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TRANSLATION

ADDITIVES TO OILS AND FUELS
(COLLECTION OF ARTICLES)

FOREIGN TECHNOLOGY DIVISION

AIR FORCE SYSTEMS COMMAND

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ADDITIVES TO OILS AND FUELS (COLLECTION OF ARTICLES)

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TABLE OF CONTENTS

Designations of the Trigonometric Functions..... vi

Preface..... 1

CHAPTER I

CONTEMPORARY REQUIREMENTS FOR QUALITY OF MOTOR AND OTHER OILS AND FUELS

Contemporary Requirements for Quality of Motor Oils, by Ye. N. Firsanova (NATI)..... 4

Technical Requirements for Quality of Diesel Fuels and Oils and Results of Tests of Some Additives, by G. A. Morozov (TsNIDI)..... 16

CHAPTER II

SYNTHESIS OF ADDITIVES

Alkylphenol Additives of Formaldehyde Condensation, by A. V. Druzhinia, G. S. Tarmanyan, M. S. Myachina and I. V. Morozova (VNII NP)..... 30

Investigation of Additives of the Type Dialkyldithiophospate Metals, by P. I. Sanin, V. V. Sher, A. B. Vipper, I. S. Glukhoded and Ye. A. Nikitskaya (Institute of Petrochemical Synthesis of the Academy of Sciences of USSR)..... 40

Synthesis of Diesterdithiophosphorous Acids and of Their Derivatives on the Basis of Substituted Phenols and Application of Them as Additives to Oil Products, by V. N. Tishkov, V. I. Isagulyants, Chang Hsiu-Cheng and N. M. Utsmiyeva (MINKh i GP)..... 54

Synthesis, Research and Application of Sulfonate Additives to Lubricating Oils, by A. M. Kuliyev, K. I. Sadykhov and M. A. Mamedov (INKhP AN AzSSR)..... 73

Synthesis of Antiwear Additives to Oils, by I. D. Afanas'yev (Leningrad Petroleum Oil Factory)..... 88

Organo-Phosphorous and Organo-Chlorine Compounds as Additives, Reducing Wear in Conditions of Threshold Friction, by Ye. S. Sheleva and P. I. Sanin (Institute of Oil-Chemical Synthesis Academy of Sciences of the USSR)..... 102

Effectiveness of Certain Organo-Molybdenum and Organo-Sulfur Compounds as Antiwear Additives to Lubricating Materials, by A. A. Fal'kovskaya, A. Ya. Vavul, Ye. M. Kheyfets, I. B. Rapoport, V. A. Listov and Ye. I. Petyakin (VNII NP)..... 108

Antioxidant Additives to Lubricating Oils on a Base of Products of Reaction of Phosphorus Pentasulfide and Terpenes, by A. M. Ravikovich and I. V. Ladyzhenskaya ("Neftegaz" Factory)..... 122

Metal Dialky[illegible]thiophosphates as Antioxidants of Lubricating Oils, by P. [illegible] Danin, V. V. Sher, L. F. Chernyavskaya, N. V. Melent'eva and I. S. Glukhoded (Institute of Oil-Chemical Synthesis of Academy of Sciences of USSR)..... 133

Synthesis of New Antioxidant Additives Type of Shielded Phenols, by V. I. Isagulyants and N. A. Pacorskaya (MINKh i GP)..... 148

Synthesis and Investigation of Antioxidizing Additives for Power Engineering and Other Oils, by A. M. Kuliyev, G. A. Zeynalova and A. [illegible] Abdinova (INKhP AN)..... 161

Synthesis of Highly Effective Depressor to Lubricating Oils on a Base Chlorine of Derivatives of Cerezine, by O. N. Il'ina (Orenburg Petroleum Plant)..... 171

Synthesis and Properties of Polyglycol Esters and Their Application as Components of Synthetic Oils and Additives, by V. I. Isagulyants, V. M. Tishkova, L. M. Emel'yanova and [illegible] A. Trushevenko (MINKh i GP)..... 181

Synthesis and Investigation of Additives Increasing Lubricating Properties of Oils, by A.M. Kuliev and A. A. Atal'yan (INKhP)... 191

Additives Ensuring Uniformity of Slow Movement of Units of Metal-Cutting Machines, by R. N. Osher (VNII NP)..... 198

C H A P T E R III

TECHNOLOGY OF PRODUCTION OF ADDITIVES

Synthesis and Technology of Production of Multicomponent Additive VNII NP-[illegible] for Lubricating Oils, by V. N. Monastyrskiy, [illegible] A. P[illegible] and M. S. Perel'miter(VNII NP)..... 204

Alkylation of Phenol by Diisobutylene in the Presence of Soviet-Produced Cation Exchange Resins as Catalyst, by V. I. Isagulyants and G. A. Ivanov (MINKh i GP)..... 213

Production of Oil-Soluble Sulfonates by [illegible] of Sulfonation of Mineral Oils by Liquid Sulfuric Anhydride in Solvents, by A. M. Ravikovich, G. G. Vinner, N. I. Levstratova, A. L. Dol'berg and Yu. N. Shekhter (Factory "Neftegaz")..... 223

Methods of Obtaining Multiash Sulfonates, by V. N. Monastyrskyy and T. K. Avaliani (VNII NP)..... 234

Improvement of Technology of Manufacture of Additive TsIATIM-339, by N. F. Karpov (Permskiy Petroleum Oil Factory)..... 247

Experience of Mastering of Industrial Installation for Production of Additive AZNII-[illegible], by M. A. Mamedov (Administration of Azerbaijan Petroleum Chemical Plant)..... 253

C H A P T E R IV

MECHANISM OF ACTION OF ADDITIVES

Investigation of Action of Additives, Containing Different Functional Groups, on Butyric Fractions and Oil, by A. M. Kuliyev and A. M. Levshina (INKhP)..... 261

About Mechanism of Action of Certain Types of Additives to Oils (Detergent, Anticorrosive and Antiscoring Additives), by Yu. S. Zaslavskiy, G. I. Shor and R. N. Shneyerova (VNII NP)..... 275

About Mechanism of Detergent Action of Additives, by P. I. Sanin, L. F. Chernyavskaya, V. V. Sher and N. V. Melent'yeva (Institute of Oil-Chemical Synthesis of Academy of Sciences of USSR)..... 285

Mechanism of Action of Detergent and Antioxidant Additives in Laquor Deposition (Working Hypothesis), by K. K. Papok..... 305

Phosphorous-Organic Compounds Reducing Wear During Friction. Mechanism of Their Action, by P. I. Sanin and A. V. Ul'yanova (Institute of Oil-Chemical Synthesis of Academy of Sciences of USSR)..... 313

New Methods and Results of Investigation of Antiwear and Antifriction Properties of Lubricating Materials, by G. V. Vinogradov (Institute of Oil-Chemical Synthesis of Academy of Sciences of USSR)..... 328

Investigation of Mechanism of Reaction of Tributyltrithiophosphite in a Hydrocarbon Medium Layers of Copper by Using Radioactive Indicators, by M. M. Kusakov, P. I. Sanin, E. A. Razumovskaya, A. V. Ul'yanova and A. P. Dekartov (Institute of Oil-Chemical Synthesis of Academy of Sciences of USSR)..... 345

Antiscoring Additives to Oils for Automobile Transmissions and Mechanism of Their Action, by I. E. Vinogradov, Ye. I. Petyakina and F. Ya. Shames (VNII NP)..... 357

Influence of Catalyst of Oil Oxidation on Anticorrosive Effectiveness of Additives Containing Various Functional Groups, by K. S. Ramayya and F. Kh. Sil's (NAMI)..... 372

Mechanism of Action and Effectiveness of Additives Increasing Lubricating Ability, by G. I. Buks (NIIcharprom)..... 381

Uses of Antioxidant Additives to Power Engineering Oil -- New in Theory and Practice, by K. I. Ivanov, Ye. D. Vilyanskaya, and A. Luzhetskiy (All-Union Power Engineering Institute)..... 401

Influence of Basic Types of Additives on Operating Properties and Oxidation of Oils in an Internal Combustion Engine, by A. V. Druzhinina, T. A. Tsiguro and V. F. Filippov (VNII NP)..... 414

C H A P T E R V

RESEARCH METHODS FOR ADDITIVE EFFECTIVENESS

Complex of Methods to Appraise the Effect of Additives on the Working Properties of Motor Oils, by K. K. Papok, A. P. Zakharov, Ye. G. Kuznetsov and A. G. Slavinskiy..... 426

Radiotracer Methods of Research of Functional Properties of Oils with Additives, by Yu. S. Zaslavskiy, G. I. Shor, R. N. Shneyerova, F. P. Lebedeva, I. A. Morozova, D. V. Ryabova, A. D. Stukin, Ye. V. Yevstigneyev, P. F. Yurchenko and V. Ya. Nizhnik (VNII NP)..... 442

A Laboratory Study of the Antioxidation Effectiveness of Motor-Oil Additives, by K. S. Ramaya, M. S. Borovaya and R. Kh. Sil's..... 451

New Method of Evaluating the Effectiveness of Antiburr Additive Actior in Oils and Fuels, by K. I. Klimov, A. V. Vilenkin and G. I. Kichkin..... 458

The Effect of Lubricating Materials and Their Additives on Formation of Pitting, by M. D. Bezborod'ko and G. S. Krivosheyn..... 467

The Effect of Oil Additives on Corrosional Wear of Bearing Alloys, by K. S. Ramayya and V. S. Zavel'skiy (NAMI)..... 477

Method of Appraisal of Working Properties of Inhibited Insulating Oils, by K. I. Ivanov, R. A. Lipsteyn, A. Ya. Mikhel'son and A. A. Luzhetskiy (VTI)..... 489

Calculating the Necessary Concentrations of Neutralizing Additives in Motor Oils, by V. D. Reznikov, N. G. Puchkov and M. S. Borovaya (VNII NP)..... 499

Method of Determining Requirements for Quality of Lubricating Oils for Tractor Motors, by S. G. Arab'yan (NATI)..... 512

C H A P T E R VI

TEST OF OILS WITH ADDITIVES ON MOTORS AND MECHANISMS AND EXPERIMENT IN THEIR USE

Tests of Oils from Sulfurous Crudes with Different Additives, by N. G. Puchkov, M. S. Borovaya, A. A. Deryabin and G. P. Belyanchikov (VNII NP)..... 524

Methods and Results of Tests of Oils with Additives on Diesel Engines of Kolomenskiy Factory, by L. G. [illegible]nov (Kolemenskiy Diesel Locomotive Factory)..... 535

Tests of Additives to Oil on a 2D100 Motor of a Diesel Locomotive While Operating on Sulfur-Bearing Fuel, by B. N. Strunge and N. F. Sinenko (Khar'kovskiy Factory of Transport Machine Building Named after V. A. Malyshev)..... 544

Results of Motor Tests of Additives Developed by the Institute of Petrochemical Processes of the Academy of Sciences of the Azerbaydzhan SSR (INKhP AN AZERB SSR) for the Improvement of Operational Properties of Fuels and Oils, by V. Ye. Bashayev (INKhP AN. Azerb. SSR)..... 556

Experiment in Using Oil Additives from Sulfur-Bearing Crudes in Diesel Locomotive Diesel Engines, by I. S. Zelenetskaya (TsNII MPS)..... 564

The Effect of Motor Oil Additives on Pitting (Point Breaking-Off) of Hydraulic Lifters, by O. S. Obleukhov, V. V. Protasov, and R. A. Trubinskaya (Moscow Automobile Plant Named after I. A. Likhachev..... 575

Method and Results of Stand Tests of Transmission Oils with Different Additives, by O. S. Obleukhov, E. N. Devyatkin and A. V. Berenfel'd (Moscow Automobile Plant im. I. A. Likhachev.. 587

Research on Effectiveness of Additive TSIATIM-339 During Prolonged Operation of High Speed and Forced Ship Diesel Engines on Sulfur-Bearing Fuels and Oils, by V. P. Korotnenko..... 596

The Effect of Viscosity of Additives on Operational Properties of Oils, by Ye. G. Semenido, V. I. Sharapov, and N. V. Shchegolev..... 604

CHAPTER VII

ADDITIVES TO FUELS

Additives to Liquid Fuels for Gas Turbine Installations, Preventing Deposits of Ashes and Vanadium Corrosion, by R. A. Lipshteyn, S. E. Khaykina, A. S. Avetisyan and T. A. Blagova (VTI)..... 619

Some Data on the Use of Anticorrosive Additives to Residual Fuels Containing Vanadium and Sulfur, by V. G. Nikolayeva, A. Ya. Dukhnina, B. I. Komarov and G. I. Levinson (VNII NP).... 631

Use of Neutralizing Substances in Motors Working on High-Sulfur Diesel Fuels, by B. V. Losikov, M. S. Smirnov, L. A. Aleksandrova, I. A. Rubinstein, L. T. Ocheretyanyy and N. Dneprov..... 642

Antioxidants for Fuels, by I. V. Rozhkov, Z. A. Sablina, A. A. Gureyev and Ye. N. Kornilova..... 654

FOLLOWING ARE THE CORRESPONDING RUSSIAN AND ENGLISH

DESIGNATIONS OF THE TRIGONOMETRIC FUNCTIONS

Russian	English
sin	sin
cos	cos
tg	tan
ctg	cot
sec	sec
cosec	csc
sh	sinh
ch	cosh
th	tanh
cth	coth
sch	sech
csch	csch
arc sin	$\sin^{-1}$
arc cos	$\cos^{-1}$
arc tg	$\tan^{-1}$
arc ctg	$\cot^{-1}$
arc sec	$\sec^{-1}$
arc cosec	$\csc^{-1}$
arc sh	$\sinh^{-1}$
arc ch	$\cosh^{-1}$
arc th	$\tanh^{-1}$
arc cth	$\coth^{-1}$
arc sch	sech^{-1}
arc csch	csch^{-1}
rot	curl
lg	log

ANNOTATION

In the collection are reports heard at Scientific and Technical Conference on Additives to Oils and Fuels, devoted to the synthesis of detergent, antioxidant, anti-corrosive, antiwear and other additives, investigation of mechanism of their action, methods of investigation of effectiveness of additives, results of laboratory, stand and operational tests of oils and fuels with different additives.

Contemporary tendencies in area of development of machines and mechanisms and requirements presented for quality of oils and fuels are briefly illustrated.

Collection is designed for workers of scientific research organizations of petroleum, machine-building and other branches of industry occupied with development, research and tests of additives, engineering-technical workers, producing additives and oil products with additives, and also for engineering-technical workers of machines and mechanisms and use of oil products.

PRISADKI K MASLAM I TOPLIVAM

Trudy Nauchno-Tekhnicheskogo Soveshchaniya

Pod redaktsiyey
S. E. Kreyna, P. I. Sanina, V. N. Monastyrskogo,
Ye. A. Eminova

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PREFACE

Increase of quality of petroleum fuels and oils is a problem of great national economic value.

The most economically expedient, and in many cases the only possible method of solution of this problem is addition to fuels and oils of special additives.

Production of additives has been developed here so far at an insufficiently fast rate and on insufficient scale, and assortment of additives is still very limited.

During the last few years different scientific research organizations have developed additives allowing us significantly to improve the operational properties of oils and fuels.

Great experience of work of engines and mechanisms on oils with additives has been accumulated.

Theory and working hypotheses have been developed, which give us the possibility of explaining mechanism of action of different additives, and new methods of laboratory appraisal of quality of oils with additives and installation for simulating work of oils in friction assemblies have been created. All this great experimental material was generalized at All-Union Scientific and Technical Conference on Additives to Oils and Fuels, convoked on initiative of GNTK SM SSSR (State Scientific and Technical Committee of Council of Ministers of the USSR),

Central Administration of NTO (Scientific and Technical Society) of Petroleum Industry and Leningrad Council of National Economy in June, 1960.

At this conference works performed were summed up, and ways of further increase of production of additives and direction in area of synthesis of new highly effective additives was outlined.

Transactions of conference on additives will be useful not only to scientists of petroleum and chemical industry, who create new additives, but also to wide circle of readers associated with the production and application of fuels and lubricants.

Editorial board

CHAPTER I

CONTEMPORARY REQUIREMENTS FOR QUALITY OF MOTOR AND OTHER OILS AND FUELS

CONTEMPORARY REQUIREMENTS FOR QUALITY OF MOTOR OILS

Ye. N. Firsanova
NATI*

Requirements for quality of lubricating oils for different internal combustion engines change depending on a number of factors, for instance, thermal state of parts lubricated by oil and temperature of oil in crankcase frequently connected with this, quality of fuel used from the point of view of content in it of sulfur, tarry substances, fractional composition, certain peculiarities of construction and material of parts, operating conditions and course of working process, conditions of operation and care of motor, period of replacement of oil and so forth.

One of the most important factors determining behavior of oil in engine is thermal state of lubricated parts, influencing both physical, and also chemical properties of motor oils.

Range of temperatures at which lubricating oils work in motor is very wide. Lubricating oils should ensure normal work both at moment of starting of cold engine at temperatures reaching -40° and below, and during work of heated engines, temperature of whose piston in zone of piston rings can reach 200-300°.

*State All-Union Scientific Research Institute of Tractors.

To guarantee easy starting of engine in winter it is necessary to use oils of low viscosity at low temperatures.

In Fig. 1 are presented viscosity and temperature characteristics of native (Soviet) winter and foreign oils, indicating good properties of oils SAE-10, all-season oils SAE-10W/30, SAE-10W/20 and others, prepared with the use of thickening additives: polymethacrylates and polyisobutylenes.

Study of influence of these oils on starting of diesel engines YaAZ-204 (Fig. 2) and D8-30 showed that with the use, for instance, of all-season oil SAE-5W/30, having 100° viscosity close to the viscosity of oil SU, but very different at -20°, moment of resistance to idling is 2.6 times less than with use of oil of industrial 50.

In Fig. 3 are given data of NAMI (Central "Order of the Red Banner of Labor" Scientific Research Institute of Automobiles and Automobile Engines), showing numbers of turns developed during starting of engine YaAZ-204 on oils with different viscosity and temperature characteristics, from which it is clear that oils with high index of viscosity ensure development by engine of significantly greater number of turns under the same temperature conditions.

Starting of a number of tractor diesel engines by starter, conducted by NATI in different winter conditions without the use of preheating, could be carried out in the case when viscosity of oil at the test temperature did not exceed 4000-5000 cs. Inasmuch as at the moment of starting of engines and work of little-heated engine the greatest magnitude of wear is observed, on tractor diesel engine D-28 an attempt was made to select the optimum viscosity, ensuring least wear of sleeves. It was found that for this engine oil with index of viscosity near 100 and viscosity 5 cs at 100° gave the best result. However, during work of engine in winter conditions under nominal load conditions the least wear was obtained on oil with viscosity of 7-8 cs and index of viscosity near 100. Therefore in norms for winter oil it is necessary to introduce value of viscosity at negative temperature (of the order of -20°).

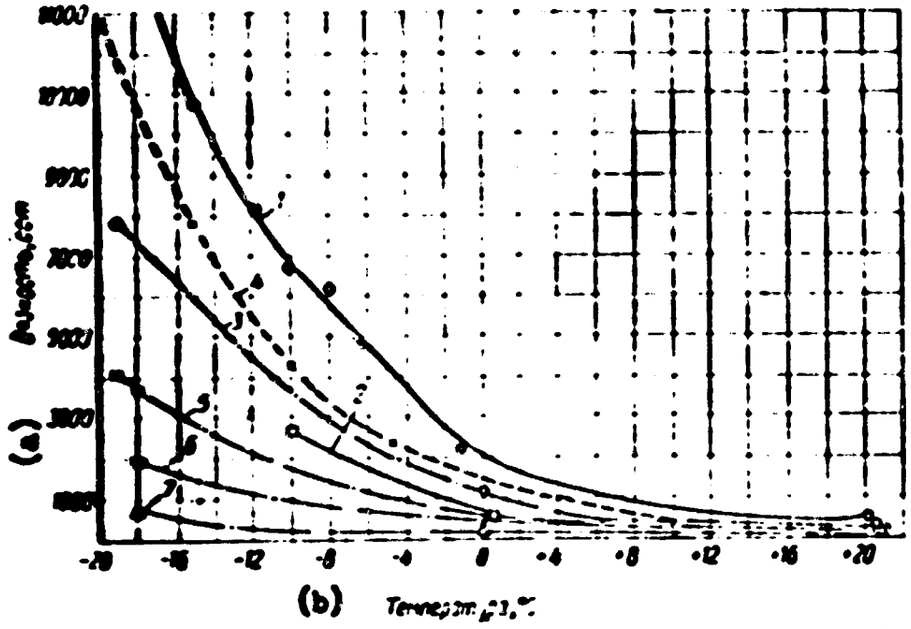


Fig. 1. Viscosity and temperature characteristic of winter oils (native [Soviet] and foreign). Oils:
1) Dp - 8; 2) SAE-10W/30; 3) AKZp-10; 4) DSp-8; 5) SAE-10W/20; 6) SAE-10W; 7) SAE-5W.
KEY: (a) Viscosity, cs; (b) Temperature, °C.

It is necessary to note that according to available source material [1], oils with high index of viscosity are consumed in motor significantly less than low-index oils.

For determination of optimum level of viscosity is necessary to consider also the index of viscosity of oil, since oils having identical viscosity at 100°, with high index of viscosity sometimes will not be in a state to ensure necessary thickness of oil film at temperatures of 50—80°, which can be observed, for instance, in bearings in initial period of work, during work on small turns, etc.

Practice of work of motor and tractor diesel engines showed that oil with index of viscosity ≈90°, with level of viscosity near 11 cs at 100° gives satisfactory results during operation. Results of introduction of oil DSp-11 with index of viscosity near 80 now still are not generalized.

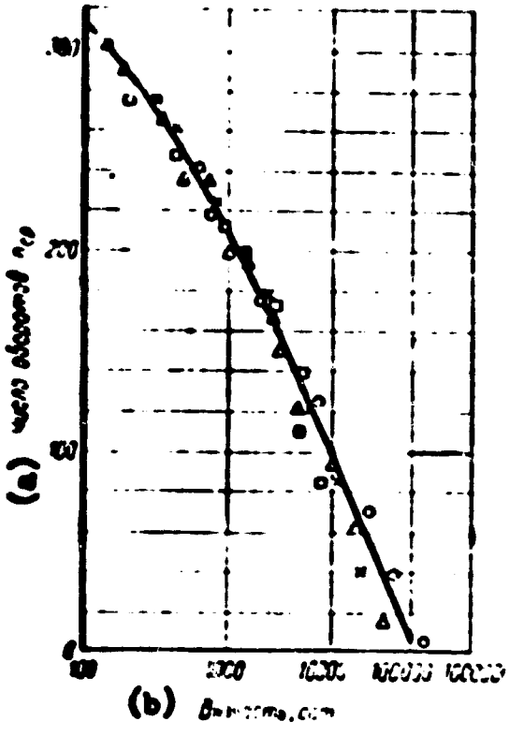


Fig. 2. Dependence of moment of resistance to idling of engine YaAZ-204 on viscosity of oils during its cranking by starter.
Oils: 0 — industrial 50;
Δ — sulfur-bearing;
x — AKZp-10;
□ — AKZp-6;
▲ — SAE-5W/30;
■ — SAE-5W/20.
KEY: (a) Number of turns, n_{ave}; (b) Viscosity, cs.

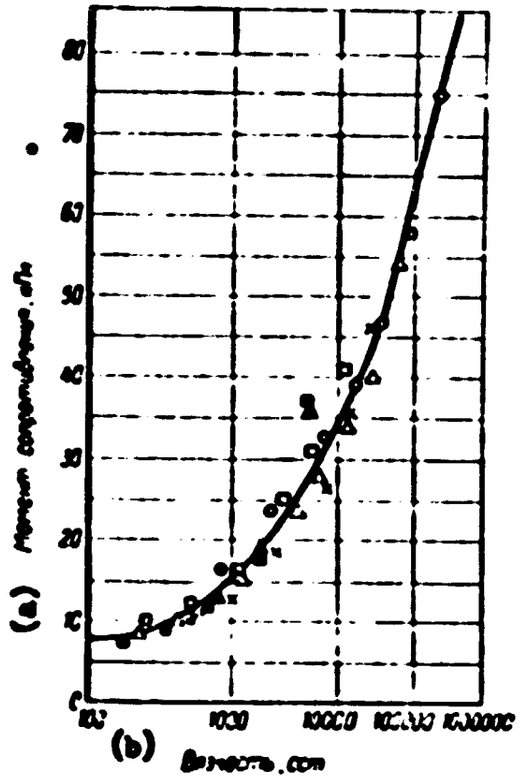


Fig. 3. Dependence of number of revolutions of engine YaAZ-204 on viscosity of oils during its cranking by starter.
Oils: 0 — industrial 50;
Δ — sulfur-bearing;
x — AKZp-10;
□ — AKZp-6;
▲ — SAE-5W/30;
■ — SAE-5W/20.
KEY: (a) Moment of resistance, kgm; (b) Viscosity, cs.

Abroad as summer oils for diesel engines oils SAE-20 and SAE-30, with level of viscosity at 98.9° ar. widely used, equal respectively to 9.4-12.1 cs and 12.1-14.6 cs.

As a result of study of thermal conditions of a number of native (Soviet) carburetor and diesel engines, it was shown (Table 1) that temperature of upper part of piston head also in some of piston rings of such engines as ZIL-121, GAZ-51, MZMA-401 [2] is significantly lower than diesel engines D-54, CMD-7(D-35 and D-38) and GMC [3], especially if we consider that automobile engines of passenger machines work on the average with load of 30-35%, cargo machines 60-70%, and tractor diesel engines 70-90% of rated power.

Table 1. Temperature of Pistons C_m = 9.15 m/sec

Engine	Temperature, °C	
	Upper part of head of piston	Crosspiece of first piston ring
Carburetor engines		
ZIL-121:		
at P_e = 100%.....	198	190
at P_e = 60%.....	175	169
GAZ-51:		
at P_e = 100%.....	192	187
at P_e = 60%.....	170	164
MZMA-401:		
at P_e = 100%.....	197	180
at P_e = 35%.....	162	147
Diesel engines		
GMC:		
at P_e = 100%.....	338	—
CMD-7:		
at P_e = 100%.....	228	First piston groove 210
at P_e = 90%.....	205	180
D-54 (cast-iron):		
at P_e = 100%.....	335	237
at P_e = 90%.....	325	232
D-54 (aluminum):		
at P_e = 100%.....	255	210
at P_e = 90%.....	250	208

During forcing of carburetor engines (increase of number of turns, increase of degree of compression, etc) the temperature in engines of new models in conditions of operation significantly is increased and from this point of view conditions of work of oil become close to conditions of work in diesel engines. Therefore abroad oil is selected depending upon conditions in which it is necessary to work the engine.

Thus, usual (regular grade) oils without additives are useful for conditions of work designated usually by letters ML and characteristic for low stress gasoline engines, not possessing any design features causing formation of deposits.

Oils of first grade (Premium), intended for work in heavier conditions (ИМ), contain antiwear and antioxidant additives, preventing formation of deposits and corrosion of bearings, caused by high temperature of oil in crankcase.

Heavy duty oils are intended for diesel engines and gasoline engines, working in heavy conditions (МС) and containing both detergent additives, and also additives preventing formation of deposits and corrosion of bearings caused by fuel used or peculiarities of construction of engine.

Use of diesel fuel with high content of sulfur and heightening of thermal conditions of diesel engines, and use of pressure feed make it necessary to create additional types of oils, designated S-1 (Supplement 1) S-2, and S-3 (Series 2, Series 3) and intended for very heavy conditions of work ДГ and ДС.

Oils, intended for conditions of work МС, pass tests on standard diesel engine Caterpillar, working on fuel with content of sulfur of 0.2%. Oil S-1 is estimated on the same engine with the use of fuel with 1% sulfur; oil S-2 is tested on engine with pressure feed (ИД) and on fuel with content of sulfur of 1%; oil S-3 passes tests on low-sulfur fuel, but on engine 1Г with great overload.

In Soviet Union until now methods of rating oils on special engines still have not been standardized; as a result of such a situation it is difficult to estimate reliably the quality of oils and correctly to classify oils with additives with the help of motor methods.

At НАТИ there was created an installation for tests of oils (УИМ-НАТИ), consisting of specially equipped one-cylinder engine; dimension and type of combustion in it correspond to diesel engine Д-54 [4].

Tests of different oils for clogging of piston by deposits during work on fuel with content of sulfur of 1% (Table 2), conducted on installation УИМ-НАТИ, showed that oils without additives and with such additives as азнии-4 and азнии-тсиатим-1, just like foreign oils of premium type, are not useful for work in diesel engine with the use of sulfur-bearing fuel.

Table 2. Appraisal of Motor Oils on Installation UIM-NATI

Type of oil	Brand of oil	Appraisal, points
Premium	SAE-30	15
	SAE-10W/30	19
For heavy conditions of work		
S-1	Essoluble MD-20	8
S-2	Rimula oil-20	8
S-2	Rimula oil-30	7
Native (Soviet) motor	D-11 + aznii-tsiatim-1*	39
	D-11 + aznii-4	38
	DS-8 + tsiatim-339 (experimental	12
	DS-11 + tsiatim-339(experimental	10
	Industrial 50	39
	Industrial 50 + tsiatim-339	15
	D-11 + tsiatim-39	19
	DS-11 + vnii np-360**	10
	AKZ + tsiatim-339	23
	DS-11 + PMS_{ya}-19	4
	DS-11 + MG-102	4

*Additive designated by number and names of institutes, AZNII (Azerbaijan Scientific Research Petroleum Institute in V. V. Kuybyshev) and Tsiatim (Central Scientific Research Institute of Aviation Fuels and Oils)

**Additive designated by number and [illegible] of the institute, All-Union Scientific Research Institute for [illegible] and Gas Refining and the Production of Synthetic Liquid Fuel

Development types of oils from sulfur-bearing crudes with additive tsiatim-339 gave better results than commercial oil according to GOST 5304-54.

During experiments with sulfur-bearing oils with additives PMS_{ya}, MG-102 and vnii np-360, significantly better results are obtained as compared to oil with additive tsiatim-339. Oils turned out to be equivalent in quality to foreign oils for heavy conditions of work S-1 and S-2 or even somewhat exceeded them. However final appraisal of oils S-2 should be obtained after tests on engine with pressure feed. Thickened oils of type AKZ_p-10 with additive tsiatim-339 gave bad results.

Data obtained on installation UDM-NATI will agree with results of tests conducted in stand and field conditions on full-scale diesel engines D-35, D-54 and KDM-46.

In order to clarify what physico-chemical properties are the most important for one or another type of tested oils, oxidizability of a number of oils of foreign firms was simultaneously determined according to methods of AzNII and NAMI (on instrument DK-2), and thermooxidizing stability in evaporators according to Papok's method and detergent properties according to PZV method.

From data given in Table 3, it is clear that premium oils SAE-30 and SAE-10W/30 possess (according to methods of AzNII and Papok) high antioxidant properties, fairly bad detergent properties according to PZV, and also give large deposit in instrument DK-2.

Oils for very heavy conditions of work of type S-2, for instance Rimula oil, conversely, have very high detergent properties and do not give any deposit at all in instrument DK-2, but have somewhat worse antioxidant properties according to method of AzNII. Thermooxidizing stability of these oils in evaporators is at very low level, which contradicts all the results of observations of work in engines where this oil gives very good results.

Oil emulsible MD-20, intended for moderately heavy conditions of work, occupies intermediate position.

Impairment of antioxidant properties of oils for increasingly heavy conditions of work can, apparently, explained by the use of even greater concentrations (reaching 20%) of detergent additives in oils, necessary to guarantee cleanness of pistons during work on sulfur-bearing fuel.

It is known that many detergents not only are not inhibitors, but, conversely, act as catalysts of oxidation. Therefore, obtaining of good results, obviously, can be ensured with optimum relationship between quantities of detergent and inhibitor in oil.

Table 3. Indices of Quality of Some Foreign Oils

Brand of oil	Oxidizability according to method of AsNTI	Detergent properties according to method of P2V	Thermooxidizing stability in evaporators according to Papok method	Formation of deposit according to method of NAMI, %
SAE-10W.....	—	3.5	—	—
SAE-20.....	—	2.5	—	—
SAE-30.....	270	3.5	91	8.5
SAE-10W/30.....	230	3.5	—	8
SAE-10W/20.....	—	2.0	—	—
Essoluble MD-20	154	0.5	—	4.3
Essoluble MD-40	—	0.5	—	—
Rimula oil-20.....	90	0	23	0
Rimula oil-30.....	110	0	15	0

In foreign practice in connection with this different compositions of calcium or barium alkylphenolates and sulfonates in mixture with thiophosphoric and other compounds as inhibitors found wide application.

For oils working in moderate conditions antioxidant properties should, apparently, predominate action of inhibitor turns out to be sufficient to prevent formation of deeply oxidized compounds; therefore large amount of detergent components is not required.

Numerous observations of NAMI and VNII NP showed that all oils for automobile engines, working in moderate conditions, give significant (up to 7%) deposit in instrument DK-2 after 50 hr of heating at 200°, and only separate samples of oils, for heavy conditions, (for instance, Shell-x-100) gave several tenth's of a percent of deposit.

Apparently, this method characterizes well oils intended for heavy conditions of work, when Papok method does not give correct characteristic of oils of this type.

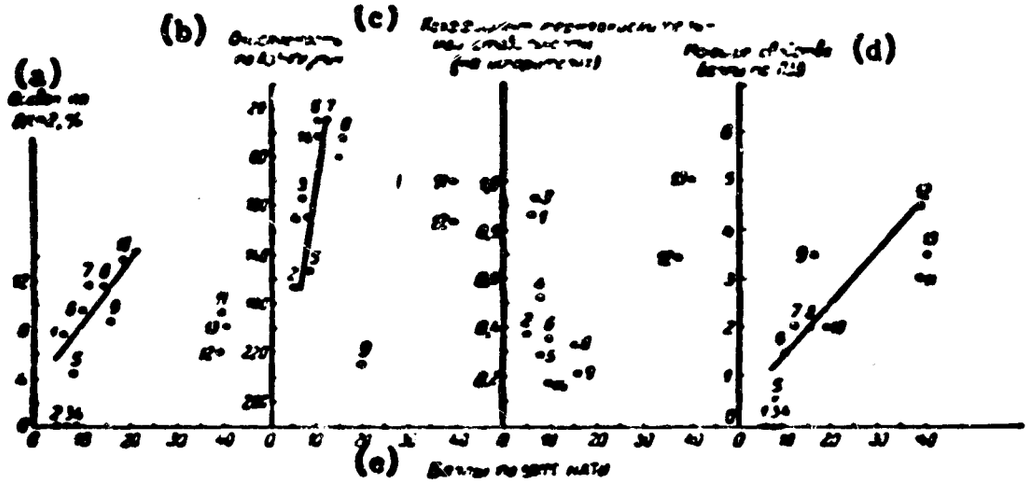


Fig. 4. Appraisal of quality of oils by laboratory and motor method.
Oils: 1) NKZ + NG-102; 2) NKZ + PMS$_{ya}$; 3) Rimula-Oil 30HD; 4) the same 20HD; 5) Essoluble 20HD; 6) NKZ + tsiatim-330 (summer); 7) the same (winter); 8) industrial 50 + tsiatim-339; 9) SAE-30; 10) Dp-11 (GOST 5304-54) + tsiatim-339; 11) Dp-11 + azniI-tsiatim-1; 12) industrial 50; 13) SAE-10W/30; 14) Ds-11 + vniI np-360.
KEY: (a) Deposit on DK = 2, %; (b) Oxidizability according to AzNII, min; (c) Coefficient of thermooxidizing stability (in evaporators); (d) Detergent properties, points according to PZV; (e) Points according to UIM-NATI.

In Fig. 4 are given results of motor appraisal of quality of native (Soviet) and foreign oils, obtained on installation UIM-NATI, and results obtained with the help of laboratory methods. Additive tsiatim-339 sharply worsens antioxidant properties of base industrial oils (SU) and DS-11. Apparently, this explains the fact that oils with this additive with insufficient detergent properties (1.5 points according to PZV) do not ensure necessary cleanness of piston during work of forced or strongly loaded motors on fuel with 1% sulfur.

Very bad detergent and weak antioxidant properties of commercial oil D-11 with additive azniI-4 lead to bad results during test of diesel engines on sulfur-bearing fuel and cause fast coking of piston rings. It is necessary however to note very great spread of points on given graphs for different native oils with additives, which indicates difficulty of imitation of conditions of work of motor in laboratory instrument.

Significant increase of antioxidant properties according to method of AzNII was obtained for oil DS-11 with additive PMS_{ya}, giving simultaneously also the best results on engines UIM-NATI and D-35, and also not giving deposit in instrument DK-2.

Good results on cleanness of piston were obtained also on oil with additive NG-102, ash content of which amounted to 2.3%. However oil with additive NG-102U, with ash content of 1.2%, had bad stability according to AzNII and in instrument DK-2, and it is doubtful whether it will give good results also on UIM-NATI.

In foreign literature recently considerable attention has been paid to neutralizing properties of oil for heavy conditions of work, connected with alkalinity of additives used.

There are data [5], from which it follows that required alkalinity of oil should be in dependence on content of sulfur in fuel used, and that for some types of oils alkalinity of additive should amount to 1 mg KOH/g for each percent of sulfur contained in fuel. These requirements, however, can change depending on the construction of engine and conditions of work; for instance for ship diesel engines, working on high-sulfur fuel, alkalinity of 40-50 mg KOH/g of oil is recommended.

Inasmuch as we do not have standardized method of determination of alkalinity, we determined it by different methods for a number of native and foreign oils, in order subsequently to establish what method of physico-chemical research appears most characteristic for appraisal of ability of additive to prevent interaction of products of combustion of sulfur-bearing fuels with metal or with molecules of oil and to decrease wear and bedding of rings.

In Table 4 are given data on determination of alkalinity (minus mg KOH/g), acid number (plus mg KOH/g) of oil, obtained by potentiometric titrating on instrument LP-5, by usual titrating in 96 and 60% alcohol with phenolphthalein and with new indicator nitrosine yellow.

From these data it is clear that as compared to foreign sample of oil, intended for work on fuel with content of 1% sulfur, native samples possess extremely unsatisfactory alkalinity.

Table 4. Determination of Alkalinity and Acidity of Oils with Additives

Oils	Method of test			
	Potentiometrically up to pH = 9.2	According to GOST 5985-51 with phenolphthalein (96% alcohol)	With phenolphthalein (60% alcohol)	With nitrozine yellow (60% alcohol)
Industrial 50 + 3% tsiatim-339.....	+0.13	—	—	—
DS_p-11.....	—	+0.5	-0.1	-0.1
DS_p-11 + 2% AFB.....	-0.6	-0.4	—	—
DS-11 + 6% vnii np-360..	-0.3	-0.4	+0.3	-0.2
DS-11 + PMS_{ya}.....	+0.4	+0.3	0	-0.8
DS-11 + $NG-102_u$.....	—	-0.6	—	—
AKZ-10 + 3% tsiatim-339.	+0.1	+0.1	0	-0.9
Foreign oil.....	-5.1	-4.1	-0.5	-7.0
Foreign oil.....	-0.2	-0.1	-0.2	-1.1

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TECHNICAL REQUIREMENTS FOR QUALITY OF DIESEL FUELS AND OILS AND RESULTS OF TESTS OF SOME ADDITIVES

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TsNIDI*

Requirements for Quality of Diesel Oils Depending on Degree of Forcing of Engines

In resolutions of conferences it was repeatedly noted that in diesel construction native lubricating oils do not ensure completely normal operation of forced diesel engines during their work on sulfur-bearing fuels. Current position requires reconsideration of existing assortment of diesel oils and presentation of increased requirements for quality of oils and additives [1]. These requirements for different types of diesel engines and conditions of their operation to a significant degree depend on thermal stress of given type of diesel engine and quality of fuel used, in particular content in it of sulfur.

Thermal stress of engine could be characterized by temperature of lateral surface of piston, especially by temperature in the area of upper piston compression rings, where the most intense scale slag formation occurs. However, similar systematized data at present are practically absent, and available results of

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measurements of temperatures are not numerous and cannot be compared with each other due to different method of determination. Therefore thermal stress must be characterized with the help of parameters determining the degree of forcing of the engine.

Thermal stress of engine depends first of all on average effective pressure P_e.

Degree of forcing of engine frequently is expressed by ratio of power on one piston, to diameter of piston N_{ts}/D.

However parameter N_{ts}/D can be used as criterion of intensity only for similar constructions of motors [2].

For comparison of intensity of different types of diesel engines, in our opinion, it is more convenient to use criterion of forcing K_ϕ, characterizing degree of use of working cylinder:

$$K_\phi = P_e C_m Z,$$

where P_e is the average effective pressure in kg/cm^2;

C_m is the average speed of piston in m/sec;

Z is the cycle coefficient (for four-cycle engines Z = 0.5, for two-cycle Z = 1.0).

There is no reason to expect growth of K_ϕ due to significant increase of C_m, since this is limited by reserve of strength of material.

Conversely, growth of P_e is possible owing to use of gas turbine pressure feed. Prospects of development of diesel construction in 1965-1975 anticipate increase of average effective pressure from P_e = 5-6 kg/cm^2 to values:

a) for four-cycle diesel engines P_e = 20-25 kg/cm^2;

b) for two-cycle diesel engines P_e = 12-14 kg/cm^2.

Increase of P_e usually entails some increase of temperature of piston. In Fig. 1 is shown increase of temperature of piston of engine 6Ch23/30 during forcing of it from 600 to 900 hp by means of use of gas turbine pressure feed. Research was conducted in TsNIDI [4].

By degree of forcing diesel engines issued by our industry can be divided into three basic groups (Table 1).

To the first group belong the most forced motors with gas turbine pressure feed, having values of K_ϕ higher than 50, average speed of piston $C_m > 9$ m/sec and temperature of piston in area of upper piston ring higher than 250° (for instance, diesel engines 9D100, 30D and others). Here come in some engines of special assignment and separate head samples of diesel engines, which pass tests at present or are in state of finishing.

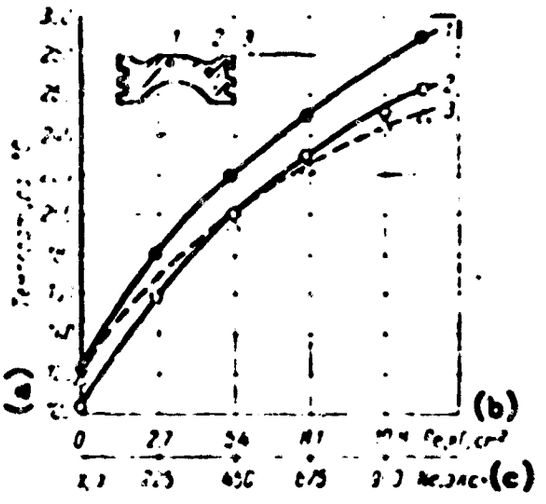


Fig. 1. Change of temperatures of piston of engine 6Ch28/30 with pressure feed (at 1000 rpm). KEY: (a) Temperature, °C; (b) P_e, kg/cm^2; (c) N_e, ehp hr.

For comparative characteristics of diesel engines of this group it is possible to list parameters of some contemporary high-forced motors of foreign firms [3] (Table 2).

To the second group belongs a number of serial forced diesel locomotive and ship diesel engines of the type 2D-100, D-50 and others with index of forcing K_ϕ from 30 to 50 and temperature of piston in region of upper compression ring of the order of 250°.

Third group includes relatively low-stress engines with values of $K_\phi < 30$, for which corresponding temperature of piston is usually lower than 250°. For example, for diesel engine Ch-10/13 it lies within limits of 210-220°.

Typical temperatures of lateral surface of piston for diesel engines of different groups are shown in Fig. 2.

Table 1. Classification of Diesel Engines by Degree of Forcing

Group of engines	Type of engine	Brand	N_e, bhp hr	n, rpm	C_m, m/sec	P_e, kg/cm^2	N_{ts}/n	K_ϕ
1. High stress diesel engines (K_ϕ >50)	Special		—	—	9—12	8—20	—	50—100
2. Diesel engines of average stress (K_ϕ from 30 to 50)	6D10,8/12.7	YaAZ-206	165	2000	8.5	5.3	25.5	45.1
	10D20,7/2 X X 25.4	2D-100	2000	850	7.2	6.2	48.3	44.6
	12ChN18/20	M-751	750	1500	10.0	7.7	34.7	38.5
	12ChN18/20	M-601	700	1400	9.35	6.7	32.4	31.5
	6ChN31.8/33	D-50	1000	740	8.15	7.7	52.2	31.4
3. Low-stress diesel engines (K_ϕ less than 30)	8D43/61	—	2000	250	5.1	5.1	58.1	26.0
	6D30/50	—	600	300	5.0	4.25	33.3	21.2
	6Ch15/18	3D6	150	1500	9.0	4.7	16.6	21.2
	4N14.5/20.5	KDM-46	93	1000	6.8	6.15	16.0	20.9
	4Ch10.5/13	—	40	1500	6.5	5.3	9.5	17.7
	6Ch12/14	K-150	80	1500	7.0	5.0	11.1	17.6
	4Ch12.5/12.5	D-14	14	1600	6.7	5.1	11.2	17.3
	4Ch12.5/15.2	D-54	54	1300	6.7	5.0	10.8	16.8
	4Ch10.5/13	D-35	37	1400	6.0	5.8	9.3	16.1
	6Ch136/45	—	600	375	5.6	5.2	27.7	14.7
	4Ch8.5/11	—	20	1500	5.5	4.8	5.8	13.2

Table 2. Characteristics of High-Forced Engines of Foreign Firms

Type, brand	N_e, bhp hr	n, rpm	C_m, m/sec	P_e, kg/cm^2	K_ϕ
MAN (6ChN30/50.....	1700	600	6.0	20	60
Cummins (ChN10.5/12.7)..	300	3600	15.2	11.4	87
Sulzert (6D18/22.5X2)...	2750	1000	7.5	12.5	94

Another essential factor, determining requirements for oil, is quality of diesel fuel. It is well-known that wear and scale formation in diesel engine are approximately proportional to content of sulfur in fuel. Therefore use of sulfur-bearing, and also heavy fuels in diesel engines without lowering of motor potential is possible only with selection of special oils with effective additives.

Perspective classification of oils for diesel engines should specify three main types of oils, which would correspond to the above-indicated three types of engines with different degree of forcing, taking into account quality of fuel used (Table 3).

Each type of oil given in Table 3 should include oils with different level of viscosity: in range from 6-8 to 20-22 cs at 100°.

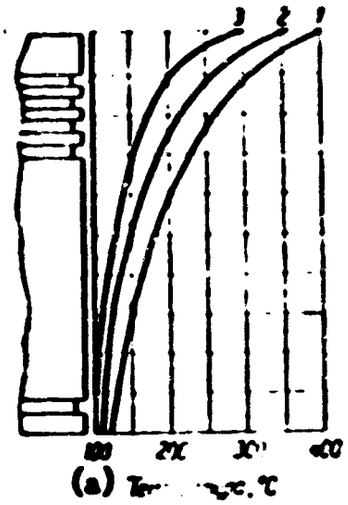


Fig. 2. Average temperature of lateral surface of piston for diesel engines with different degree of forcing. KEY: (a) Temperature, °C.

In special group one should single out special cylinder oils (for instance, emulsion), intended for big low rpm ship diesel engines of the Burmeister and Payn type, working on heavy fuel. Production of these diesel engines here at present is limited.

Basic indices of operational quality of oils of different types in accordance with the given diagram during appraisal of them on laboratory installations must approximately satisfy requirements given in Table 4.

However, final fitness of oil for given conditions of work should be determined only as a result of motor tests. With this wear of engine working on sulfur-containing fuel and tested oil with additive does not have to exceed wear on low-sulfur fuel and standard oil.

Development of standard methods of motor tests and standard engines — simulators, intended for appraisal of oils and additives is very necessary.

Table 3. Classification of Diesel Oils on the Basis of Their Conditions of Work in Engine

Type of Oil	Purpose
For specially heavy conditions of work	For lubrication: a) high-stress diesel engines of 1-st group, having value of $K_\phi > 50$, during their work on sulfur-bearing fuel (content of sulfur up to 1.0%) b) diesel engines of 2-nd group (k_ϕ from 30 to 50) during their work on high-sulfur fuel (content of sulfur more than 1.0%)
For heavy conditions of work	For lubrication of diesel engines of 2-nd group (K_ϕ from 30 to 50) during their work on sulfur-containing fuel (content of sulfur up to 1.0%)
For normal conditions of work	For lubrication: a) low-stress diesel engines of 3-rd group ($K_\phi < 30$) during their work on sulfur-bearing fuel; b) diesel engines of 2-nd group during their work on low-sulfur fuel (content of sulfur less than 0.5%)

Table 4. Operational Qualities of Oils

Type of Oil	Index of viscosity, not less than	Detergent properties according to PZV, points, not more than	Degree of corrosion according to Pinkevich on lead plate, g/m², not more than
For specially heavy conditions of work.....	90—120	0.0	8.0
For heavy conditions of work	90—120	0.5	8.0
For normal conditions of work	90—120	3.0	8.0

Oil refining industry at present issues only oils corresponding in quality to oils for usual conditions of work (oil with additive tsiatim-339*). As oils for

*Additive designated by number and name of the institute, Central Scientific Research Institute of Aviation Fuels and Oils.

heavy conditions of work can be considered oils with phosphorous-containing additives vnii np-360* and mni ip-22**. Oils for specially heavy conditions of work here now are absent.

Basic Requirements for Quality of Diesel Fuel

For selection of fuel for definite group of engines one proceeds first of all from the number of revolutions, since precisely the rpm rate of engine determines period of time expended on process of combustion.

However, the above-considered diagram of division of engines into three groups by degree of forcing can be used also for determination of basic types of fuels ensuring reliable operation of these groups of engines.

1. For high speed forced diesel engines with direct injection, with speed of piston more than 9 m/sec, it is necessary to use low-sulfur distillate fuel with narrow fractional composition, obtained by processing of low-sulfur crudes or by hydropurification.

With this is desirable further limitation of the content of actual resins and increase of cetane number of winter and Arctic grades of fuel.

2. For less stressed high speed and part of low speed diesel engines diesel fuel GOST 305-58 with content of sulfur not more than 1.0% can be used, under conditions of use of oils with sufficiently effective additives.

3. For low rpm diesel engines of great power (type D 74/160) heavy fuel can be used (of type of motor DT-1) with saturated content of sulfur 1.5%, with additive and other indices coordinated with the consumer.

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*Additive designated by number and name of the institute, All-Union Scientific Research Institute for Oil and Gas Refining and the Production of Synthetic Liquid Fuel.

**Moscow Petroleum Institute.

Results of Tests of Some Additives to Fuels and Oils, Conducted at TsNIDI

For determination of comparative effectiveness of additives to diesel oils at TsNIDI brief motor tests of additives of different types were conducted (alkylphenol, phosphorous-containing, sulfonate and others). Tests were conducted on engines of type Ch10.5/13 on fuel of GOST 305-58 (content of sulfur 0.8%) and on high-sulfur fuel (content of sulfur 1.4-1.6%), and oil DS-11.

Along with motor tests laboratory investigations of oil DS-11 with different additives were conducted; in particular, the corrosion capacity of oil (according to Pinkevich) and inclination of oils to varnish formation (on instrument of Kyuregyan) was determined.

Results of these investigations (Table 5) correspond to results of motor tests.

Table 5. Influence of Additives on Varnish Formation and Corrosion Capacity of Oil DS-11 During Appraisal on Laboratory Installations

Index	Oil DS-11					
	Without additive	3% tsiatim-339	3% azniI-7*	6.5 % vniI np-371	6% vniI np-360	6% ip-22
Period of varnish formation on instrument of Kyuregyan, min..	12.5	23.0	24.5	—	34.0	45.0
Corrosion capacity according to Pinkevich, g/m^2:						
on lead.....	-8.2	-5.4	-3.0	-3.2	-1.76	-0.85
on plumbous bronze.....	-1.6	-0.43	-0.50	-0.75	-0.50	+1.68

*Additive designated by number and name of the institute, Azerbaijan Scientific Research Petroleum Institute im. V. V. Kuybyshev.

Test of additives on engines of type Ch-10.5/13 during work on high-sulfur fuel (content of sulfur 1.6%) are described in formerly published works of TsNIDI [5, 6].

Main results of these tests reduce to the following.

1. Wear of piston rings increases during work on high-sulfur fuel and oil without additives 1.5-2 times as compared to wear on fuel of GOST 305-58 and the same oil. Wear of sleeves increases especially sharply.

2. Additive aznii-7, taken in concentration of 5.0%, does not give sufficient lowering of wear, although with this absence of sticking of piston rings was noted.

3. Additives vnii np-360 and mni np-22 with respect to wear and detergent properties showed good results (Fig. 3).

However, during all tests of high-sulfur fuel with use of the indicated additives to oil lowering of wear of bushings of cylinders to level existing for standard fuel (GOST 305-58) couldn't be achieved.

In Fig. 4 is shown wear of bushing of cylinder of diesel engine Ch-10.5/13 during work on fuels with different content of sulfur and the influence of additives on lowering of wear.

Results of brief (60-hour) tests of different additives on engine 2Ch-10.5/13 during work on fuel of GOST 305-58 (content of sulfur 0.8%) are presented in Table 6.

In table are given also indices of quality of worked oil, which characterize the influence of additive on properties of oil. Tests were conducted without adding of oil and without use of filter of fine purification; this can explain high values of acid number.

Results of motor tests and appraisal of oils with different additives on laboratory installations permit to divide these oils into separate groups according to increasing effectiveness:

a) oils with alkylphenol additives of type tsiatim-339 and aznii-7;

b) oils with phosphorous-containing additives of the type vnii np-360 and mni ip-22;

c) oils with high-ash sulfonate additives of type $ФМС_{уа}$, NG-102, SB-2.

Tests of additive vnii np-371, obtained by condensation of alkylphenols with formaldehyde, showed that it exceeds additive tsiatim-339 in antiwear properties.

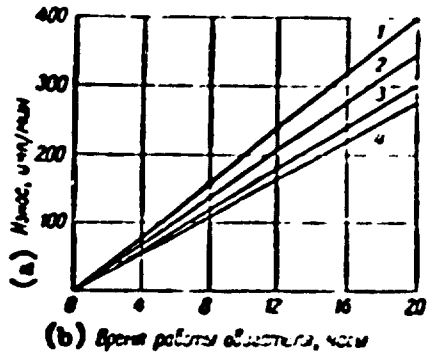


Fig. 3. Wear of piston rings of engine Ch8.5/11 during work on fuel of GOST 305-58 (content of sulfur 0.8%) and oils with different additives (method of radioactive isotopes).
1) oil D-11 without additive; oil DS-11 with additive; 2) 3% aznii-7; 3) 4.5% ip-22; 4) 6% vnii np-360.
KEY: (a) Wear, inp/min; (b) Time of work of motor, hrs.

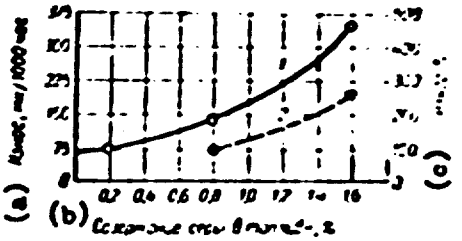
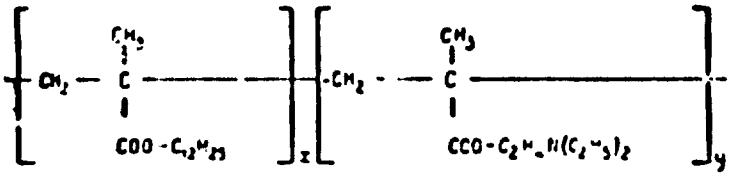


Fig. 4. Wear of bushing of cylinder of engine Ch10.5/13 depending on content of sulfur in fuel.
1) during work on oil without additive; 2) during work on oil with additive vnii np-360.
KEY: (a) Wear, mcoul/1000 hr; (b) Content of sulfur in fuel, %; (c) Wear, %.

Of significant interest are ash-free additives of type VNI-1, offered by VNIINEFTEKhIM*, which represent copolymers of lauryl-α-thacrylate with aminoderivatives of methacrylate. Certain additives of this type, described in foreign literature [8], have the following diagram of structure:



Long-range aspect of nitrogen-containing additives was noted also by S. E. [illegible] [7].

Given tests of additives of type VNI-1 showed that these additives, taken in very small concentration, significantly lower wear of engine, although they possess insufficient detergent properties. Therefore given additives can be recommended for carrying out of further tests as component of additives, including active detergent component.

*All-Union Scientific Research Institute of Petrochemical Processes.

Table 6. Results of Tests of Oil DS-11 With Additives on Engine 2Ch-10.5/13

Fuel	Additive to oil	Wear						Scale formation		Indices of worked oil	
		Last piston ring		Total wear of all piston rings		General wear of engine with respect to content of iron in oil		Number of stuck rings, piece	State of skirt of piston: surface, covered with varnish (in %) & color	Ash content %	Acid number mg KOH/g of oil
		g	%	g	%	g	%				
Diesel fuel of GOST 305-58 (content S = 0.8%)	Without additive	0,10	100	0,22	100	1,25	100	2 (completely)	50 dark-brown	0,91	1,90
	3% tsiatim-339	0,087	87	0,216	98	0,87	70	1 (partially)	10 light-brown	0,56	1,28
	6% vnii np-360	0,05	50	0,09	40	—	—	0	Clean	1,70	0,80
	8% PMS_{ya}-19	0,032	32	0,083	38	0,25	20	0	"	1,87	0,79
	15% NG-102_u	0,026	26	0,059	28	0,30	24	0	"	1,01	0,22
	5% SB-2	0,018	18	0,091	40	0,30	24	0	"	1,03	0,68
	4-5% vnii np-371	0,04	44	0,130	60	—	—	1 (partially)	10 light-brown	0,88	0,73
	0.5% VN-1	0,04	40	0,11	50	0,52	41	2 (partially)	10 light-brown	0,44	0,94
	Without additive	0,007	67	0,21	95	1,0	80	2 (partially)	30 dark-brown	0,20	1,81

Tests of additive vnii np-111 to diesel fuel showed its relatively small effectiveness with respect to antiwear and antiscale properties.

Formerly tested additive to fuel (zinc naphthenate) gave significant lowering of wear of bushings, but with this was observed increase of amount by weight of deposit on piston [5]. Tests of this additive on engine 2D100 at Kharkov factory did not give positive results.

Conclusion

Analysis of results of tests of sulfur-bearing fuels and oils with different additives permits to present diagram (Table 7), showing which oil and with which additives for each group of diesel engines it is possible to use with use in them of fuels with different content of sulfur. This diagram is correct for experimental and industrial additives known at present; it should be examined with the appearance of new more effective additives.

Table 7. Division of Oils by Types of Engines

Group	Type of engine	Fuel with content of sulfur, %		
		to 0.2	to 1.0	More than 1.0
1	Special and perspective diesel engines with high pressure feed	D-11 with additive tsiatim-339 or aznii-7	None	None
2	Forced diesel engines of type 2D100	The same	DS-11 with additive of type vnii np-360	None
3	Low stress diesel engines of type Ch-10.5/13	D-11 GOST 5304-54; DS-11 GOST 8581-57	DS-11, D-11 with additive aznii-7 or tsiatim-339	None

Analysis of obtained results shows that further research works must be directed to obtaining of additives with high detergent and antiwear properties, which would ensure creation of oils for specially heavy conditions of work, intended for lubrication of high-stress diesel engines, working on sulfur-bearing fuels.

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CHAPTER II

SYNTHESIS OF ADDITIVES

ALKYLPHENOL ADDITIVES OF FORMALDEHYDE CONDENSATION

A. V. Druzhinia, G. S. Tarranyan, M. S. Myachina,
and I. V. Morozova
VNII NP*

Aldehydes of different types for the last 10-15 years have been widely used for synthesis of motor oil additives. There is extensive literature about additions of detergents, antioxidant and of the anticorrosive type, synthesized with application of aldehydes [1, 2]. Especially stressed is high effectiveness of additives of alkylphenol formaldehyde condensation.

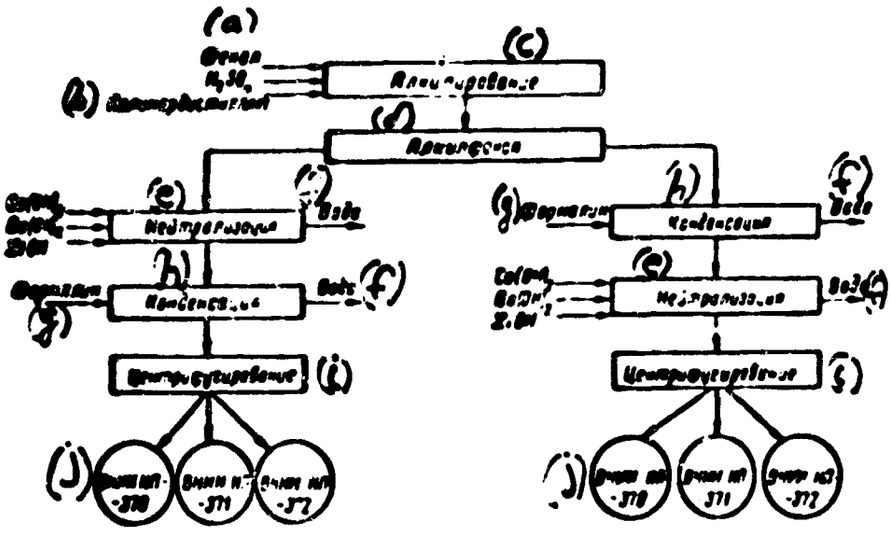
This reaction of formaldehyde condensation [3] can take place in the presence of a small quantity of condensing catalyst, as which we apply acid (HCl, H_2SO_4) and alkali (oxide and hydroxide of metals).

Preparation additives vnii np-370 and vnii np-371 is carried out in alkaline medium; furthermore, the possibility was checked of condensation of alkylphenol in presence of catalyst AFSK (alkylphenol sulfo acid).

Calcium and barium salts of products of alkylformaldehyde condensation possess high detergent properties, remove scorching of piston rings, decrease a number of carbon and act as anticorrosive agents.

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Flow chart of obtaining alkylphenol additives of aldehyde condensation in presence of AFSK (alkylphenol sulfo acid).
KEY: (a) Phenol; (b) Polymer distillate; (c) Alkylation; (d) Alkylphenol; (e) Neutralization; (f) Water; (g) Formalin; (h) Condensation; (i) Centrifuging; (j) VNII NP-*.

The figure is a flow chart showing the obtaining of two additives of alkylphenol formaldehyde condensation developed in VNII NP: calcium vnii np-370 and barium vnii np-371.

Additives vnii np-370 and vnii np-371 can be prepared in existing works in the production of additive tsiatim-339**. Here is excluded the use of catalyst -- benzo sulfo acid, as a result of which the necessity in washing alkylphenol falls, and thereby the problem of liquid phenol waste is positively solved.

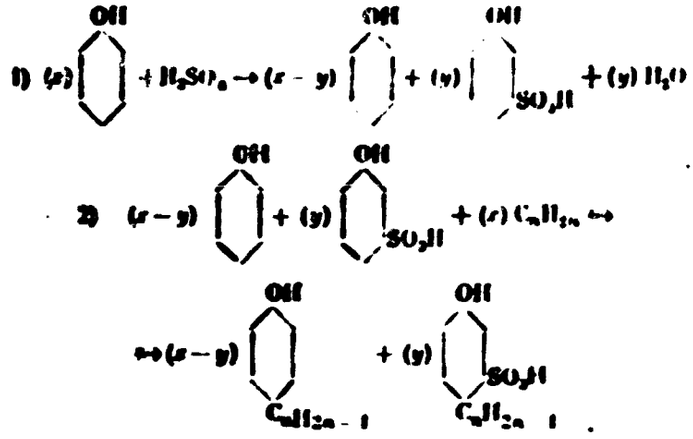
Synthesis of Additive VNII NP-371. Condensation in Alkaline Medium.

Alkylation. During alkylation a wide fraction of polymer distillate (240% in proportion to the phenol which is used). For obtaining alkylphenol sulfo acid 98% sulfuric acid is used in quantity of 8% of the total quantity of phenol and polymer distillate.

*Ed. Note. The different additives are designated by the initials VNII NP, which stands for the All-Union Scientific Research Institute for Oil and Gas Refining and the Production of Synthetic Liquid Fuel.

**Ed. Note. Additive is designated by the initials standing for the Central Scientific Research Institute of Aviation Fuels and Lubricants, developers of the additive.

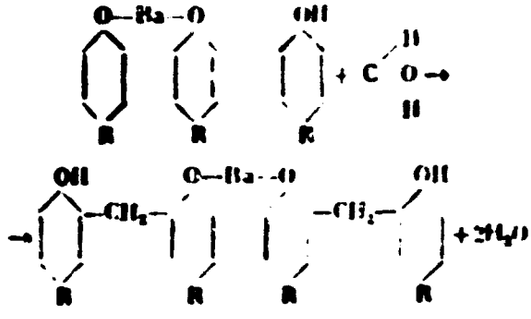
It is assumed that reaction of alkylation goes according to the following diagram.



Preparation of Alkylphenolate of Barium. To obtain alkylphenolate barium we take 1 mole of barium oxide octahydrate on 2 moles alkylphenol. The treatment of alkylphenol by barium oxide hydrate is carried out at 120°.

Condensation. For condensation a 37% aqueous solution of formaldehyde is used calculated from two moles of formaldehyde per 1 mole barium alkylphenol and 2 moles of alkylphenol. Condensation is conducted at a temperature of 70-72°. As diluent industrial oil 12 (axle oil 2) is used.

It is assumed that condensation takes place according to the following diagram:



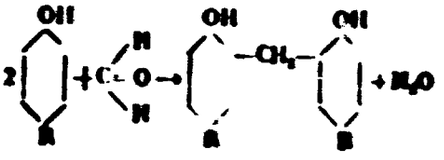
The obtained additive vnii np-371 has the following physico-chemical properties

Ash content, %.....	13—16.5
Content Ba, %.....	7—9
Alkalinity, milligram KOH.....	26—30
Kinematic viscosity at 100°, cs.....	17—80
Content of mechanical impurities, %.....	0.02—0.2

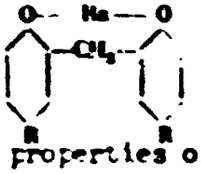
Synthesis of calcium additive vnii np-370 and lithium additive vnii np-372 is carried out according to a diagram analogous to the diagram for obtaining additive vnii np-371, with the only difference being that instead of hydrate of barium oxide is used calcium oxide is used to obtain additive vnii np-370 and hydrate of lithium oxide for obtaining additive vnii np-372. Treatment of alkylphenol by calcium oxide and by a hydrate of lithium oxide is conducted at a temperature of 80°. It is necessary to note that preparation of additive vnii np-370 may be carried out also with a smaller quantity of alkylphenol.

Synthesis of Additive VNII NP-371. Condensation in Presence of APSK

During synthesis of additive vnii np-371 with condensation in an acid medium, the obtained alkylphenol at first is subjected to condensation by a 37% aqueous solution of formaldehyde calculated from 1 role of formaldehyde per 2 moles alkylphenol. In this case the catalyst of condensation is alkylphenol sulfo acid, forming in the alkylphenol during alkylation. It is assumed that reaction of condensation takes place according to the following diagram.



Then condensed alkylphenol is processed by barium oxide octahydrate calculated from 1 mole of barium oxide octahydrate per 1 molecule of condensed alkylphenol. Treatment of condensed alkylphenol by barium hydroxide is conducted in an oil-diluent. The obtained additive, apparently, has the following structure:



Below are the physico-chemical properties of this additive.

Ash content, %..... 18—20
Content Ba, %..... 11—12
Kinematic viscosity at 100°, cs....52.8—82.6

Influence of Quantity of Reagents on Physico-Chemical Characteristic of Additives VNII NP-370 and VNII NP-371

For clarification of influence of different factors on quality of additives vnii np-370 and vnii np-371 a number of investigations was conducted. The role of catalyst AFSK and influence of quantity of formaldehyde and alkylphenol and quality of the additive obtained was investigated.

The role of AFSK during synthesis of addition was determined by the radiometric method. A sample of additive vnii np-370 on alkylphenol was obtained with use of sulfur-35 labeled sulfuric acid. In the synthesized sample of the additive were revealed the sulphogroup, whose content in additive in the conversion to sulfuric acid constituted 3.1%.

Influence of Quantity of Formaldehyde on Physico-Chemical Characteristic of Additives VNII NP-370 and VNII NP-371

To manifest influence of formaldehyde on properties of obtained additive of alkylphenol formaldehyde condensation experiments were conducted using a different quantity of formaldehyde. Thus, for 4 moles of alkylphenol 0.5; 1; 1.5; 2; 3, and 4 moles of formaldehyde were taken.

Results of the investigation are given in Table 1. According to this table, best results with respect to content of calcium are obtained during expenditure of 2 moles of formaldehyde for 4 moles of alkylphenol (experiments 170, 182, 183, and 184).

Table 1. Influence of Quantity of Formaldehyde on Physico-Chemical Properties of Additive VNII NP-370

No experiment	Ratio of reagents, moles: Alkylphenol	Kon	Formaldehyde	Ash Content, %	Content Ca, %	Kinematic viscosity at 100°, cs	Molecular weight
172	4	1	0.5	4.97	1.17	[illegible]	[illegible]
[illegible]	4	1	1.0	6.11	[illegible]	[illegible]	[illegible]
[illegible]	4	1	1.5	7.58	2.11	[illegible]	[illegible]
170	4	1	2	8.31	2.65	[illegible]	[illegible]
[illegible]	4	1	2	7.91	2.31	[illegible]	[illegible]
[illegible]	4	1	2	8.31	2.46	[illegible]	[illegible]
[illegible]	4	1	3	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	4	2	3	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	4	2	4	[illegible]	[illegible]	[illegible]	[illegible]

Influence of Quantity of Alkylrhenol on Quality of Additive

A number of investigations was conducted in synthesis of additive vnii np-370 and vnii np-371 with application of different quantity of alkylphenol (c 0.5, 1 and 2 moles alkylphenol for 1 mole alkylphenolate. Research showed that with decrease of quantity of alkylphenol is observed a lowering of ash content and viscosity of calcium additive vnii np-370. In all three cases good solubility of additive in oil is kept.

During synthesis of barium additive (vnii np-371) with decrease of quantity of alkylphenol ash content and viscosity of additive is increased and its solubility in oil worsens. For instance, a sample of barium additive, synthesized from 2 moles alkylphenol, dissolves well in oil, with one mole of alkylphenol, it dissolves badly (a turbid solution will be formed), and with 0.5 mole of alkylphenol it is not dissolved at all in oil (Tables 2 and 3).

Table 2. Influence of Quantity of Alkylphenol on Physico-Chemical Properties of Additive VNII NP-370

No. experiment	Quantity of alkylphenol taken for condensation with 1 mole alkylphenolate, moles	Kinematic viscosity at 100°, cs	Ash content, %	Content Ca in addition, %	Molecular weight	Content of phenol in driven off water, %	Solubility in oil
107	2	51.99	7.75	2.27	493	0.212	Good
108	1	32.21	7.18	2.11	460	0.207	Good
109	0.5	25.06	6.7	1.97	465	0.198	Good

High-Ash Additives of Alkylphenol Condensation

Investigations have been made on the increase of ash content of additives of alkylphenol formaldehyde condensation. Work was conducted in two directions.

1. Increase of ash content of ready additives of vnii np-370 and vnii np-371 by treating them by an additional quantity of oxide or hydroxide of metal.

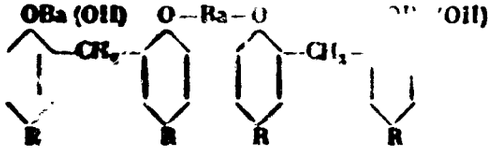
2. Obtaining additives of alkylphenol formaldehyde condensation in presence of activators.

Table 3. Influence of Quantity of Alkylphenol on Physico-Chemical Properties of Additive VNII NP-371

No. experiment	Quantity of alkylphenol taken for condensation with 1 mole alkylphenolate, moles	Kinematic viscosity at 100°, cs	Ash content, %	Content Ba in addition, %	Molecular weight	Solubility in oil
129	2	62.68	15.1	8.85	487	Good
130	1	Gelatinous mass	15.24	9.0	409	Bad
131	0.5	Greasy consistency	15.97	8.4	392	Is not dissolved

Additional Treatment of Additives VNII NP-371 by Hydrate Barium Oxide

Proceeding from the assumed formula of additive vnii np-371, the assumption was made that ash content of additive can be increased by means of substituting hydroxide of metal for hydrogen of hydroxyl group. It was assumed to obtain additive of the following structural formula:



Research in increase of ash content of additive was conducted on a developed type of additive vnii np-371. Below are physico-chemical properties of this sample of additive.

Ash content, %..... 12.9
Content Ba, %..... 7.6
Kinematic viscosity at 100°, cs..... 19.9
Mechanical impurities, %..... 0.19
Alkalinity, milligram KOH..... 29.5
Content of water, %..... 0.3

With the shown purpose, a factory sample of additive vnii np-371 was subjected to additional treatment by hydrate of barium oxide from a calculated 2 moles hydrate oxide on 1 molecule of additive.

However, for selection of optimum quantity of barium hydroxide, research was conducted not only with theoretically necessary quantity of hydrate barium oxide, but also with smaller and larger quantities than the theoretically necessary. The sample of additive additionally was processed with a calculated quantity of hydrate barium oxide at various temperatures; it was established that optimum temperature is 145°.

During additional treatment by hydrate of barium oxide, ash content of additive is increased twice, and viscosity in an insignificant degree (Table 4). From data of the table it is clear that 25% or even 18% hydrate of barium oxide is sufficient (instead of theoretically necessary quantity of 35% in batch of additive in the case when it is diluted by oil-diluent in 1:1 ratio).

Table 4. Influence of Expenditure of Barium Oxide Hydrate on Physico-Chemical Properties of Additive

Indices	Developed type of additive VNII NP-371				
	prior to treatment by hydrate of barium oxide	after treatment by different quantity $Ba(OH)_2 \cdot 8H_2O$, % of initial additive			
		70	35	25	18
Ash content, %.....	12.9	25.8	26.2	24.9	21.6
Content Ba, %.....	7.6	15.8	15.4	14.64	12.72
Kinematic viscosity at 100°, cs.....	19.9	32.2	25.7	25.4	21.19
Mechanical impurities, %..	0.19	—	—	0.027	—
Alkalinity, milligram KOH.	39.5	34.5	—	36.1	32.3

Containing Additives of Alkylformaldehyde Condensation in Presence of Activators

Investigations of products of alkylphenol condensation showed that products of this type can be obtained by different methods. Depending upon quantity of formaldehyde salts of products of alkylphenol formaldehyde condensation can be liquid or viscous at normal temperature.

High-alkali calcium salts of alkylphenols of formaldehyde condensation were synthesized using a larger quantity of formaldehyde and calcium oxide than during synthesis of additive vnii np-370. Synthesis was conducted in presence of an activator.

On 1 mole alkylphenol were taken 1 mole of formaldehyde and 1 mole oxide of metal. Synthesis was carried out in two stages. At first alkylphenol was prepared according to the diagram used for synthesis of additives vnii np-370 and vnii np-371, and then in process of one operation obtaining of products of alkylphenol formaldehyde condensation with simultaneous transformation of them into calcium salts was carried out. Oil-diluent was used 2 times more than alkylphenol for condensation.

In Table 5 are physico-chemical properties of synthesized samples of fully replaced calcium salt of products alkylformaldehyde condensation.

Table 5. Physico-Chemical Properties of Calcium Additive of Alkylphenol Formaldehyde Condensation, Obtained in Presence of Activator

No experiment	Ash Content, %	Content Ca, %	Alkalinity mg KOH	Kinematic viscosity at 100°,	Molecular weight	Color according to NPA
264	12	3.53	53	12.91	394	7.5
282	10.3	3.04	43.1	12.9	—	8.0

When the quantity of formaldehyde and calcium oxide is raised to 1 mole on 1 mole alkylphenol, high-ash and high-alkali calcium additives are obtained with a content up to 3.0-3.53% calcium in the additive.

It is necessary to note that barium additive of alkylphenol condensation (vnii np-371) possesses effective anticorrosive properties and very reliably protects metal from corrosion during application of antiwear additives of the chlorinated paraffin type. Furthermore, the obtained additives of formaldehyde condensation have good color.

Additives vnii np-370 and vnii np-371 passed bench test on different motors according to 100-hour method with sulfurous automobile oil AS-9.5 and diesel oil AS-5. Positive results were obtained.

Mixture vnii np-371 with additive of sulfate type (PMS_{ya}) was tested on motor YaAZ-204 and on a one-cylinder motor IT-9-3 with positive results.

Along with obtaining alkylphenol additives of formaldehyde condensation additives were synthesized on the basis of treatment of barium alkylphenolate in a solution of propylene oxide alkylphenol. Preliminary investigations of the obtained additives by the radiometric method showed that in small concentrations (order of 1.0%) these additives possess high dispersive properties. This direction of works deserves further development.

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INVESTIGATION OF ADDITIVES OF THE TYPE DIALKYLDITHIOPHOSPHATE METALS

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In works published earlier [1-4] it was shown that salts of acid esters of dialkyldithiophor acid (dialkyldithiophosphate) of the general structure $(RO)_2$ PSSMe SSP $(OR)_2$ are active polyfunctional additives to lubricating oils. It was established that additives of this type possess detergents, anticorrosive, and antiwear properties and are, furthermore, antioxidants, and certain are depressors and de-emulsifiers. Individual properties for dialkyldithiophosphates are expressed in various degree and deperd on their structure.

In the mentioned works were determined basic regularities connecting activity of additives and their structure, and basic ways of synthesis of technical additives of this type are outlined.

We have carried out synthesis and conducted research of a number of technical additives of the dialkyldithiophosphate type. Research of these additives, besides being practical, also had scientific value. Comparative research of technical additives of different structure gave new material on dependence of activity of additives on their structure and about the mechanism of action of additives. The obtained results at the same time allowed a more definite recommendation of the individual additives for specific conditions of use.

Dialkyldithiophosphates of metals (additive of type DF) were synthesized, proceeding from technical alcohols. By a known means (action of alcohols with phosphorus pentasulfide) were obtained acid esters of dithiophosphorous acids, which then were reduced into corresponding salts of metals. Structure of obtained additives is represented in Table 1.

Table 1. Structure of Technical Additives of the Type Dialkyldithiophosphate Salts

No.	Additives	Formula
1	DF-1	$[(RO)_2PSS]_2Ba$; R C_{20} C_{24}
2	DF-2	$[(RO)_2PSS]_2Ba$; R C_{16} C_{20}
3	DF-12	$[CH_3-(CH_2)_3-CH(C_2H_5)-CH_2O)_2PSS]_2Ba$
4	DF-5	$[(RO)_2PSS]_2Zn$; R C_{20} C_{24}
5	DF-8	$[CH_3-(CH_2)_5-CHO)_2PSS]_2Zn$
6	DF-9	$[CH_3-(CH_2)_3-CH(C_2H_5)-CH_2O)_2PSS]_2Zn$
7	DF-10	$[CH_3-(CH_2)_5-CHO]_2PSSZnSSP[OCH_2CH(CH_3)_2]_2$
8	DF-11	$[CH_3-(CH_2)_3-CH(C_2H_5)-CH_2O]_2PSSZnSSP[OCH_2CH(CH_3)_2]_2$

Additives DF-1, DF-2, and DF-12 constituted barium dialkyldithiophosphate, the remaining additives -- zinc dialkyldithiophosphate.

To obtain additives DF-1 and DF-5 technical high-molecular alcohols were used, obtained by direct oxidation of fraction of paraffin (petroleum or synthetic), evaporating within the limits of 330-390°; to obtain additive DF-2 -- alcohols obtained by oxidation of fraction of synthetic paraffin, evaporating within limits of 270-320°. The molecular weight of alcohols corresponds to C_{20} -- C_{24} and C_{16} -- C_{20}. A number of additives was obtained on the basis of octyl alcohols. Thus, additive DF-8 was obtained on the basis of secondary octyl alcohol, n-octanol-2, and additives DF-9 and DF-12 -- on the basis of primary octyl alcohol 2-ethyl-hexanol,

known in industry as isooctyl alcohol. Each of additives DF-10 and DF-11 was obtained from two alcohols — isobutyl and octyl and contained thus radicals of a different structure: additive DF-10 — isobutyl and secondary octyl, additive DF-11 — isobutyl and isooctyl. The practical value of compounds of the last type is also confirmed by reference [5]. All synthesized additives were studied and were applied in the form of their solutions in light oil in a 1:1 ratio.

Content of phosphorus, sulfur and metal in investigated additives is given in Table 2. Given values pertain to 50% solutions of additives in oil; calculated values correspond to formulas of Table 1.

For carrying out comparative tests of additives oil DS-8 from sulfurous oils was used, obtained by mixing 86% distillate and 14% residual components.

Table 2. Results of Additive of the Type Dialkyldithiophosphate Metals

Additive	Molecular weight of dialkyldithiophosphates (calculated)	Metal, %		Phosphorus, %		Sulfur, %	
		calculated	found	calculated	found	calculated	found
DF-1	1516—1740	4.53—3.93	4.20	2.04—1.78	1.63	4.28—3.68	3.40
DF-2	1293—1516	5.31—4.53	4.64	2.39—2.04	1.93	4.95—4.23	4.23
DF-12	844.5	8.17	7.9	3.66	3.29	7.59	—
DF-5	1444—1668	2.26—1.95	1.8	2.14—1.85	1.93	4.44—3.75	3.37
DF-8	772.5	4.23	4.18	4.01	3.34	8.30	9.02
DF-9	772.5	4.23	3.90	4.01	3.84	8.30	8.18
DF-10	660.3	4.95	5.00	4.69	4.66	9.70	9.49
DF-11	660.3	4.95	5.28	4.69	4.50	9.70	9.55

Influence of additives on detergent, de-emulsifying, anticorrosive, and antiwear properties of oil DS-8 was investigated; also influence of additives on low-temperature properties of oil DS-8 (depression of solidification point) and on its stability was established.

Dialkyldithiophosphate metals are typical surface-active materials. The action of such additives on some of the shown properties of oil is determined first of all by their surface activity — ability to be adsorbed on boundary of two phases.

Surface activity of additives determines detergent and depressor action of additives, their action as de-emulsifiers and partly as anticorrosive additives, i.e., in those cases when mechanism of action is caused by adsorption of additives and presence of two phases in system.

The influence of structure of hydrocarbon radicals on surface activity of compounds is known. It is interesting to compare in this respect, compounds containing different metals, and namely zinc and barium dialkyldithiophosphate, serving as the subject of present research.

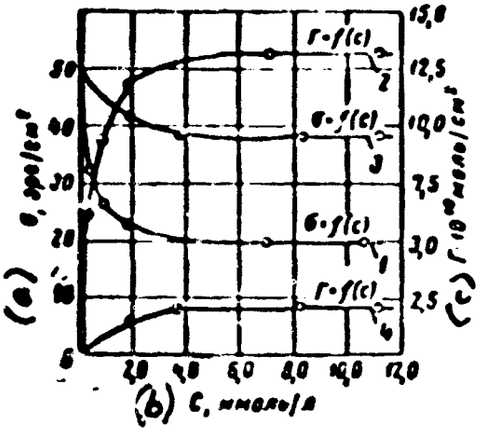


Fig. 1. Isotherms of surface tension $\sigma = f(c)$ and isotherms of adsorption $G = f(c)$ of solutions of barium dioctadecyldithiophosphates zinc in vaseline oil on boundary with water.
1 and 2 — barium dialkyldithiophosphate $[(C_{18}H_{37}O)_2\ PSS]_2\ Ba$;
3 and 4 — zinc dialkyldithiophosphate $[(C_{18}H_{37}O)_2\ PSS]_2\ Zn$.
KEY: (a) σ, erg/cm^2; (b) C, m mole/l; (c) $G \cdot 10^{10}$ mole/cm^2.

Isotherms of surface tension on boundary of two phases were removed: solution of additive in hydrocarbon medium (vaseline oil) — water. As additives pure preparations of barium and zinc di-n-octadecyldithiophosphates. Surface tension $\sigma_{1,2}$ was determined at a temperature of 77.5° by finding the biggest pressure drops, using an instrument of P. A. Rebinder [6]; relatively high temperature was necessary for increase of solubility of barium di-n-octadecyldithiophosphate in vaseline oil.

Isotherms of surface tension $\sigma = f(c)$ and isotherms of adsorption $G = f(c)$ corresponding to them for both dialkyldithiophosphates are shown in Fig. 1.

In Fig. 1 it is clear that surface activity of barium di-n-octadecyldithiophosphate is significantly higher than for zinc di-n-octadecyldithiophosphate. Limit adsorption G_∞ corresponding to total saturation of adsorptive layer, for the first compound constitutes $13.1 \cdot 10^{-10}$, for the second $2.0 \cdot 10^{-10}$ mole/cm^2.

Calculated from these values, the area occupied by one molecule in the adsorption layer, for dialky dithiophosphate of barium constituted 12.6 $\mathring{A}^2$, and for zinc dialkyldithiophosphate 81.1 $\mathring{A}^2$.

On the basis of obtained results, it is possible to assume that in cases when mechanism of action of additives is determined mainly by their adsorption on boundary of two phases, barium dialkyldithiophosphate will be more active additives than zinc dialkyldithiophosphate; at the same time optimum concentration of salts of zinc will be lower than optimum concentration of salts of barium. As will be shown, this conclusion was confirmed during comparative investigations of technical additives.

Detergent Action of Additives

The mechanism of detergent action of additives is very complicated, and up to now not fully clarified. Basic property of majority of detergent additives is their ability to disperse insoluble products of aging and incomplete combustion of hydrocarbons of oil and fuel and to stabilize suspension of these products in oil. Detergent additives like surface active material are adsorbed on insoluble particles formed in oil, preventing thereby their adhesion and precipitation on motor parts.

Earlier, during investigation of individual salts of dialkyldithiophosphate, it was shown that their detergent action depends on length of hydrocarbon radicals. With increased length of hydrocarbon radicals of molecule of additive the detergent action of additive increases [1].

In Table 3 are given results of determination of detergent properties of oil DS-8, containing different technical additives.

Determinations were conducted on laboratory one-cylinder motor PZV [7] in more rigid conditions than are standard. As follows from data of Table 3, all additives of the considered type are detergent additives; however, their activity in this respect is relatively low. The latter, apparently, partly is caused by properties of the oil itself, since other types of oils are more sensitive with respect to detergent action of dialkyldithiophosphates.

Table 3. Influence of Additives of the Type Dialkyldithiophosphate Metals on Properties of Oil DS-8
Concentration Additives in Oil 3.5 %

Additive	Detergent properties of oil		De-emulsification (quantity of undecomposed emulsion), %	Corrosionability, g/m²	
	Points	Quantity of varnish precipitation, g		Oil DS-8	Oil MT-16 (Pmba)
Oil without additive	4.0—4.5	0.35	22	2.2	33.7
DF-1	2.5	0.15	0	0.9	2.1
DF-2	4.0	0.30	0	1.8	3.2
DF-12	3.0	0.25	4	—	4.2
DF-5	3.0	0.20	12	4.9	10.9
DF-8	4.0	0.30	16	4.7	13.5
DF-9	2.5	0.05	18	3.8	11.5
DF-10	3.0	0.15	16	4.4	11.2
DF-11	3.0	0.10	18	5.6	8.3

Quantity of deposits and varnish precipitation on piston of motor PZV in presence of additives is lowered by 1.0-1.5 point. The most effective turned out to be additive DF-1 (high-molecular barium dialkyldithiophosphate), in presence of which detergent action of oil corresponded to 2.5 points (for pure oil 4.0-4.5 point). Dialkyldithiophosphate of barium of smaller molecular weight (DF-2 and DF-12), just as high-molecular dialkyldithiophosphate of zinc (DF-5), possessed less detergent action. This is in full agreement with above-indicated influence of nature of metal (barium and zinc) and length of hydrocarbon radicals on surface activity of dialkyldithiophosphates.

Influence of Additives on Fluidity of Oil at Low Temperatures

From obtained dialkyldithiophosphate only additive DF-1 possessed the properties of a depressor. Temperature of thickening of oil DS-8 (-15°) in presence of 3.5%

addition DF-1 was lowered to -37°; depression of temperature of thickening thus constituted 22°. Other additives did not lower temperature of thickening of oil.

Specific action of additive DF-1 as a depressor, just as detergent action of this additive, is in accordance with its heightened surface activity as compared to other additives, which are either salt of zinc, or salt of barium of smaller molecular weight. As was shown earlier, depressor action of additives of different structure is in direct dependence on their surface activity (adsorptive characteristic) [8].

De-emulsion

Certain dialkydithiophosphate metals as surface active material are typical de-emulsifiers, able to destroy emulsions formed by hydrocarbons of oils and water [3].

De-emulsifying action of technical additives of the considered type was determined according to the already described method [9]: there was established the quantity of standard oil — water emulsion, remaining undestroyed after centrifuging during 30 minutes in presence of different additives preliminarily dissolved in oil. The obtained results are given in Table 3.

From data of Table 3 it follows that de-emulsifying action of technical additives, as one should have expected, also is in direct dependence on their surface activity. Barium dialkyldithiophosphates are stronger de-emulsifiers than zince dialkyldithiophosphates, but in a number of barium dialkyldithiophosphates — compound of the biggest molecular weight. Thus, additive DF-1 and DF-2 in the test conditions completely destroyed the emulsion, whereas in presence of additive DF-12 part of emulsion remained undestroyed (quantity of undestroyed emulsion constituted 4% as opposed to 22% in absence of additive). Although zinc dialkyldithiophosphates are weak de-emulsifiers, in a number of these additives the most active de-emulsifier was the additive of the biggest molecular weight, containing the longest hydrocarbon radicals (DF-5).

Anticorrosive Properties of Additives

According to the most wide-spread opinion, anticorrosive additives chemically interact with metal, forming on its surface a protective film, which protects metal from corrosion [10]. Recently the assumption was expressed that this is the most effective film formed on metal surface as a result of adsorption of molecules of additives [11].

Earlier [1] it was shown that the basic element determining anticorrosive properties of metal dialkyldithiophosphates is sulfur; anticorrosive properties of these compounds depend also on nature of metal.

Anticorrosive properties of technical additives of the type metal dialkyldithiophosphates are determined according to the method of NAMI [State All-Union "Order of Labor Red Banner" Automobile and Automobile Engine Scientific Research Institute] [12]; corroding action of oil with additives — according to decrease of weight of lead plate (in g/m^2) during influence on it of products of oxidation of oil in standard conditions.

Since corrosiveness of pure oil DS-8, obtained from sulfurous oils, is very insignificant (2.2 g/m^2), also corresponding determination were also conducted for additives with oil MT-16 from Emba oils; corrosiveness of pure oil MT-16 constitutes 33.7 g/m^2.

From data of Table 3 it follows that all technical additives possess strong anticorrosive action, while several are more effective than barium dialkyldithiophosphate (DF-1, DF-2 and DF-12); corrosiveness of oil MT-16 in presence of barium dialkyldithiophosphates is lowered approximately 10 times. Anticorrosive action of different zinc dialkyldithiophosphates is practically equal (corrosiveness of oil MT-16 is lowered 3 times) and does not depend on magnitude and structure of hydrocarbon radicals.

Besides determination of anticorrosive action of additives by the method of NAMI, also corrosion action of the additives themselves on copper plates (M-1) was

studied which, apparently, depends on thermal stability of additives.

With this goal were tested 3.5% solutions of additives in a butyric base of oil VNII NP-1 (oil for automatic transmissions of automobiles). Copper plates were kept in oil for 3 hours at temperatures of 130°, 140°, and 150°, after which formation of sulfurous copper was visually determined. As was established, low-molecular dialkyldithiophosphates at high temperatures corrode copper in the least degree. At a temperature of 150° oil containing additives DF-12, DF-8, DF-9, DF-10, and DF-11, absolutely did not change surface of copper plate.

Wear During Friction in Conditions of High Loads

In recent years a number of works have been published, dedicated to research of metal dialkyldithiophosphates, especially zinc dialkyldithiophosphates as additives lowering wear during friction in conditions of high loads [5, 13, 14]. Additives of this type turned out to be very effective during application in specific conditions of friction of cam — pusher pair in V-shape automobile engines: the additives prevent development of pitting of pushers, frequently observed in these conditions. Apparently, the action of metal dialkyldithiophosphates as antiwear additives is caused by their chemical interaction with metal of friction surface.

As was established in the example of other thiophosphororganic compounds, in conditions of high loads and heightened temperatures, in places of contact the additive is decomposed with formation of chemically active compounds, which in turn react with metal of friction surface, forming a sulfide-phosphide film [15]. Thermal stability of compounds, therefore, plays an essential role in mechanism of action of antiwear additives.

Tests of antiwear properties of technical additives -- dialkyldithiophosphates of metals — were conducted on a four-ball friction machine. Spheres prepared of steel ShKh-9 12.7 mm diameter were used. Relative speed of slip of surfaces of friction of spheres was around 0.25 m/sec.

For all samples of oil with additives curves of dependence of wear were obtained (average diameter of spot of wear on lower spheres in mm) from total axial load (in kg).

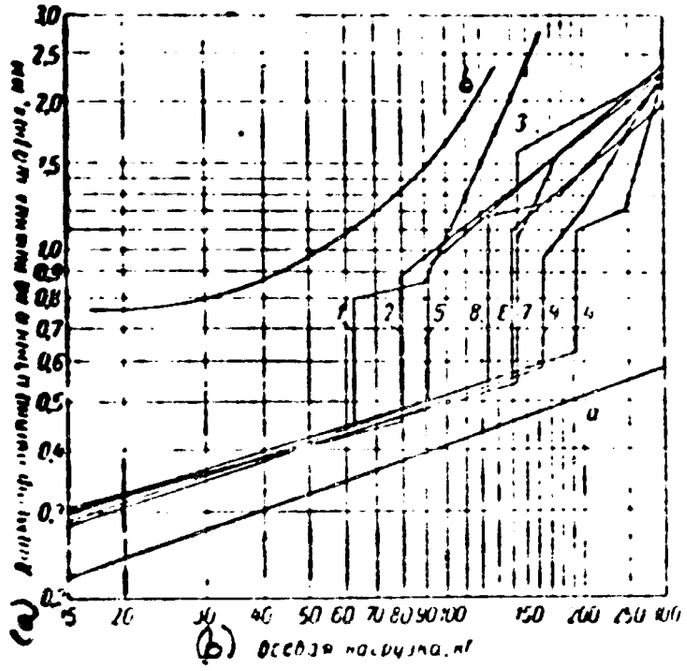


Fig. 2. Influence of metal dialkyldithiophosphates on wear during friction.
Oil DS-8; concentration of additive in oil 3.5%.
a—line of elastic deformation; b—wear during dry friction; 1—oil without additive; oil with additive: 2—DF-1; 3—DF-2; 4—DF-12; 5—DF-5; 6—DF-8; 7—DF-9; 8—DF-10; 9—DF-11.
KEY: (a) Diameter of spot of wear on lower spheres, mm; (b) Axial load, kg.

Critical loads were defined as loads at which wear is increased (break of curves on graphs of Fig. 2), caused by local breaks of butyric and "seizing" of surfaces of friction.

In Fig. 2, and also from data of Table 4, it is clear that all investigated additives sharply increase critical load sustained by oil during friction, where the most effective in this respect turned out to be barium and zinc dialkyldithiophosphates of the least molecular weight, containing in the molecule relatively short hydrocarbon radicals. Antiwear properties of high-molecular dialkyldithiophosphates (DF-1 and DF-5) are expressed noticeably weaker than for the low-molecular. Increase of antiwear properties of dialkyldithiophosphates with decrease of length of hydrocarbon radicals contained in their molecules, may be seen especially graphically in comparison of wear — load curves (see Fig. 2) in a number of barium salts (DF-1, DF-2 and DF-12).

Table 4. Influence of Additives of the Type Metal Dialkyldithiophosphates on Properties of Oil DS-8
Concentration of Additives in 3.5% Oil

Additive	Wear, critical load P_k, kg	Stability	
		Thermo-oxidizing stability, minutes	Content of resins in processed oil, %
Oil without additive	64	19	15.2
DF-1	80	65	7.0
DF-2	145	50	—
DF-12	194	66	—
DF-5	92	60	8.0
DF-8	142	66	5.4
DF-9	145	62	6.0
DF-10	125	63	7.3
DF-11	165	56	6.8

There is indication that effectiveness of zinc dialkyldithiophosphates with respect to preventing of pitting of pushers is higher the lower their thermal stability is; where temperature of decomposition of these compounds lies below 150° [14]. According to our data the temperature of the beginning of decomposition dialkyldithiophosphates of zinc and barium lies within the limits of 140-160°.

Influence of Additives on Stability of Oil

It was established that additives of the type metal dialkyldithiophosphates increase thermo-oxidizing stability of oil DS-8; they delay also formation of soluble resins in oil during its test on PZV setup.

Thermo-oxidizing stability of oil was determined by standard method [16]. From data of Table 4 it is clear that all technical additives significantly (approximately 3 times) increase thermo-oxidizing stability of oil DS-8. In this case any influence of structure of additive was not revealed: during test of all additives close results were obtained.

Determined also was influence of additives on resin formation in conditions of operation of PZV setup. From data of Table 4 it is also clear that all additives almost in identical degree (approximately 2 times) lower content of resins, forming in oil during work of motor.

The question about influence of dialkyldithiophosphates of metals on stability of oil is considered in more detail in a special report [17].

Concentrations of Additives

In the above described research the concentrations of additives constituted 3.5% of oil. Consequently, depending upon molecular weight of additives their molar content in oil, and also quantitative content in oil of metal, phosphorus, and sulfur was different that could have value during comparative estimate of additives. In connection with this, in this work in all cases parallel tests were conducted of oil DS-8, containing equimolecular quantities of additives, namely 1.05 mole on 100 g oil. Content of phosphorus in all additives constituted 0.065%, sulfur 0.13%, barium (in barium salts) 0.146%, zinc (in zinc salts) 0.069%. Concentrations by weight of additives, corresponding to the used equimolecular concentration, were, naturally, different: 3.5% DF-1; 3.0% DF-4; 3.3% DF-5; 1.7% DF-8 and DF-9; 1.6% DF-10 and DF-11; 1.8% DF-12. Majority of additives thus was tested in concentrations by weight less than 3.5%.

It was established that in those cases when mechanism of action of additives depends on their surface activity (for instance, detergent action of additives), action of zinc dialkyldithiophosphates is changed (drops) due to decrease of concentration by weight in smaller degree than action of similar barium dialkyldithiophosphates (DF-1 and DF-5, DF-12 and DF-9). This phenomenon is in accordance with the fact that optimum concentration of salts of zinc should be lower than optimum concentration of salts of barium.

Conclusions

As a result of conducted synthesis and research investigation of a number of technical additives of the type dialkyldithiophosphates of barium and zinc it was established that:

1) additives of this type possess detergent, anticorrosive, and antiwear properties and are, furthermore, antioxidants, and some of them are depressors and, de-emulsifiers;

2) separate properties of dialkyldithiophosphate metals as additives to lubricating oils are expressed in different degree and depend on structure of additives;

3) properties of additives — dialkyldithiophosphate metals, which depend on their surface activity (detergent and de-emulsifying action; partly anticorrosive action; depression of temperature of thickening of oils) in the greatest degree appear for high-molecular barium dialkyldithiophosphates. Other properties of additives (antiwear properties) are expressed stronger for relatively low-molecular metal dialkyldithiophosphates.

Properties of first type of dialkyldithiophosphates are in accordance with their adsorptive characteristic;

4) in practical relation, the greatest interest is in additive DF-1 (heightened detergent, anticorrosive and de-emulsifying property) and additive DF-11 (heightened antiwear properties).

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SYNTHESIS OF DIESTERDITHIOPHOSPHOROUS ACIDS AND OF THEIR DERIVATIVES ON THE BASIS OF SUBSTITUTED PHENOLS AND APPLICATION OF THEM AS ADDITIVES TO OIL PRODUCTS

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Chang Hsiu-Cheng, and
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MINKh i GP*

Diesterdithiophosphorous acids and their salts during the last 10 years have found wide application abroad [1, 2] as highly effective multifunctional additives to lubricating oils for engines with stressed operating conditions. Namely this type of phosphorous additives turned out to be the most effective as compared to other phosphorous additives and quickly occupied first place, displacing all other types of phosphorous additives on the foreign market.

We studied the reaction of phosphorous pentasulfide with substituted phenols, conducted synthesis on the basis of obtained diesterdithiophosphorous acids of multifunctional additives and investigated dependence of activity additives on their composition and structure. The following types of phosphorous additives are obtained on the basis of substituted phenols:

1) calcium, barium and zinc salts of diestherdithiophosphorous acids;

*Moscow Order of Labor of the Red Banner Institute of the Petroleum Chemical and Gas Industry named for Academician I. M. Gubkin.

2) ash-free additives in the form of binary compounds of diesterdithiophosphorous acids with aliphatic amines and amides, and also in the form of triesters of dithiophosphorous acid;

3) phenolates 2.2 methylene-bis (6-dithiophosphoric acid methyl 4-tert-octyl phenol);

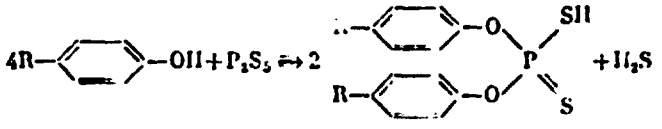
4) salts of esters of diamidodithiophosphorous acid.

Synthesis of Diesterdithiophosphorous Acids and of Their Salts

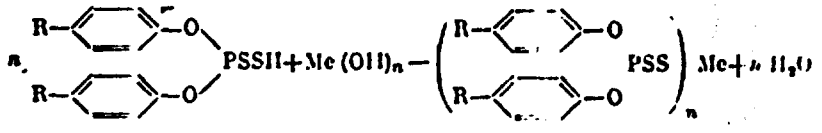
Initial raw material for synthesis of diesterdithiophosphorous acids was a homologic series of substituted phenols with alkyl radicals from C_4 to C_{12}, disulfides of these, phenols, and also bisphenols with methylene cross-link. Synthesis of alkyl-and aryl-substituted phenols and their derivative sulfide and disulfides is described in [3, 4]. Therefore, here are presented only the results of research of initial alkylphenols, obtained for their further processing on additives (Table 1).

Diesterdithiophosphorous acids were obtained by the reaction of above-indicated substituted phenols or bisphenols in a solution of toluene. Reaction took place 1-1.5 hours at a temperature of 110° according to the following diagram:

1st stage



2nd stage



where R — alkyl radical from C_4—C_{12}; Me—Ca, Ba, Zn; n equals 1 or 2.

The obtained diesterdithiophosphorous acids after determination of acid number (Table 2) and establishment of end of reaction were changed into a salt of calcium, barium, and zinc by neutralization by corresponding oxides or hydroxides of metals

(zinc salts were obtained by neutralization of diesterdithiophosphorous acid by zinc acetate).

After separation of insoluble impurities by filtration and distillation of solvent, the ready additive was investigated.

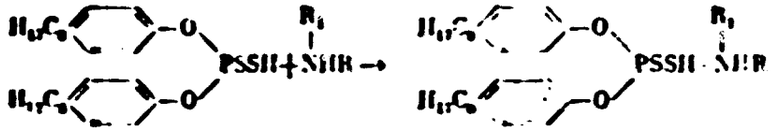
The obtained compounds, their formulas, and results of their investigation are given in Tables 3, 4, 5.

Ash-free additives were obtained in two types:

1) in the form of binary compounds of diesterdithiophosphorous acid with aliphatic amines or amide and

2) in the form of triesters of dithiophosphorous acid.

Binary compounds were obtained according to the following diagram:



where R — alkyl radical; R_1 -- alkyl radical or hydrogen.

As organic bases primary and secondary aliphatic amines were used: α-methyl stearylamine, octadecylamine, guanidine, and also diamide of sebacic acid.

Binary compounds were synthesized by heating diesterdithiophosphorous acid with corresponding amines or amide in a benzene medium. Reaction took place for 1 hour (with guanidine, 5 hours) at a temperature of 40°. When diamide of sebacic acid was used as an organic base, reaction took place at a temperature of 160°.

In Table 6 are given formulas and results of investigation of the obtained compounds.

Ash-free additives in the form of tri-esters of dithiophosphorous acid were obtained during the reaction of diesterdithiophosphorous acid with propylene oxide according to the following diagram:

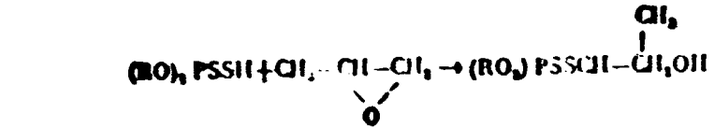


Table 1. Character[illegible] Initial and Intermediate Products (Alkylphenols and Disulfides of Alkylphenols)

Compounds	Molecular weight		Content of groups OH, %		Content of Sulfur, %		d^{20}	n_D^{20}	MR		Melting point, °C	
	Calculated	Found	Calculated	Found	Calculated	Found			Calculated	Found	Source material	Found
tert-Butylphenol.....	150	150	11.3	11.3	—	—	—	—	—	—	97-[illegible]	98
tert-Amylphenol.....	164	165	10.4	10.3	—	—	—	—	—	—	[illegible]	[illegible]
tert-Amylphenol disulphide.	390	388	8.72	9.64	—	—	—	—	—	—	—	—
sec-Heptiphenol.....	192	192	8.25	9.3	55.4	59.0	0.9420	1.5040	—	—	—	[illegible]
Disulfide of sec-heptiphenol.....	446	452	7.6	7.8	—	—	—	—	—	—	—	—
tert-Octylphenol.....	206	208	8.25	8.24	—	—	—	—	—	—	73-75	—
Disulfide of mono-tert-octylphenol.....	474	473	7.17	7.24	13.5	12.24	—	—	—	—	—	—
Disulfide of di-tert-octylphenol.....	698	690	4.8	4.7	—	—	—	—	—	—	—	—
2,2-methylene-bis (4-di-tert-octylphenol).....	424	443	8.01	8.35	—	—	—	—	—	—	—	—
2.2-methylene-bis (4.6 di-tert-octylphenol).....	648	541	5.24	5.0	—	—	—	—	—	—	—	—
sec-Octylphenol.....	206	204	8.25	8.29	60.62	64.0	0.9295	1.5025	—	—	—	[illegible]
Disulfide of 2-ethyl-hexylphenol.....	206	199	8.25	9.5[illegible]	—	—	0.9525	1.5110	[illegible]	[illegible]	—	[illegible]

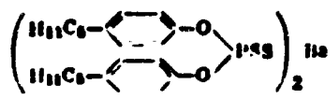
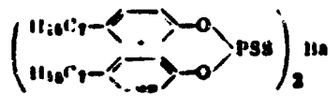
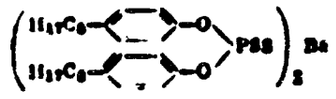
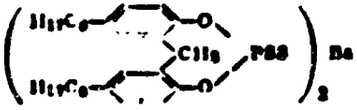
Table 2. Characteristics of Diesterdithiophosphorous Acids

Acid	Acid number, milligram KOH	
	Calculated	Found
tert-Butylphenol diesterdithiophosphorous..	142	141.4
tert-Amylphenol diesterdithiophosphorous...	132.6	129.2
tert-Octylphenol diesterdithiophosphorous..	110.5	111.0
Disulfide-tert-octylphenol diesterdithiophosphorous.....	98.5	103.0
2.2-methylene-bis-4-tert-octylphenol diesterdithiophosphorous.....	107.0	105.5
bis-Heptyl diesterdithiophosphorous.....	117.1	107.5
2-ethylhexylphenol diesterdithiophosphorous.....	110.6	106.5
Disulfide-2-ethylhexylphenol diesterdithiophosphorous.....	98.5	97.3

Table 3. Calcium of Salts Diesterdithiophosphorous Acid

Calcium salt of diesterdithiophosphorous acid on a base of	Content, %							Useful properties of oil MT-16 with 1.5% additive		
	Ash	Calcium		Phosphorus		Sulfur		thermooxidizing stability at 260°, minutes	coefficient of varnish formation A,	detergent properties with respect to PZV, points
		Calculated	Found	Calculated	Found	Calculated	Found			
Monoalkylphenol disulphide (IP-22k, alkali)..	32.1	3.4	11.9	5.28	5.0	21.8	15.0	48	0.56	0.5—1
Dialkylphenol disulphide (IP-22k, alkali).....	21.4	2.4	9.0	3.82	4.1	15.7	13.3	43	0.60	1
Monoalkylphenol disulphide (IP-22k, neutral, antioxidant).....	9.2	3.4	1.7	5.25	5.95	21.8	13.3	86	0.32	2—2.5
Dialkylphenol disulphide (Academy of Sciences-22k, neutral, antioxidant)...	10.7	2.46	2.0	3.82	5.76	15.7	13.8	84	0.31	—
Monoalkylphenol (IP-150k, alkali).....	18.0	3.8	4.0	5.9	4.8	12.2	9.9	52	0.55	1
Monoalkyldiphenol (neutral, antioxidant).....	15.7	3.8	3.03	5.9	5.0	12.2	10.0	91	0.27	—

Table 4. Barium Salts of Diesterdithiophosphorous Acid

Formula of compound	Content, %							Performance properties of oil MT-16 with 1.5% additive		
	Ash	Barium		Phosphorous		Sulfur		Thermo-oxidizing stability at 260°, minutes	Coefficient of varnish formation K_v	Detergent properties with respect to PZV, points
		Calculated	Found	Calculated	Found	Calculated	Found			
	34.5	14.0	16.5	6.35	6.0	13.1	14.6	67.5	0.39	1.5–2
	30	12.5	13.4	5.7	5.4	11.7	10.0	57	0.5	2
	28	12.0	10.5	5.4	4.9	11.2	10.0	78	0.34	3
C 5% additive										
	19.4	11.5	15.3	5.3	4.9	10.9	8.5	95	0.2	1.0–1.5

(Table 4 Continued)

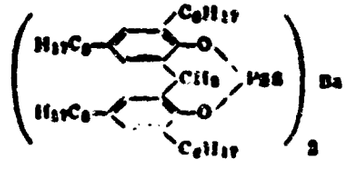
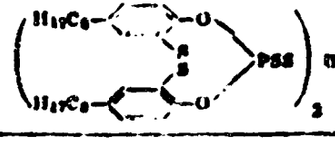
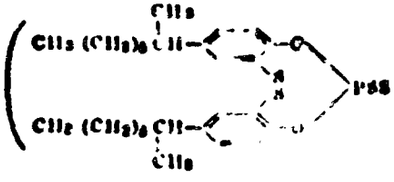
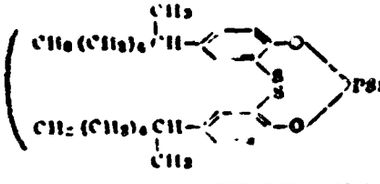
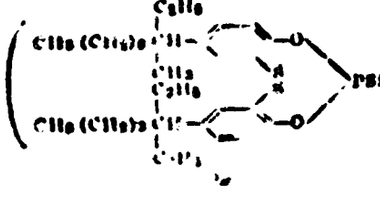
	25	5.0	14.8	3.8	3.7	7.8	6.4	C 5% additive 68	0.3	1.0—1.5
	20	10.8	9.0	4.8	4.4	20.0	21.0	71	0.39	2
	20.8	12	14.1	5.4	5.2	11.2	10.3	87	0.4	Temperature of thickening −26°
	27.8	11.8	14.8	5.3	5.0	22	—	78	0.3	Temperature of thickening −25°
	22.6	10.6	13.0	4.8	4.7	20	—	88	0.3	Temperature of thickening −15°

Table 5. Zinc Salts of Diesterdithiophosphorous Acid

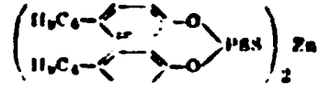
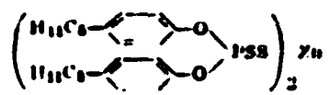
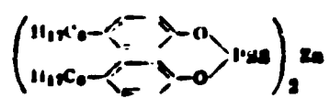
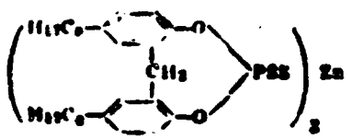
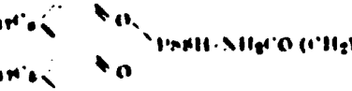
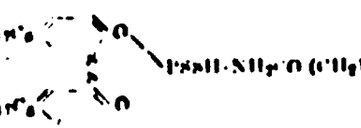
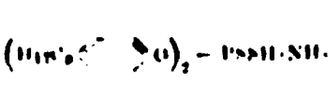
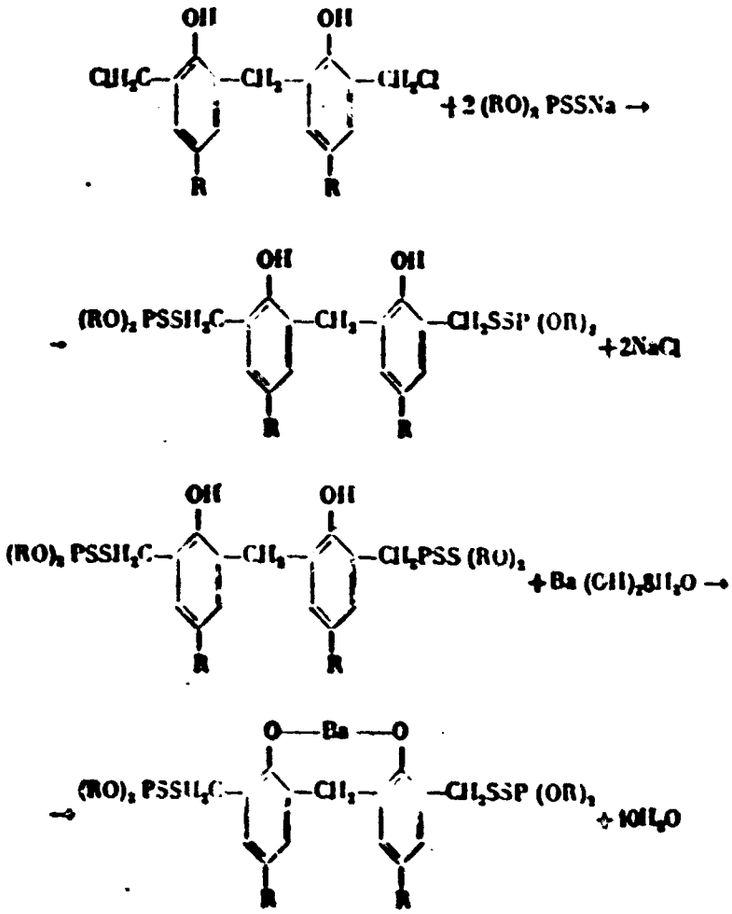
Formula of compound	Content, %							Performance properties of oil MT-16 with 1.5% additive		
	Ash	Zinc		Phosphorous		Sulfur		Thermo oxidizing stability at 260°, minutes	Coefficient of varnish formation K_a	Detergent properties with respect to PZV, points
		Calculated	Found	Calculated	Found	Calculated	Found			
	19.9	7.03	7.59	7.27	6.50	15.01	14.2	50	0.5	4—4.5
	—	7.16	6.1	6.85	6.10	14.1	13.2	61	0.6	—
	16.1	6.06	5.0	5.76	5.25	11.9	11.7	74	0.6	4—4.5
	15.8	5.1	3.1	5.16	—	21.3	—	66	0.6	—
	19.0	5.87	4.2	5.2	—	11.8	—	72	0.6	—

Table 6. Binary Compounds of Diesterdithiophosphorous Acid With Aliphatic Amines and Amide

Formula of compound	Content, %				Performance properties of oil MT-16 with 1.5% additive						
	Nitrogen		Phosphorous		Thermo oxidizing stability at 150°C, minutes	Thermo oxidizing stability at 200°C, minutes	Coefficient of varnish formation K_n	Volatility	Working fraction, %	Critical temperature, °C	Detergent properties with respect to PZV, points
	Calculated	Found	Calculated	Found							
	1.61	0.15	3.61	3.8	108	75	0.36	45.0	54	270	4—4.5
	1.6		3.7	3.5	62	66	0.4	57.0	63	270	—
	2.3	—	5.11	4.8	65	50	0.5	55.0	65	260	—
	2.0	—	5.0	4.9	78	57	0.5	52.0	66	265	3—3.5
	7.1	7.0	5.1	5.0	—	76	0.25	—	—	—	—

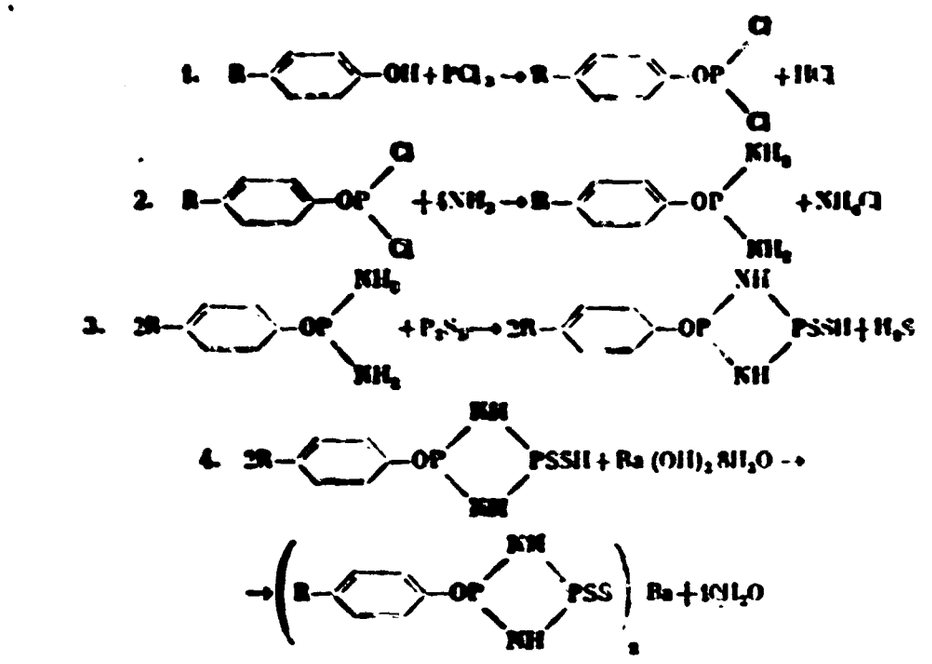
To diesterdithiophosphorous acid in solution of benzene, slowly heated up to 70° (1 hour), from a liquid-drop funnel (immersed in mixture) was added propylene oxide. Reaction was finished, when test for methyl orange showed neutral reaction. After removal of surplus oxide of propylene and solvent — benzene — distillation of the ready additive was investigated. Results of investigation and formulas of obtained compounds are given in Table 7.

A third group of synthesized compounds of the type phenolates 2.2-methylene-bis (6-dithiophosphoric acid methyl 4-tert-octylphenol) was obtained by condensation of chloromethyl alkylphenol or its disulfide with sodium salt of diesterdithio-phosphorous acid in a solution of ethyl alcohol during heating for 1.5-3 hours at a temperature of 70-80°.



Results of investigation obtained compounds and their formulas are presented in Table 8.

Additives of the 4-th group of salt types from esters of diamidodithiophosphorous acid were obtained according to the following diagram:



In the beginning, by heating at 50° for 4 hours a halide compound of phosphorous and n-tert-octylphenol or its disulfide in a solution of toluene, acid chloride of ester of phosphorous acid was obtained, which during subsequent interaction of it with gaseous arronia in conditions of cooling of reaction mixture by ice was turned into ester of diamidophosphorous acid. After distillation of a light solvent — toluene and its replacement by a kerosene solvent, the obtained product reacted with phosphorous pentasulfide for 2 hours at a temperature of 179-185°. After separation of residue of phosphorous pentasulfide by filtration and distillation of kerosene ester of diamidodithiophosphorous acid was obtained. Salts of this compound were obtained by treating the ester by hydrate barium oxide. By this means two compounds were obtained.

Results of investigation and formulas of obtained compounds are given in Table 9.

Table 7. Ash-Free Additives of the Type Triesthers of Dithiophosphorus Acid

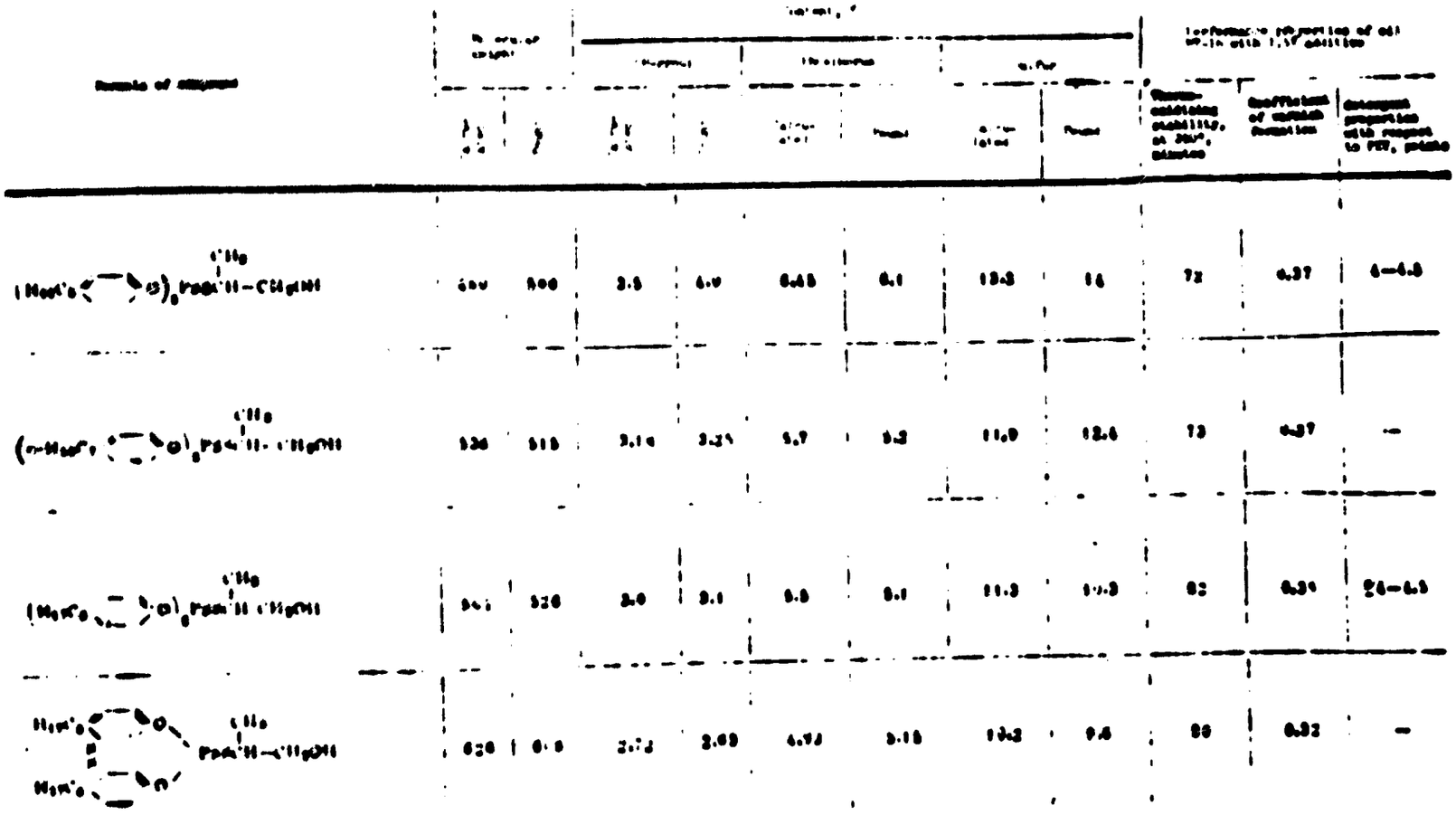


Table 8. Characteristics of Obtained Compounds of the Phenolates Type

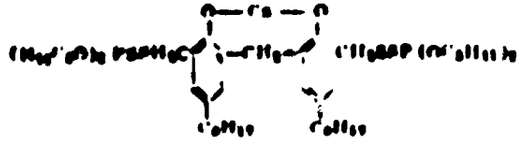
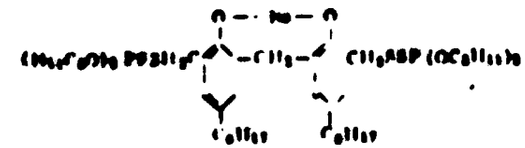
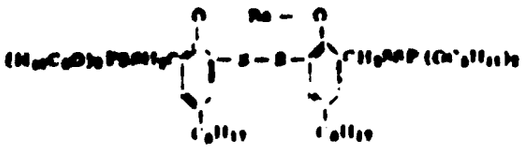
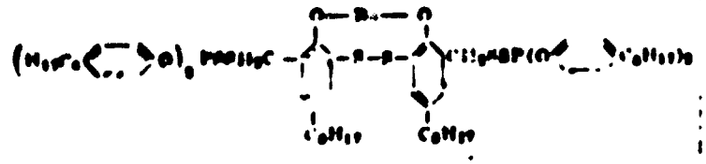
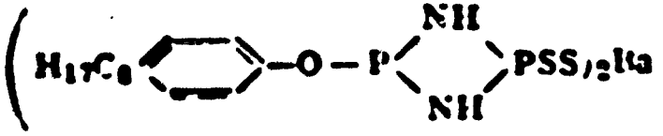
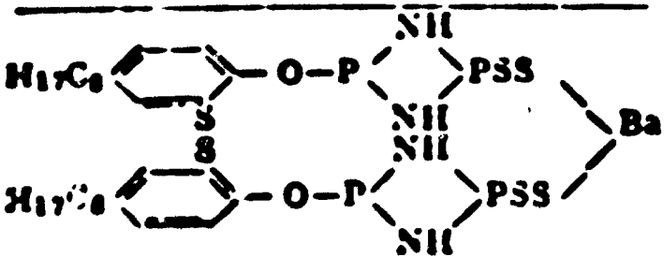
Formula of compound	Content, %				Performance properties of oil MK-14 with 1.5% additive				
	Barium		Phosphorus		Thermo-oxidizing stability, at 200°, minutes	Volatility, weight %	Boiling fraction, %	Critical temperature, °C	Halogen properties with respect to F-76 points
	Calculated	Found	Calculated	Found					
	3.9 calculated	3.5	6.18	5.9	54	54.1	65	290	2
	12.4	11.8	5.[illegible]	5.3	71	49.0	51	275	2
	11.9	12.8	5.3	4.8	72	54.0	50	270	2
	8.4	9.8	3.8	3.2	90	48.0	60	270	2

Table 9. Salt of Esters of Diamidodithiophosphorous Acid

Formula of compound	Content, %				Performance properties of oil MT-16 with 1.5% additive			
	Nitrogen		Phosphorous					
	Calculated	Found	Calculated	Found	Thermooxidising stability at 250° C, hours	Volatility/varnish, %	Working fraction, %	Detergent properties with respect to PZV, points
	6.5	—	14.4	12.5	72	59.0	41	2
	6.2	6.0	13.5	12.2	65	51.0	46	2—2.5

NOTE: For dissolution in oil the above additive was mixed with trialkylphenol in a 1:1, ratio.

Discussion of the Obtained Results

Compounds obtained in the form of calcium salts of diesterdithiophosphorous acid, are effective multifunctional additives, possessing antioxidant and detergent properties (see Table 3). A peculiarity of these compounds is the possibility of obtaining them both in the form of an alkali, and also in the form of neutral salts. When they are obtained in the form of alkali salts with a high content of calcium (near 12%), they show high detergent properties (0.5–1 point with respect to PZV) and a lowered antioxidant effect, the coefficient of varnish formation $K_л$ = = 0.5—0.6 (sample 1 and 2, Table 3). Neutral calcium salts of diesterdithiophosphorous acid (sample 3, Table 3) with low Ca content (near 2%) are effective antioxidant additives. Their detergent properties are insignificant.

Due to revealed regular dependence of increase of antioxidant properties of calcium salts of diesterdithiophosphorous acid with decrease of calcium content in a molecule of additive, during a simultaneous certain lowering of detergent properties, it is possible to obtain an additive of this type in numerous variants with given properties.

Of numerous additives, at present there is interest in: 1) alkali calcium salt of disulfide octylphenol diesterdithiophosphorous acid with Ca content near 12% (multifunctional additive IP-22k), which showed high quality during numerous motor tests; 2) neutral calcium salt disulfide octylphenol diesterdithiophosphorous acid with Ca content near 2% (antioxidant additive of Academy of Sciences-22k) as an effective oxidizer for work in conditions of high temperatures.

Preliminary experiments showed that this additive (Academy of Sciences-22k) can be applied as a component for formation of compositions with sulfonate additives MC-102u, SB-3, and others, with which it is well combined (Table 10).

Table 10. Results of Tests of Sulfonate SB-3 and of Additive of Academy of Sciences-22k

Compound	Thermo oxidizing stability at 260°, minutes	Coefficient of varnish formation K_a	Detergent properties with respect to PZV, points
10% sulfonate SB-3 in oil MT-16.....	16	2.3	0.5
4.5% antioxidant addition of Academy of Sciences-22k in oil MT-16.....	80	0.33	2.0—2.5
9% mixture (2:1) sulfonate SB-3 with antioxidant additive of Academy of Sciences--22 in oil MT-16.....	87	0.30	0.5

During investigation of barium salts of diesterdithiophosphorous acid (see Table 4), obtained in the form of neutral salts, it was shown that with respect to their own performance characteristics they differ little from similar calcium salts; obtaining them is connected with consumption of expensive barium oxide hydrate and, therefore, without damaging quality of the additive, barium can be replaced by calcium.

From data in Table 5 it is possible to see that zinc salts of diesterdithiophosphorous acid have high antioxidant properties; they do not show detergent properties. The highest antioxidant properties are possessed by zinc salt of diesterdithiophosphorous acid on an octylphenol base, and also a similar bispheno with a methylene or disulfide cross-link.

Preliminary tests of mixtures of zinc salts of diesterdithiophosphorous acid with sulfonate additives was showed that they combine worse with the latter than calcium antioxidant additive of the Academy of Sciences-22k which it is possible to see from data of Table 11.

Table 11. Results of Tests of Sulfonate NG-102u and Anti-Oxidizers

Compound	Additive in oil, %	Thermo oxidizing stability at 260°, minutes	Coefficient of varnish formation $K_л$	Detergent properties with respect to PZV, points
Sulfonate NG-102u (detergent component).....	6	18	1.9	—
Dithiophosphate of zinc (antioxidant additive on an alkylphenol base).....	4.5	77	0.38	1.5
Calcium antioxidant additive (Academy of Sciences-22k).....	4.5	80	0.33	2—2.5
Mixture of sulfonate NG-102u and dithiophosphate of zinc (2:1).....	6	38	0.70	—
Mixture of sulfonate NG-102u and calcium antioxidant additive of Academy of Sciences-22k (2:1).....	6	72	0.37	—

It was established (see Table 6) that ash-free additives, obtained in the form of binary compounds of diesterdithiophosphorous acid with amines, do not possess detergent effect and according to the nature of their own action can be attributed to antioxidant additives. The best additive of this type turned out to be a guanidine additive, showing high antioxidant properties (thermo-oxidizing stability for 70 minutes at 260° and $K_л = 0.25$).

Ash-free additives of the type triesters of dithiophosphorous acid did not reveal detergent properties (see Table 7). Introduction of propylene oxide in molecule of diesterdithiophosphorous acid favorably influenced antioxidant properties of all obtained compounds. The best additive of this type turned out to be an additive obtained on a base of diesterdithiophosphorous acid, containing

in the composition of its own molecule an octylphenol radical (thermo-oxidizing stability of 80-82 minutes at 260° and K_2 = 0.32 — 0.38).

It is necessary to note the practical value of triesters of dithiophosphorous acid as effective antioxidant additives. Their value increases if one considers that these compounds are excellent solvents of a number of difficult-soluble substances. They prevent loss of additives from butyric solutions in the form of deposit, therefore, they can be applied as additives stabilizing the butyric solutions of additives.

Investigation of organic phosphorous compounds of third group of the type alkylphenol phenolates, containing in side chain of benzene nucleus a substituted diesterdithiophosphorous acid (see Table 8) showed that with respect to their own performance characteristics they differ little from additives of the first group of the type diesterdithiophosphorous acids, but obtaining them is connected with a somewhat more complicated technology, hampering their manufacture. It was revealed that content of alkylphenol groups in structure of compound determines their activity as additives.

Preliminary results of the investigation of performance properties of nitrogen-containing additives of the fourth group of the type diamidodithiophosphorous acids (see Table 9) did not show any noticeable difference as compared to compounds of first group of type diesterdithiophosphorous acids. However, the possibility is not excluded that presence of nitrogen improves certain special necessary properties of oils, not revealed by preliminary investigation.

Conclusions

1. On a base of diesterdithiophosphorous acid are synthesized 35 different compounds, some of them in an almost analytically pure form. These compounds constitute certain types of multifunctional and antioxidant additives.

2. Synthesis of multifunctional additive IP-22k (alkali—calcium salt of diesterdithiophosphorous acid) is adopted on an industrial scale; antioxidant additives — neutral calcium salt of diesterdithiophosphorous acid and glycol ester of diesterdithiophosphorous acids are selected as the most effective as a result of laboratory tests of their performance properties.

3. Antioxidant additive of Academy of Sciences-22k shows good compatibility with certain sulfonate additives; it significantly increases antioxidant effect of the latter and can be recommended for formation of additive compositions.

4. As a result of conducted investigation the possibility is established of obtaining neutral and alkali salts of diesterdithiophosphorous acids with given properties, either heightened antioxidant or dispersive.

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SYNTHESIS, RESEARCH, AND APPLICATION OF SULFONATE ADDITIVES TO LUBRICATING OILS

A. M. Kuliyev, K. I. Sadykhov, and M. A. Mamedov
INKhP AN AzSSR*

The authors carried out synthesis of a number of salts of sulfonic acids of alkyl aromatic hydrocarbons and studied the effectiveness of their action on oils depending upon molecular weight, structure, and also upon character of metal entering in their composition.

Selection of alkyl aromatic hydrocarbons as raw material for synthesis of sulfo salts is explained by the fact that during sulfonation of petroleum distillates sulfonic acids are formed, basically owing to the alkyl aromatic hydrocarbons in the raw material.

Alkyl aromatic hydrocarbons were synthesized by means of alkylation of benzene, napthalene, tetralin, phenol, and chlorobenzene by unsaturated hydrocarbons and alkyl halides in the presence of catalysts.

Alkyl-derivative aromatic hydrocarbons were subjected to sulfonation by sulfuric acid or oleum to obtain corresponding sulfonic acids, from which different metallic salts subsequently were obtained [1] by treating their corresponding

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carbonates by salts [2]. Sulfo salts were separated from inorganic impurities by extraction by ethyl alcohol or benzene.

To study influence of nature of metal on detergent and dispersive properties of sulfo salts, besides the calcium and barium salts of sulfonic acids, sulfonated alkyl aromatic hydrocarbons, were obtained, and also cobalt, lead, strontium, and copper salts of sulfo acids of sulfonated alkylbenzene (Table 1) were investigated.

Synthesized salts of sulfonic acids of alkyl aromatic hydrocarbons of different structure were investigated with respect to their solubility in oils and other solvents. As solvents water, ethyl alcohol, toluene, and industrial oil 50 (machine SU) were used.

Research showed that solubility of salts of sulfonic acids in different solvents basically depends on their molecular weight.

With increase of number of carbon atoms in side alkyl chain, i.e., with increase of molecular weight of sulfonic acids, solubility of sulfo salts in water and alcohol decreased, and their solubility in toluene and industrial oil 50 was increased.

Barium salts of sulfonic acids as compared to corresponding calcium sulfo salts showed best solubility in toluene and oil and the worst — in water and alcohol.

Sulfo salts of alkyl napthaline are dissolved much better in oils than corresponding sulfo salts of alkyl benzenes.

To study influence of chemical nature sulfo salts on quality of lubricating oil samples of industrial oil 50 with different sulfo salts, well dissolved in oil were prepared and investigated. Stability against oxidation according to the method of AzNII [Azerbaydzhan Scientific Research Institute], corrosiveness according to Pinkevich method on plates prepared from lead, and detergent properties according to method of PZV (Tables 2-4) were determined.

As can be seen from given data, all sulfo salts lower the stability of oils against oxidation and, consequently, catalyze the process of oxidation. The catalyzing action of barium salts of sulfo acids on oxidation of oils is possibly stronger than that of calcium. The least catalyzing action on oxidation of oils is shown by cobalt salt of isocetylbenzenesulfonic acid. Strontium salt conducts itself just as calcium, does.

Introduction of hydroxyl group in the composition of aromatic nucleus of isocetylbenzenesulfonic acid increases antioxidant action of additive. With an additive of 1% barium or calcium salts of isocetylbenzenesulfonic acid stability of industrial oil 50 is increased; induction period of oxidation is increased from 5 to 30 minutes, and time of absorption of 20 ml of oxygen from 175 to 205-219 minutes.

Results of test of different sulfo salts in a mixture with industrial oil 50 according to Pinkevich method showed a certain dependence of their corrosion properties on chemical composition. It is clarified that with an increase of number of carbon atoms in side alkyl chain of sulfo salts, their corroding action in oils is increased.

Salts of different metals of the same sulfonic acids unequally act on corrosion aggressiveness of oils. Barium salts of sulfonic acids are more corrosional-aggressive than corresponding calcium salts. Strontium and cobalt salts of isocetyl-benzenesulfonic acid with respect to corrosion action are close to calcium salt, and lead and copper salts to corresponding barium salt.

With increase of number of carbon atoms in side alkyl chain of sulfo salts, their detergent properties are increased. Comparison of properties of calcium and barium salts of the same sulfonic acid showed that barium sulfo salts with respect to detergent and dispersive properties are more effective than calcium salts. Of other salts of sulfonic acids, cobalt salts possess the best properties. Lead salt acts like barium, and strontium like calcium salt.

Table 1. Physico-Chemical Properties of Synthesized Salts of Sulfonic Acids

№ п/п	Synthesized compound	Assumed empirical formula	Molecular weight		Content of sulfur, %		Ash content in the form $MeSO_4$, % (calculated on sulfo salt)	
			Found	Calculated	Found	Calculated	Found	Calculated
1	Calcium salt of p-toluenesulfonic acid.....	$(CH_3-C_6H_4-SO_3)_2Ca$	—	382	16,43	16,75	35,6	35,6
2	Barium salt of p-toluenesulfonic acid.....	$(CH_3-C_6H_4-SO_3)_2Ba$	—	479,36	12,99	13,35	48,89	48,62
3	Calcium salt of p-ethylbenzenesulfonic acid.....	$(C_2H_5-C_6H_4-SO_3)_2Ca$	—	410,0	15,52	15,60	33,78	33,20
4	Barium salt of p-ethylbenzenesulfonic acid.....	$(C_2H_5-C_6H_4-SO_3)_2Ba$	—	507,3	12,30	12,62	44,79	46,01
5	Calcium salt of isopropylbenzenesulfonic acid.....	$(C_3H_7-C_6H_4-SO_3)_2Ca$	—	438	14,56	14,61	31,51	31,08
6	Barium salt of isopropylbenzenesulfonic acid.....	$(C_3H_7-C_6H_4-SO_3)_2Ba$	—	535,3	11,62	11,96	43,47	43,52
7	Calcium salt of sec-butylbenzenesulfonic acid.....	$(C_4H_9-C_6H_4-SO_3)_2Ca$	—	466	13,70	13,73	29,46	29,18
8	Barium salt of sec-butylbenzenesulfonic acid.....	$(C_4H_9-C_6H_4-SO_3)_2Ba$	—	563,3	11,01	11,36	41,41	41,36
9	Calcium salt of isoctylbenzenesulfonic acid.....	$(C_8H_{17}-C_6H_4-SO_3)_2Ca$	—	578,0	11,16	11,07	24,36	23,52
10	Barium salt of isoctylbenzesulfonic acid.....	$(C_8H_{17}-C_6H_4-SO_3)_2Ba$	—	675,3	9,56	9,49	35,42	34,48
11	Calcium salt of isododecylbenzenesulfonic acid.....	$(C_{12}H_{25}-C_6H_4-SO_3)_2Ca$	684,2	690,0	9,01	9,27	19,14	19,71
12	Barium salt of isododecylbenzenesulfonic acid.....	$(C_{12}H_{25}-C_6H_4-SO_3)_2Ba$	779,5	787,3	8,01	8,12	29,34	29,59
13	Calcium salt of isocetylbenzenesulfonic acid.....	$(C_{16}H_{33}-C_6H_4-SO_3)_2Ca$	794,0	802,0	7,54	7,98	16,58	16,95
14	Barium salt of isocetylbenzenesulfonic acid.....	$(C_{16}H_{33}-C_6H_4-SO_3)_2Ba$	890,1	899,3	6,97	7,11	25,89	25,90
15	Strontium salt of isocetylbenzenesulfonic acid.....	$(C_{16}H_{33}-C_6H_4-SO_3)_2Sr$	841	849,6	7,50	7,58	21,01	21,61
16	Lead salt of isocetylbenzenesulfonic acid.....	$C_{16}H_{33}-C_6H_4-SO_3)_2Pb$	961,1	962,2	6,43	6,60	30,39	31,28
17	Cobalt salt of isocetylbenzenesulfonic acid.....	$(C_{16}H_{33}-C_6H_4-SO_3)_2Co$	812,8	820,0	7,30	7,79	18,03	18,87
18	Copper salt isocetylbenzenesulfonic acid.....	$(C_{16}H_{33}-C_6H_4-SO_3)_2Cu$	816,4	825,5	7,15	7,75	18,54	19,32

(Table 1 Continued)

№ п/п	Synthesized compound	Assumed empirical formula	Molecular weight		Content of sulfur, %		Ash content in the form $MeSO_4$, % (calculated on sulfo salt)	
			Found	Calculated	Found	Calculated	Found	Calculated
19	Calcium salt of alkylbenzenesulfonic acid (from chloroparaffin).....	—	455,0	895,0	3,05	6,23	8,90	13,25
20	Barium salt of alkylbenzenesulfonic acid (from chloroparaffin).....	—	1013,2	1153,3	3,90	5,69	14,1	20,74
21	Calcium salt of isocetylnaphthalenesulfonic acid...	$(C_{16}H_{33}-C_{10}H_6-SO_3)_2Ca$		658,0	9,12	9,53	19,83	20,06
22	Barium salt of isocetylnaphthalenesulfonic acid...	$(C_{16}H_{33}-C_{10}H_6-SO_3)_2Ba$		777,3	8,11	8,25	29,31	30,05
23	Calcium salt of isododecylnaphthalenesulfonic acid...	$(C_{12}H_{25}-C_{10}H_6-SO_3)_2Ca$	577,0	770,0	7,95	8,10	17,16	17,21
24	Barium salt of isododecylnaphthalenesulfonic acid...	$(C_{12}H_{25}-C_{10}H_6-SO_3)_2Ba$	689,3	867,3	7,09	7,21	25,08	25,5
25	Calcium salt of isocetylnaphthalenesulfonic acid...	$(C_{16}H_{33}-C_{10}H_6-SO_3)_2Ca$	815,1	910,0	7,01	7,09	15,22	15,36
26	Barium salt of isocetylnaphthalenesulfonic acid...	$(C_{16}H_{33}-C_{10}H_6-SO_3)_2Ba$	940,3	999,3	6,12	6,30	21,01	21,31
27	Calcium salt of isotetracosylnaphthalenesulfonic acid.....	$(C_{24}H_{49}-C_{10}H_6-SO_3)_2Ca$	1115,1	1135,0	5,61	5,68	11,98	12,07
28	Barium salt of isotetracosylnaphthalenesulfonic acid.....	$(C_{24}H_{49}-C_{10}H_6-SO_3)_2Ba$	1215,1	1224,3	5,12	5,23	18,01	18,16
29	Calcium salt of isocetylphenolsulfonic acid.....	$(C_{16}H_{33}-C_6H_3OH-SO_3)_2Ca$	831,1	826,0	7,01	7,07	16,12	16,29
30	Barium salt of isocetylphenolsulfonic acid.....	$(C_{16}H_{33}-C_6H_3OH-SO_3)_2Ba$	936,3	918,3	6,65	6,87	21,30	21,50
31	Calcium salt of isocetyltetralinsulfonic acid.....	$(C_{16}H_{33}-C_{10}H_{10}-SO_3)_2Ca$	859	900,0	6,92	7,03	15,15	15,91
32	Barium salt of isocetyltetralinsulfonic acid.....	$(C_{16}H_{33}-C_{10}H_{10}-SO_3)_2Ba$	996,3	990,3	6,30	6,45	21,51	21,12
33	Calcium salt of isocetylmonochlorobenzenesulfonic acid.....	$(C_{16}H_{33}-C_6H_3Cl-SO_3)_2Ca$	853,0	853,1	7,03	7,31	15,79	15,97
34	Barium salt of isocetylmonochlorobenzenesulfonic acid.....	$(C_{16}H_{33}-C_6H_3Cl-SO_3)_2Ba$	963,9	979,3	6,14	6,29	21,51	21,01

Table 2. Influence of Number of Carbon Atoms in Side Alkyl Chains of Sulfo Salts on Effectiveness of Their Action

Product	Assumed empirical formula of sulfo salt	Detergent properties with respect to PZV, points	Stability according to method of AzNII, minutes		Corrosiveness according to Pinkevich method	
			Induction period	Time of absorption of 20 ml of oxygen	Acid number, milligram KOH	Corrosion of lead plate, g/m^2
Industrial oil 50	—	5–5.5	5	175	0.21	59.34
Industrial oil 50 with additive:						
1% barium salt of isocetylnaphthalene-sulfonic acid.....	$(C_{16}H_{33}-C_{10}H_6-SO_3)_2Ba$	4.5	6	72	—	35.78
1% barium salt of isododecylnaphthalene-sulfonic acid.....	$(C_{12}H_{25}-C_{10}H_6-SO_3)_2Ba$	3.5	5	68	0.36	38.74
1% barium salt of isocetylnaphthalene-sulfonic acid.....	$(C_{16}H_{33}-C_{10}H_6-SO_3)_2Ba$	2.0–2.5	7	61	0.43	55.07
1% barium salt of isotetracosyl-naphthalenesulfonic acid.....	$(C_{24}H_{49}-C_{10}H_6-SO_3)_2Ba$	1.5–2.0	6	56	0.51	67.77

Introduction of hydroxyl group in composition of aromatic nucleus of sulfo salts and chlorine insignificantly affects detergent and dispersive ability of sulfo salts.

In sulfo salts the majority of the carriers of the detergent properties are assumed to be sulfo groups connected with different metals.

If one were to approach from this point of view, then the sulfo salt with the smaller molecular weight, i.e., containing short side with long side chains, since in low-molecular sulfo salts the ratio of sulfo group to hydrocarbon radical is larger than in sulfo salts containing long side chains. Obtained data did not

confirm this position. Apparently, besides the above-mentioned factor the effectiveness of action of salts is influenced by solubility in hydrocarbons, character and magnitude of radicals, structure and nature of molecules of sulfo salts, response of oils to separate salts of sulfonic acids, nature of metal, and others.

Obviously, one of the decisive factors affecting detergent, dispersive, anti-corrosive, stabilizing, and other properties of sulfo salts is their catalytical action on oxidation of oils.

Depending upon nature of sulfo salts, the direction and speed of oxidation of oils sharply change, and character of products of oxidation is changed which significantly affects effectiveness of action of sulfo salts.

Also depressor properties of salts of sulfonic acids were studied (Table 5).

It was clarified that with increase of molecular weight the depressor properties of synthesized sulfo salts are increased.

Study of action of different sulfo salts on detergent and dispersive properties of oils showed that for a detergent component of the additives it is desirable to use barium salts of sulfonic acids of sulfonated alkyl aromatic hydrocarbons with long paraffin chains. These sulfosalts also possess depressor properties.

Positive results obtained during investigation of salts of sulfonic acids of alkyl aromatic hydrocarbons as detergent additives, made subsequent research possible in the direction of synthesis and selection for motor and tractor oils of the most effective detergent additive on a base of sulfo salts obtained from sulfonated oil products.

For that high-molecular petroleum fractions were sulfonated, containing in composition alkyl aromatic hydrocarbons with long paraffin chains, for instance, petrolatum from Surakhany selected oil, depressor AzNII, butyric fraction of Romashkino oil (fr. 400-500°), concentrate and wide solar oil fraction of Surakhany selected oil and other. Ready Baku oils of different molecular weight

Table 3. Influence of Nature of Metal on Effectiveness of Action of Sulfo Salts

Product	Assumed empirical formula of sulfo salt	Detergent properties with respect to PZV, points	Stability according to method of AzNII, minutes		Corrosivity according to Pinkevich method	
			induction period	time of absorption of 20 ml of oxygen	acid number, milligram KOH	corrosion of lead plate, g/m²
Industrial oil 50	—	5—5.5	5	175	0.21	59.34
Industrial oil 50 with additive:						
1% calcium salt of isocetylbenzene-sulfonic acid.....	$(C_{16}H_{33}-C_6H_4-SO_3)_2Ca$	3.5-4.0	5	64	0.26	43.31
1% barium salt of isocetylbenzene-sulfonic acid.....	$(C_{16}H_{33}-C_6H_4-SO_3)_2Ba$	3.0	6	49	0.38	62.09
1% strontium salt of isocetylbenzene-sulfonic acid.....	$(C_{16}H_{33}-C_6H_4-SO_3)_2Sr$	3.5-4.0	7	61	0.79	42.15
1% lead salt of isocetylbenzene-sulfonic acid.....	$(C_{16}H_{33}-C_6H_4-SO_3)_2Pb$	3.0	8	103	0.92	64.71
1% cobalt salt of isocetylbenzesul-fonic acid.....	$(C_{16}H_{33}-C_6H_4-SO_3)_2Co$	2.5	16	145	0.91	44.47
1% copper salt of isocetylbenzene-sulfonic acid.....	$(C_{16}H_{33}-C_6H_4-SO_3)_2Cu$	4.5	9	119	0.89	44.47

and viscosity were also subjected to sulfonation: solar oil-spindle oil, transformer, turbine, industrial oil 50, motor oil, AK-10, diesel oil of selective purification with kinematic viscosity 11 and 14 cs at 100°, and also oils AS-5 and AS-9.5 from eastern oils.

Also investigated were high-molecular alkyl aromatic hydrocarbons, obtained as a result of reaction of alkylation of benzene and phenol with chlorinated Grozn'ye paraffin and wide solar oil fraction.

Table 4. Influence of Character of Aromatic Nucleus and Functional Groups on Effectiveness of Action of Sulfo Salts

Product	Assumed empirical formula of sulfo salt	Detergent properties with respect to PZV, points	Stability according to method of AzNII, minutes		Corrosivity according to Pinkevich method, (50 hours)	
			induction period	time of absorption of 20 ml of oxygen	acid number, milligram KOH	corrosion of lead plate, g/m²
Industrial oil 50	—	3–5.5	5	175	0.21	59.34
Industrial oil 50 with additive:						
1% calcium salt of isocetylbenzenesulfonic acid	$(C_{16}H_{33}-C_6H_4-SO_3)_2Ca$	3.5–4.0	5	64	0.20	43.31
1% barium salt of isocetylbenzenesulphonic acid	$(C_{16}H_{33}-C_6H_4-SO_3)_2Ba$	3.0	6	49	0.33	62.00
1% calcium salt of isocetylnaphthalenesulfonic acid	$(C_{16}H_{33}-C_{10}H_6-SO_3)_2Ca$	3.5	7	86	0.29	22.46
1% barium salt of isocetylnaphthalenesulfonic acid	$(C_{16}H_{33}-C_{10}H_6-SO_3)_2Ba$	2.0–2.5	7	62	0.43	55.07
1% calcium salt isocetyltetralinsulfonic acid	$(C_{16}H_{33}-C_{10}H_{10}-SO_3)_2Ca$	4.0	7	81	0.37	42.64
1% barium salt of isocetyltetralinsulfonic acid	$(C_{16}H_{33}-C_{10}H_{10}-SO_3)_2Ba$	3.5	5	54	0.41	58.53
1% calcium salt of isocetylphenolsulfonic acid	$(C_{16}H_{33}-C_6H_3(OH)-SO_3)_2Ca$	4.0	31	219	0.29	63.08
1% barium salt of isocetylphenolsulfonic acid	$(C_{16}H_{33}-C_6H_3(OH)-SO_3)_2Ba$	3.5	30	205	0.36	71.72
1% calcium salt of isocetylmonochlorobenzenesulfonic acid	$(C_{16}H_{33}-C_6H_3Cl-SO_3)_2Ca$	3.0–3.5	7	97	0.31	41.83
1% barium salt of isocetylmonochlorobenzenesulfonic acid	$(C_{16}H_{33}-C_6H_3Cl-SO_3)_2Ba$	3.0	5	56	0.34	67.44

Table 5. Influence of Salts of Sulfonic Acids on Temperature of Thickening of Oil AK-15

Product	Assumed empirical formula of sulfo salt	Pour point, °C*	Depression of temperature of thickening, °C
Oil AK-15.....	—	-3 - -5	—
Oil AK-15 with additive:			
1% barium salt of isocetylbenzene-sulfonic acid.....	$(C_{16}H_{33}-C_6H_4-SO_3)_2Ba$	-4 - -6	1
1% calcium salt of alkylbenzene-sulfonic acid (alkylation of benzene by chlorinated paraffin)...	$(C_{21}H_{43}-C_6H_5-SO_3)_2Ca$	-20 - -22	17
1% barium salt of alkylbenzene-sulfonic acid (alkylation of benzene by chlorinated paraffin)...	$(C_{21}H_{43}-C_6H_5-SO_3)_2Ba$	-20 - -22	17
1% barium salt of isocetylnaphthalenesulfonic acid...	$(C_{16}H_{33}-C_{10}H_6-SO_3)_2Ba$	-3 - -6	0
1% calcium salt of isotetracosyl-naphthalenesulfonic acid.....	$(C_{24}H_{49}-C_{10}H_6-SO_3)_2Ca$	-20 - -22	17
1% calcium salt of isotetracosyl-naphthalene-sulfonic acid.....	$(C_{24}H_{49}-C_{10}H_6-SO_3)_2Ba$	-20 - -22	17
1% barium salt of isocetylphenol-sulfonic acid.....	$(C_{16}H_{33}-C_6H_3OH-SO_3)_2Ba$	-4 - -6	1
1% barium salt of isocetylmonochlo-robenzenesulfonic acid.....	$(C_{16}H_{33}-C_6H_3Cl-SO_3)_2Ba$	-4 - -6	1

From shown products of sulfonic acid these were obtained by sulfonation:

1) sulfuric acid or oleum;

2) sulfuric acid or oleum with subsequent isolation of sulfonic acids by solvents;

3) sulfuric anhydride.

On a base of sulfonic acids, obtained by the above methods, were synthesized different salts of them. Of three methods of sulfonation the most convenient was sulfonation by sulfuric anhydride.

The conducted synthesis of high-ash (alkali) sulfonates and developed a technology of obtaining them. It was clarified that by the method of "re-saponification" of the detergent component of additive aznii-5* a high-ash sulfonate additive can be obtained, containing 3 times more metal than the usual detergent component of additive aznii-5. However, results of tests of high-ash and usual sulfonates on different motors did not show a particular difference between them.

Industrial application of additive aznii-4 and aznii-5 were developed and obtained on the basis of given works.

Recently developed is the technology of a more effective sulfonate additive SB-3, barium salt of sulfonic acids of sulfonated diesel oil (selective purification) viscosity 11 cs at 100°. Oil D-11 with additive SB-3 in a quantity of 5.8 and 10% was subjected to laboratory research (Table 6).

In Table 6 are given also results of tests of sulfonate additives PMS$_{ya}$ (VNII NP) and NG-102 (Moscow "Neftegaz" factory).

Best results with respect to detergent and antioxidant properties were obtained during test of oil D-11 in mixture with 10% additive SB-3. The same results are obtained during use of additive SB-3, synthesized on a base of calcium salts.

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*Ed note: aznii = AzNII; the additive is named for the institute.

Table 6. Results of Laboratory Tests of Oils with Different Sulfonate Additives

Product	Ash content, %	Detergent properties with respect to PZV, points	Corrosivity according to Pinkevich method (on plates from lead), g/m²	Oxidation according to method of VTI [F. Dzerzhinskiy All-Union Heat Engineering Institute] (14 hours at 160°)	
				Quantity of deposit, %	Acid number, milligram KOH
Diesel oil D-11 of selective purification (Baku raw material)	—	5—5.5	30.0	0.41	1.88
Diesel oil D-11 with additive					
5% SB-3	0.46	1.0-1.5	5.5	0.55	2.99
8% SB-3	0.67	0.5-1.0	2.3	0.61	3.97
10% SB-3	0.76	0.5	2.9	0.036	5.85
10% additive SB-3 (Ca-salt)	0.27	0.5	Absent	0.027	1.32
10% PMS_{ya}	1.15	0.5-1.0	The same	0.018	0.97
15% NG-104	0.81	0.5-1.0	6.3	2.91	0
Diesel oil DS-11 (from eastern raw material)	—	4.5-5.0	12.3	0.056	1.5
Diesel oil DS-11 with additive					
10% SB-3	0.76	0.5	1.6	0.012	3.08
10% PMS-19	1.21	0.5	1.3	0.065	2.91
15% NG-102	0.84	0.5	9.9	0.036	3.67

During laboratory tests of diesel oils with three new sulfonate additives (SB-3, PMS_{ya} and NG-102) the best result with respect to detergent and other properties was obtained with additive SB-3, although oil from this additive had a smaller ash content than with the remaining additives.

Not all sulfonate additives act the same during oxidation. The biggest deposit will be formed during oxidation of oil D-11 (Baku raw material) with 15% additive NG-102. A characteristic of that sample is the fact that during determination of quantity of deposit (not soluble in gasoline) according to method of VTI, all soluble additive in oil passes into deposit and acid number of oxidized oil corresponds to zero. We checked this repeatedly and in all cases the same results were obtained.

During oxidation of diesel oil D-11 from eastern oils in mixture with additive NG-102 the given phenomenon is not observed, and quantity of deposit from oxidized oil corresponds to 0.036%.

Everything said once again confirms the existing opinion about the fact that effectiveness of action of additives depends also on quality of base oils, i.e., on their origin and degree of purification.

It is necessary also to note that acid number of oil D-11 after oxidation is strongly increased when there is added to it 10% additive SB-3; however, in spite of this, when oil D-11 with 10% additive SB-3 is tested on different motors, increased wear is not observed and among the tested sulfonates (SB-3, PMS_{ya} and NG-102) the least wear is shown by this sample of oil with additive.

Introduction of additive SB-3 in industry will make it possible to completely guarantee lubricating oils by highly effective additive and to sharply improve their performance properties.

It is necessary to note that production of additive SB-3 may be carried out on existing industrial installations in the production of additives aznii-4 and aznii-5 without any changes and does not require substantial investments.

The possibility of application of additive SB-3 to diesel oil was investigated. For that laboratory tests of this addition were conducted both in the pure form and also in mixture with different antioxidant additions (barium salt of product of condensation of alkylphenol and formaldehyde — BFK, vnii np-354, vnii np-353 and zinc salt of sulfur-phosphorous-containing additive obtained on a base of nsaturated hydrocarbons). Samples of industrial oil 50 were prepared with the shown additives and their detergent properties were determined according to method of PZV, corrosion according to Pinkevich method, and stability according to method of VTI.

With the addition of additive SB-3 to industrial oil 50 the detergent properties and corrosivity of initial oil are improved, the quantity of deposit

after 14 hours of oxidation at a temperature of 160° almost does not change, and acid number is sharply increased (Table 7).

Table 7. Results of Laboratory Tests of Oils with Sulfonate and Antioxidant Additives

Product	Detergent properties according to PZV, points	Corrosion by the Pinkevich method (on plates from lead) g/m²	Oxidation according to VTI method (14 hours at 160°)	
			Quantity of deposit, %	Acid number, milligram KOH
Industrial oil 50.....	5.0—5.5	68.0	0.69	1.1
Industrial oil 50 with additive:				
10% SB-3.....	0.5—1.0	27.6	0.64	4.95
10% additive (80% SB-3 + 20% BFK).....	0.5—1.0	15.5	0.048	1.61
10% additive (66.6% SB-3 + 33.4% BFK).....	0.5—1.0	4.0	0.034	0.43
10% additive (80% SB-3 + 20% vnii np-354).....	0.5	Absent	0.080	0.86
10% additive (66.8% SB-3 + 33.4% vnii np-354).....	0.5	Absent	0.020	1.07
10% additive (50% SB-3 + 50% additive vnii np-354	—	0.7	0.030	1.93
10% additive (80% SB-3 + 20% vnii np-353).....	—	1.8	0.016	0.79
10% additive (80% additive SB-3 + 20% zinc salt of sulfur-phosphorous-containing additive, obtained from cracking-kerosene).....	0.5—1.0	4.4	0.28	1.18

Compounding of additive SB-3 with different antioxidants gives satisfactory results both on anticorrosive properties, and also on stability.

Best results in quantity of deposit and acid number after oxidation are obtained when additive SB-3 is mixed with additive BFK in a 2:1 ratio, and with additives vnii np-354 and vnii np-353 in a 4:1 ratio.

On the basis of these data short-term (50-hour) tests of a number of samples were conducted on a one-cylinder motor UIM-3. Best results are obtained when additive SB-3 is mixed with additive BFK in a 2:1 ratio (tests are conducted on motor UIM-3, total evaluation in points).

DS-11 NKZ + 3% additive tsiatim-339.....	15.0
The same + 10% additive SB-3.....	9.8
The same + 10% additive (66.6% SB-3 + 33.4 BFK)....	5.3
The same + 10% additive (80% SB-3 + 20% vnii-354)..	11.4
The same + 6% additive vnii np-360.....	9.05
The same + 5% additive aznii-7 (purified).....	16.75

Given data indicate that in the case of use of additive SB-3 on motors operating on sulfurous fuel, it is necessary to add antioxidant additives. For this purpose, of the antioxidants investigated by us the most effective and accessible can be considered additive BFK.

Reference

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SYNTHESIS OF ANTIWEAR ADDITIVES TO OILS

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Obtaining Sulfurous Antiwear Additives on an Ethylene Sulfide and Fatty Acid Base

Work has been done on obtaining and laboratory testing esters of diethanoldisulfide and fatty acids as antiwear additives:

$$RCOOCH_2CH_2-S-S-CH_2CH_2OOCR,$$

where R — alkyl radical.

Obtaining the shown products consists of three stages.

1. Synthesis of ethylene sulfide from oxide of ethylene and thiourea:

$$\underset{\diagdown\,O\,\diagup}{CH_2-CH_2} + H_2NCSNH_2 \rightarrow \underset{\diagdown\,S\,\diagup}{CH_2-CH_2} + H_2NCONH_2$$

2. Synthesis of β-mercaptoethyl ester by reaction of ethylene sulfide and fatty acid:

$$\underset{\diagdown\,S\,\diagup}{CH_2-CH_2} + R-C(=O)-OH \rightarrow RCOOCH_2CH_2SH$$

3. Oxidation of β-mercaptoethyl ester by atmospheric oxygen in presence of traces of Fe^{+2}:

$$2RCOOCH_2CH_2SH + \tfrac{1}{2}O_2 \rightarrow \begin{matrix} RCOOCH_2CH_2-S \\ | \\ RCOOCH_2CH_2-S \end{matrix} + H_2O$$

In a number of carbonaceous acids acetic, propionic, isovaleric, C_5 — C_6 fraction of synthetic acids and chlorinated (content of chlorine 8-10% by weight) fraction of the same acids were investigated. In Table 1 are given physico-chemical properties of obtained additives.

Table 1. Properties of Additives of the Sulfide and Disulfide Type

Product	Acid number, milligram KOH	Ester number, milligram KOH	Content, %		n_D^{20}	d_4^{20}	Pour point, °C	Viscosity, cs	
			Sulfur	Chlorine				At 100°	At -30°
Ester of acetic acid and diethanoldisulfide.....	0.55	468	26.4	0	1.5012	1.1825	-60 flows	2.52	974
Ester of propionic acid and diethanoldisulfide.....	0.48	420	23.6	0	1.4878	1.1440	-60 flows	2.25	858
Ester of isovaleric acid and diethanoldisulfide.....	0.49	344	19.7	0	1.4774	1.0672	-60	2.21	487
Ester of synthetic acids of fraction C_5—C_6 and diethanoldisulfide.....	0.57	293	18.3	0	1.4720	1.0489	-60	2.27	462
Ester of synthetic chlorinated acids of C_5—C_6 fraction and diethanoldisulfide.	—	—	14.4	5.53	—	1.039	-60	2.60	837
Ester of isovaleric and dioxydisulfide.	—	—	29.0	0	1.472	1.0212	-60	2.83	682
Ester of acetic acid and thiodiglycol...	0.82	—	15.5	0	—	1.013	-60	2.09	—
Ester of carbonaceous acids of C_5—C_6 fraction and thiodiglycol.....	0.14	—	10.75	0	—	1.007	-23	2.64	—
Ester of carbonaceous acids of C_5—C_6 fraction and dioxydisulfide.....	0.32	—	10.1	0	—	1.047	-60	4.19	1571

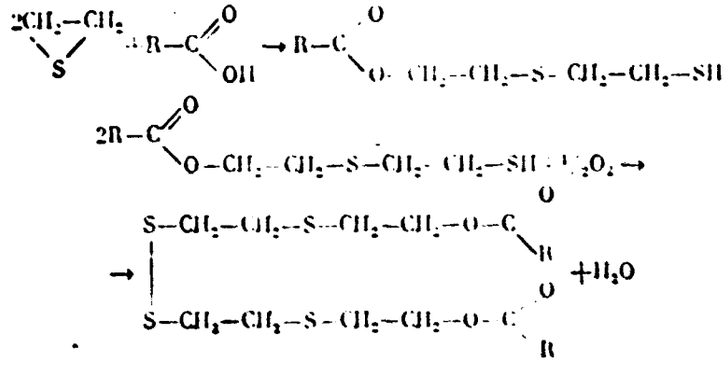
The obtained products constitute synthetic diester oils, containing in chain in exchange for oxygen cross-links one or several atoms of sulfur.

Physico-chemical properties of the studied products — temperature of thickening, viscosity characteristic, and others — are not inferior to those properties of usual synthetic oils near to them in nature.

For preliminary establishment of performance properties synthesized additives were added in different ratios to synthetic and mineral oils, after which the obtained mixtures were tested on a four-ball machine (their antiscratching and antiwear properties were studied) and on VTI apparatus (stability was determined). Results of these tests are given in Table 2.

With introduction of additives in oil 36/1 durability of butyric film significantly increases. Synthetic oil 36/1 with respect to certain additives possesses larger response than petroleum.

To increase content of sulfur in additive synthesis of dioxydisulfides was carried out by reaction of two molecules of ethylene sulfide with one molecule of carbonaceous acid according to the diagram



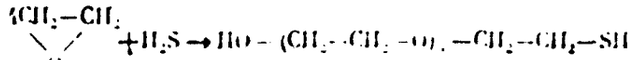
Results of tests on four-ball machine showed that with increase of sulfur content in oil by more than 30%, P_k is increased by only 15%. This observation confirmed that content of sulfur itself does not fully determine effectiveness of additive.

Table 2. Results of Tests of Antiwear Properties and Thermochemical Stability of Additives of the Sulfide and Disulfide Type

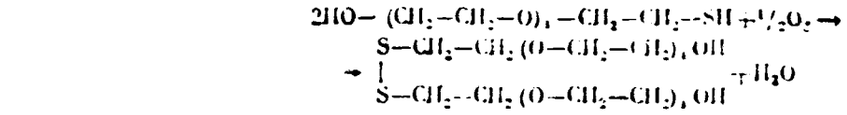
No. sample	Product	Pour point, °C	Acid number, milligram, KOH	Viscosity, cs		Content in oil, %		Critical load P_k, kg (four-ball machine)	Analysis of oxidized oil			Corrosivity (change of weight of plates), milligram cm^2	
				at 100°	at -30°	Sulfur	Chlorine		Viscosity 100°, cs	Acidity, milligram KOH	Deposit, %	Kh-15	AK-4
1	Synthetic oil 36/1.....	-60	0.36	3.71	—	0	0	54	4.09	1.80	0.006	None	
2	Synthetic oil 36/1 with additive: ±10% ester of acetic acid and diethanoldisulfide.....	-60	1.46	3.30	871	2.7	0	310	3.86	1.03	0.0009	0.16	0.16
3	10% ester of propionic acid and diethanoldisulfide.....	-60	—	3.20	743	2.4	0	240	—	—	—	—	—
4	10% ester of isovaleric acid and diethanoldisulfide.....	-60	0.62	3.35	913	2.0	0	100	5.69	5.6	0.007	0.007	0.09
5	10% esters of acids C_5—C_6 and diethanoldisulfide.....	-60	0.47	3.86	944	1.9	0	100	3.86	2.8	0.001	0.007	0.09
6	10% esters of chlorine-substituted acids C_5—C_6 and diethanoldisulfide.....	-60	2.12	3.41	834	1.44	0.55	260	4.18	9.11	0.426	+0.52	-2.08
7	10% ester of isovaleric acid and dioxydisulfide	-60	—	3.40	830	2.9	0	115	—	—	—	—	—
8	10% diester of acetic acid and thiodiglycol.	-60	0.82	3.62	878	1.55	0	100	3.58	1.36	None	0.04	None
9	10% diester of carbonaceous acids C_5—C_6 and thiodiglycol.....	-60	0.41	3.42	—	1.07	0	70	3.74	0.76	0.002	None	
10	Petroleum base transmission oil.....	—	—	—	—	—	—	50	—	—	—	—	—
11	Petroleum base transmission oil with additive 10% ester of acetic acid and diethanoldisulfide.	-11	—	15.56	—	2.6	—	118	—	—	—	—	—
12	10% ester of acids C_5—C_6 and diethanoldisulfide.....	—	—	—	—	1.9	0	100	—	—	—	—	—

Realization of synthesis of additives of the above type in sufficient measure is complicated and can turn out to be difficult in industrial design. In accordance with this investigations were conducted in synthesis of products close in nature, proceeding from such accessible materials as ethylene oxide, hydrogen sulfide, and carbonaceous acids. Depending upon temperature conditions of reaction and ratio of initial materials, different products are obtained.

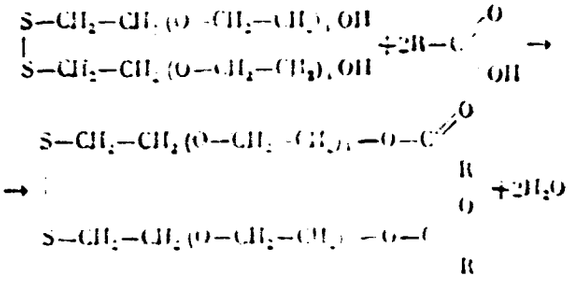
1. During reaction of 1 mole hydrogen sulfide and 4 moles ethylene oxide in the presence of traces of water at a temperature of 0-3° is obtained mercaptatetraethylene glycol:



The latter by oxidation by atmospheric oxygen is turned into corresponding dioxydisulfide:

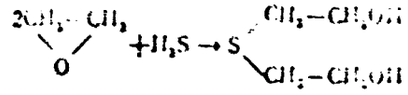


The obtained products are catalytically esterfied by synthetic fatty acids:



Characteristics of product obtained with participation of carbonaceous acids C_5—C_6, are given in Table 1.

During reaction of 2 moles ethylene oxide and 1 mole hydrogen sulfide at a temperature of 40-60° is obtained a widely known product — thiodiglycol:



By esterification of the latter by carbonaceous acids is obtained a synthetic oil of the polyglycol type, in which one central oxygen cross-link is replaced by sulfur.

All the above products are mobile liquids, possessing low temperature of thickening, good viscosity characteristics, and full solubility in synthetic and petroleum oils. Results of tests of antiwear properties, given in Table 2, give a basis for considering their effective components of synthetic oils.

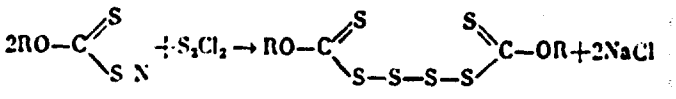
Some synthesized additives (derivatives of thiodiglycol) show increased heat resistance. Thus, test of mixtures of synthetic oil 36/1 with derivatives of thiodiglycol, prepared without participation of inhibitors, showed their increased heat resistance as compared to such for synthetic oil 36/1.

Antiwear Additives to Oils on a Base of Xanthogenates of Alcohols and Dichloroethane

The section of alcohols as basic initial raw material of xanthogenates was based on their exceptionally high adhesion properties, due to which they found wide application as flotation agents during ore concentration of nonferrous metals.

By themselves xanthogenates of alcohols cannot be used as antiwear additives due to insolubility in hydrocarbon and synthetic oils, thermal instability, and aggressiveness with respect to metals. An attempt to use for these purposes dixanthogenates (in particular, diproxide) failed, since these compounds at a temperature of 100° in the presence of red copper are decomposed with the formation of elementary sulfur.

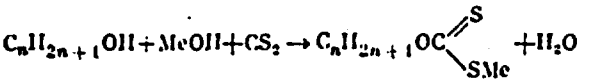
An attempt was undertaken to connect xanthogenates by sulfide cross-link by means of treatment first of sulfur monochloride:



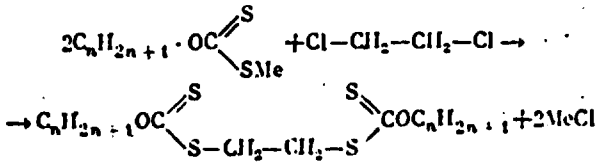
The obtained products are readily soluble in synthetic and mineral oils, possess great adhesion ability, are inert to steel, but are decomposed at a temperature 100° by red copper and its alloys.

The following stage of research was synthesis of dixanthogenate ester of ethylene glycol, proceeding from xanthogenates of alcohols and dichloroethane. The process in this case goes according to the following diagram:

1st stage — formation of alcohol xanthogenates



2nd stage — formation of total glycol ester of xanthogenic acid:



Condition of carrying out synthesis is the following.

1st stage: reaction in the cold during mixing of concentrated solution of caustic soda with alcohols and reaction of the formed alcoholate of alcohols at room temperature and mixing with carbon bisulfide.

2nd stage: reaction at 70° and mixing of aqueous solution of alcohol xanthogenates with dichloroethane. Further washing by water, distillation of surplus of dichloroethane and low-boiling products of synthesis, and drying of additives are carried out at temperatures not exceeding 100°.

In laboratories additives were synthesized on a base of xanthogenates of ethyl, isopropyl, butyl, isobutyl, and other alcohols.

In Table 3 are given physico-chemical properties of the obtained additives. With the exception of derivative ethylenexanthogenate all synthesized products are readily soluble in synthetic and mineral oils and are easily mobile (even at sub-zero temperatures) liquids, whose addition to synthetic and mineral oils does not worsen quality of the latter (Table 3).

In the laboratory of our factory, in VNII NP [All-Union Scientific Research Institute of the Petroleum Industry] and on stands of the Likhachev factory and others were studied antiscoring and antiwear properties of synthesized products.

Table 3. Properties of Additives Synthesized on a Base of Xanthogenates of Alcohols

Additive	Pour point, °C	Specific gravity g/cm²	Viscosity, cs		Content, %		Critical load P_k, kg (four-ball machine)	Diameter of mark of wear, mm
			at -10°	at +50°	Sulfur	Chlorine		
Ethylene diethyl-xanthate LE-24.....	-35 (crystal)	—	12.28	2.38	52.3	0.09	130	0.97
Ethylene diisopropyl-xanthate LZ-23.....	Below -45.1	1.1900	21.49	3.30	44.2	0.24	130	0.91
Ethylene diisobutyl-xanthate LZ-6/9.....	Below -60°	1.1326	50.22	5.05	40.1	0.20	160	0.91
Ethylene diisobutyl-xanthate LZ-25.....	Below -60°	1.2207	151.06	7.45	38.8	0.92	140	0.91
Ethylene diisoamyl-xanthate LZ-19.....	Below -60°	—	28.50	3.35	33.1	2.15	140	0.91
Ethylene dixanthate and alcohols C_5—C_6 LZ-22	-37° (crystal)	0.9872	56.45	5.11	21.1	0.85	126	0.80
Ethylene diisopropyl-xanthate (crystal) LZ-23k.....	+49°	—	—	—	40.25	—	100	1.03
Ethylene diisobutyl-xanthate (crystal) LZ-25k.....	+37.5°	—	—	—	37.1	—	160	0.86
Butylxanthol.....	Below -60°	1.154...	52.13	4.92	28.9	5.08	130	0.97
Amylxanthol.....	Below -60°	1.1347	58.44	4.90	27.6	5.50	130	0.91

NOTE: Antiwear properties of additives, with the exception of additive LZ-24, were tested in spindle oil AU. Antiwear properties of additive LZ-24 were tested in synthetic oil 36/1. Quantity of additive in oil in all cases guaranteed a sulfur content of 1.5%.

In the first place regulation was carried out on a four-ball machine (Table 3 and Fig. 1).

In Table 3 and in Fig. 1 it is clear that all products synthesized by us are good scoring inhibitors and in known measure antiwear additives to synthetic and petroleum oils.

Investigations of the VNII NP completely confirmed our conclusions.

Additive LZ-6/9, synthesized from presently accessible butylxanthogenate, passed successfully all control performance tests, and the All-Union Government Standard is foreseen for its application in the production of transmission oils. At present additive LZ-6/9 is prepared on a semi-industrial scale.

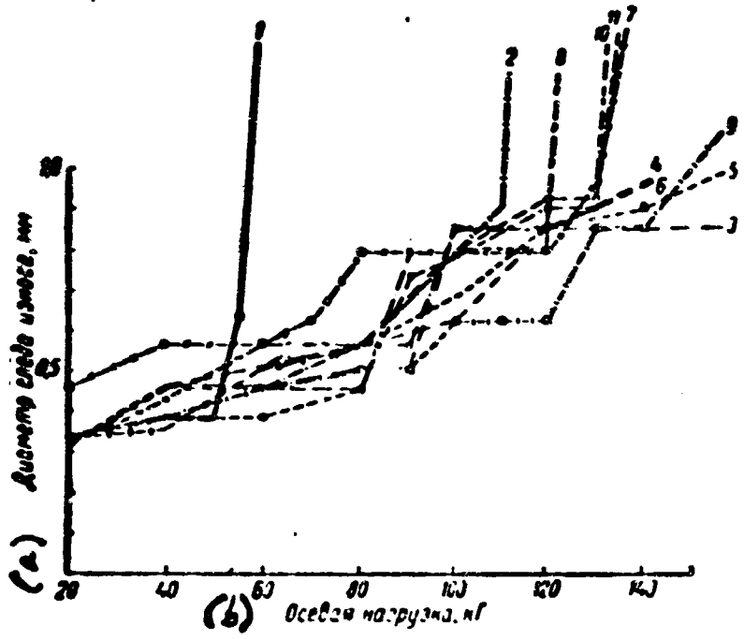


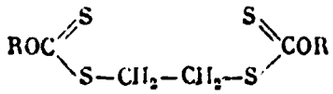
Fig. 1. Tests of oils with antiwear additives on a four-ball machine.
1—spindle oil AU; spindle oil AU with additive: 2—LZ-23k; 3—LZ-25k; 4—LZ-6/9; 5—LZ-25; 6—LZ-19; 7—synthetic 36/2 + LZ-24; spindle oil AU with additive: 8—LZ-22; 9—LZ-23; 10—butylxanthol; 11—amylxanthol.
KEY: (a) Diameter of mark of wear, mm; (b) Axial load, kg.

As the most promising initial raw material subsequently appears the use of isopropyl and isobutyl alcohols.

Additives of the Crystal Xanthogenate Type

The unpleasant odor and dark color of additives of the LZ-6/9 type, in our opinion, are explained by presence of impurities formed from products of decomposition of xanthogenates by water.

For removal of these deficiencies were synthesized crystal compounds of the type



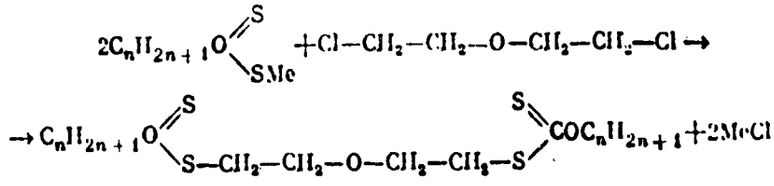
The latter differ from additives of the LZ-6/9 type by the fact that they are individual compounds, whereas the first are a rather complicated mixture of products of synthesis with a predominance of basic component.

Such type of products were obtained from isopropyl and butyl xanthogenates. Both esters -- crystal substances of white or slightly yellowish color -- are practically deprived of odor, are readily soluble in synthetic and mineral oils. Introduction of them in oils in quantities which ensure 2% by weight of sulfur, is effective (see Table 3); it increases their antiwear properties, not worsening the remaining physico-chemical properties of oils.

Synthesis of such additives is carried out with use of freshly prepared xanthogenates in a solution of dehydrated alcohol.

Additives of the Xanthol Type

To increase thermal stability of additives of the xanthogenate type synthesis was carried out of a product, called by us "xanthol," starting from butylxanthogenate and chlorex, i.e., β β'-dichlorodiethyl ester:



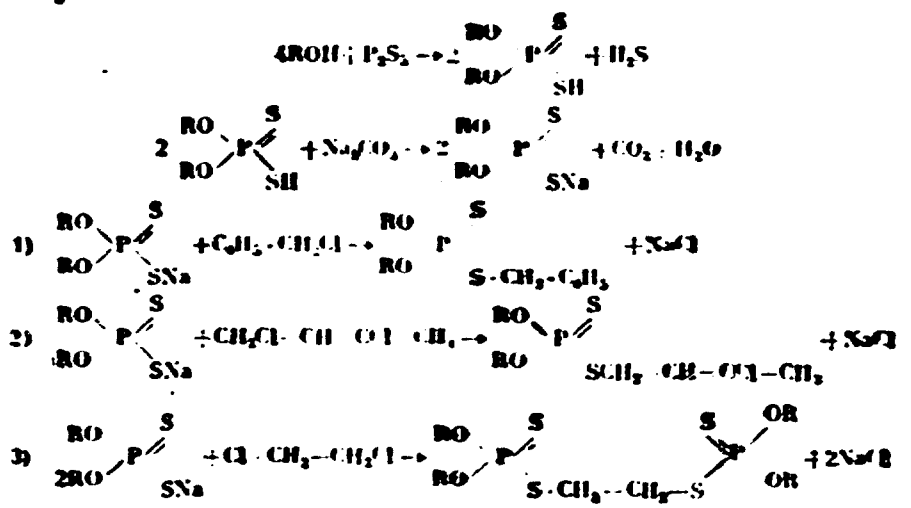
Xanthol is thermally stable up to a temperature of 130°, however, as compared to additive LZ-6/9 it possesses lowered effectiveness. The latter is connected with an increase of number of atoms in cross-link, connecting two xanthogenate groups. Additives of similar type can be recommended for those cases where increased stability of additive is required.

Sulfur and Phosphorous-Containing Antiwear Additives

All the above sulfur-containing additives possess basically antiscoring properties. For a complex resolution of problem it is necessary to combine in a number of lubricating oils both antiscoring and also antiwear properties. The latter, as is known, are ensured in the very best manner by the presence of atoms of phosphorous in molecule of additive. Structure of molecule has a very important value here.

After exploration operations, we synthesized a number of compounds, constituting esters of low-molecular dialkyldithiophosphorous acids. Synthesis of these compounds was conducted by means of condensation of sodium salts of low-molecular dialkyl-dithiophosphorous acids with the following chlorine-derivatives: benzyl chloride; 1.3-dichlorobutene-2; dichloroethane. Dialkyldithiophosphorous acids were obtained by treatment of ethyl, isopropyl, isobutyl, n-butyl, and isoamyl alcohols by phosphorous pentasulfide.

Diagram of syntheses:



Properties of obtained additives are given in Table 4.

Corrosion tests of additives, conducted according to the All-Union Government Standard for transmission oils, gave a satisfactory result.

Thermal stability according to method of VTI was satisfactory.

Table 4. Properties of Additives of the Low-Molecular Dialkyldithiophosphorous Acid Esters Type

Chlorine derivative, taken for synthesis	Alcohol, taken for synthesis of dialkyl-dithiophosphorous acids	Pour point, °C	Viscosity at 20°, cs	Content of sulfur, %	Content of phosphorus (caldulated), %	Content of chlorine %	Tests on four-ball machine		
							% additive to spindle oil AU	Critical load P_k, kg	Diameter of mark of wear at P_k, mm
Benzyl chloride	Isopropyl	-54	10.06	20.1	10.05	—	—	—	—
	Isobutyl	-60	13.47	18.2	9.10	—	5	120	0.55
	Isoamyl	-61	14.82	16.9	8.45	—	5	100	0.55
1.3-dichloro-butene-2	Ethyl	-65 (flows)	3.80	21.0	10.50	11.34	5	170	0.70
							7.5	180	0.72
	Isopropyl	-65 (flows)	6.20	19.6	9.80	9.36	—	—	—
	Isobutyl	-65 (flows)	9.30	17.9	8.90	9.20	—	—	—
	Isoamyl	-65 (flows)	10.8	16.2	8.10	7.80	5	120	0.62
							7.5	150	0.63
Dichloro-ethane	n-Butyl	-65	10.75	20.36	10.18	—	—	—	—
	Isoamyl	-65 (flows)	17.29	18.66	9.33	—	5	150	0.74

Study of antiwear properties on four-ball machine showed that all obtained additives are typically antiwear, since under critical loads the diameter of the wear mark was significantly less than during application of additives containing one sulfur (see Table 4 and Fig. 2).

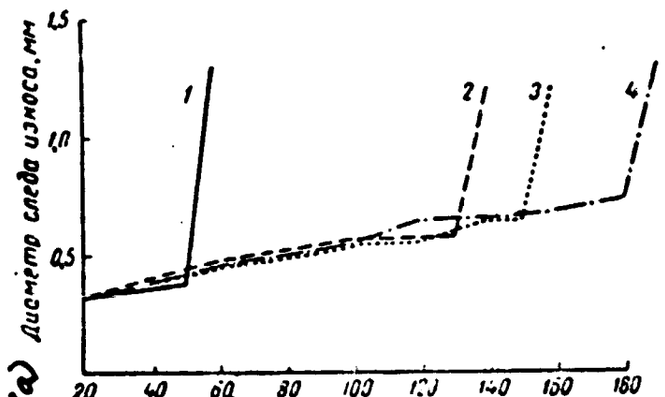


Fig. 2. Tests of oils with antiwear additives on four-ball machine.
1—spindle oil AU; spindle oil AU with additive: 2—7.5% diisobutyldithiophosphate, condensed with chlorous gasoline; 3—7.5% diisoamyldithiophosphate, condensed with 1.3-dichlorobutene-2; 4—7.5% diethyldithiophosphate, condensed with 1.3-dichlorobutylene-2.
KEY: (a) Diameter of mark of wear, mm; (b) Axial load, kg.

Activity of the tested antiwear additives increases in a number with decrease of length of hydrocarbon radicals taken for synthesis of alcohols.

Conclusions

1. Synthesized on the basis of thiourea, oxide of ethylene and carbonaceous acids, sulfur-containing products can serve as components of petroleum and synthetic oils, improving their antiwear properties.

2. Close antiwear properties are possessed by synthetic sulfur-containg oils, obtained on the basis of oxide of ethylene, hydrogen sulfide and carbonaceous acids.

Positive properties of products are their heightened thermochemical stability and relative simplicity of obtaining.

3. Very effective antiscoring properties are possessed by additives to petroleum and synthetic oils, synthesized on the basis of xanthogenates of low-molecular monatomic alcohols, from isopropyl to amyl inclusively, and dichloroethane.

Depending upon conditions of carrying out synthesis, it is possible to obtain liquid and crystal products. The latter differ from the former by the almost total absence of odor and color. Replacement during synthesis of dichloroethane by Chlorex leads to formation of additives possessing somewhat lowered antiscoring activity, but great thermochemical stability.

4. Additives obtained on the basis of dithiophosphates of ethyl, isopropyl, butyl, and amyl alcohols and 1.3-dichlorobutene-2, are readily soluble in mineral and synthetic oils, are neutral, contain sulfur, phosphorous and chlorine, do not corrode copper and steel, impart antiwear properties to oils and have satisfactory thermal stability.

Products obtained from dithiophosphates of isopropyl, butyl, and amyl alcohols*, on the one hand, and benzyl chloride or dichloroethane, on the other, can also present interest as antiwear additives.

*Derivatives of dithiophosphates of ethyl alcohol in this case are not soluble in mineral oils.

ORGANO-PHOSPHOROUS AND ORGANO-CHLORINE COMPOUNDS AS ADDITIVES, REDUCING WEAR IN CONDITIONS OF THRESHOLD FRICTION

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During research of different organo-chlorine and organo-chlorine-phosphorous compounds as additives reducing wear during friction, high activity was shown by compounds containing the $-CCl_3$ group [1, 2].

As a result of tests of monochloralkanes (No. 1) and tetrachloroalkanes (No. 2-4), obtained by telomerization (polymerization of ethylene in the presence of carbon tetrachloride), it was established that specific activity of tetrachloroalkanes is explained by the presence in their molecule of the $-CCl_3$ group owing to the relatively mobile chlorine by which a chloride film will be formed on surface of metal.

1. $CH_3(CH_2)_5CH_2Cl$
2. $CCl_3CH_2CH_2Cl$
3. $CCl_3(CH_2)_4CH_2Cl$
4. $CCl_3(CH_2)_5CH_2Cl$
5. $ClCH_2PO(OC_4H_9)_2$
6. $CCl_3PO(OC_2H_5)_2$
7. $CCl_3PO(OC_4H_9)_2$
8. $CCl_3PO(OC_6H_5)_2$
9. $CCl_3PO[N(CH_3)C_{10}H_{21}]_2$
10. $(ClCH_2CH_2O)_3P$
11. $CCl_3CH_2OP(OCH_2CH_3)_2$
12. $(CCl_3CH_2O)_3P$
13. $[CCl_3C(CH_3)_2O]_3P$

Compounds, containing the $-CCl_3$ group and phosphorus, for instance, esters of trichloromethylphosphine acid (No. 6-8) by their effectiveness exceed tetrachloroalkanes. Action of additives of this type is formed from simultaneous influence of trichloromethyl group (chloride film) and phosphorus, more correctly, of the

phosphorous compound obtained as a result of decomposition of additive and forming of phosphide film. As one should have been led to expect, considering results of tests of tetrachloroalkanes esters of monochloromethylphosphine acids (No. 5) are less active than esters of trichloromethylphosphine acid.

Specific influence of $-CCl_3$ group on antiwear properties of organo-phosphorous compounds was shown also at comparative research of esters of phosphorous acid (No. 10 and 11).

During tests of solutions of diethyl and dibutyl esters of trichloromethyl-phosphine acid (No. 6 and 7) in an experimental type of oil of high degree of purification on a four-ball friction machine the critical loads were accordingly 167 and 182 kg. During tests balls of steel ShKh-9 with a diameter of 12.7 mm were used, and relative speed of slip of surfaces of friction of balls constituted 0.25 m/sec [3].

Increasing the number of $-CCl_3$ groups in a molecule of organo-phosphorous compound, antiwear additives can be obtained, in the presence of which oil will sustain still larger loads without signs of jamming (No. 12 and 13).

Dibutyl ester of trichloromethylphosphine acid as an active additive to lubricating oils (additive Chloreth-40), we studied more widely.

Initially a pure preparation of dibutyl ester of trichloromethylphosphine acid was obtained, proceeding from dichloroanhydride trichloromethylphosphine acid and butyl alcohol according to the equation

$$CCl_3PCl_2 + 2C_4H_9OH + 2(C_2H_5)_3N \rightarrow CCl_3PO(OC_4H_9)_2 + 2(C_2H_5)_3N \cdot HCl$$

By this method may be obtained pure ester of trichloromethylphosphine acid with a boiling point of 124-125° (2 mm Hg); $d_4^{20} = 1.2219$; $n_D^{20} = 1.4590$. The content of chlorine in it is 33.93%.

However, realization of synthesis, especially in obtaining large quantities of ester, is complicated by necessity of using as initial product dichloroanhydride trichloromethylphosphine acid, the synthesis of which is relatively complicated [4].

Dibutyl ester of trichloromethylphosphine acid we, therefore, obtained by reaction of tributylphosphite and carbon tetrachloride according to G. Kamay and L. P. Egorova [5]; tributylphosphite in turn was obtained, proceeding from butyl alcohol and trichlorous phosphorus [6]. Consequently, the obtaining of additive — dibutyl ester of trichloromethylphosphine acid — is carried out in two stages according to the following equations:

$$3C_4H_9OH + PCl_3 + 3(C_2H_5)_3N \rightarrow (C_4H_9O)_3P + 3(C_2H_5)_3N \cdot HCl$$

$$(C_4H_9O)_3P + CCl_4 \rightarrow CCl_3PO(OC_4H_9)_2 + C_4H_9Cl$$

Obtaining Tributylphosphite $(C_4H_9O)_3P$

To a solution of butyl alcohol (3 moles) and triethylamine (3 moles) in benzene (800 cm^3) gradually during mixing and cooling is added a solution of trichlorous phosphorus (1 mole) in a small quantity of benzene. Butyl alcohol, triethylamine and benzene have to be dry. Temperature in beginning of reaction is around -5 to -8°; toward the end of the reaction the temperature may be increased to 15°. After addition of all the trichlorous phosphorus, the reaction mixture additionally was mixed for 2 hours at room temperature.

Falling crystal deposit of hydrochloric acid triethylamine was filtered rapidly, benzene was driven off, and the remainder was distilled in a vacuum.

Hydrochloric acid triethylamine may be removed also by other means — treatment of reaction mixture by a 1% solution of soda with subsequent washing by water. The yield of tributylphosphite is around 70% of the theoretical. The pure preparation of tributylphosphite was distilled at a temperature of 120-122° (7 mm Hg) and had $d_4^{20} = 0.9192$, $n_D^{20} = 1.4310$.

Obtaining Dibutyl Ester of Trichloromethylphosphine Acid $CCl_3PO(OC_4H_9)_2$

A solution of tributylphosphite (1 mole) in carbon tetrachloride (2 moles) is heated with reflux condensor 6 hours on a boiling water bath. Then in a vacuum (around 30 mm) surplus of carbon tetrachloride and a low-boiling byproduct, chlorous butyl, are given off.

The remainder obtained in such a way -- not quite pure dibutyl ester of trichloromethylphosphine acid -- had $d_4^{20} = 1.1870$ and $n_D^{20} = 1.4540$. Distilled in vacuum (3 mm Hg) the ester had $d_4^{20} = 1.1996$, $n_D^{20} = 1.4580$; its yield was 70%. Content of chlorine in a number of preparations of butyl ester of trichloromethylphosphine acid (additive Chloreth-40), obtained by this method without distillation, constituted around 30% (according to theory 34.1%).

From given data it follows that additive Chloreth-40 obtained by the assumed method, does not constitute a fully pure preparation of dibutyl ester of trichloromethylphosphine acid. The latter is in accordance with source material [5, 7]. Thus, Kamay and Egorova [5] obtained a preparation of ester, which was distilled at a temperature of 145-146° (7-10 mm Hg) and had a specific gravity $d_0^{17} = 1.1814$ and $n_D^{20} = 1.4521$.

In obtaining tributylphosphite by reaction hydrogen chloride is given off, which should be bound by triethylamine. Furthermore, if initial reagents, and namely butyl alcohol, triethylamine and benzene, contain moisture, then the last one will react with three-chlorous phosphorus also with formation of hydrogen chloride:

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

Part of the hydrogen chloride can react with tributylphosphite according to equation [10]:

$$P(OC_4H_9)_3 + HCl \rightarrow (C_4H_9O)_2POH + C_4H_9Cl$$

Incomplete ester of phosphorous acid (dibutylphosphite) is distilled at a temperature of 115° (10 mm Hg) and has $d_4^{20} = 0.9888$ and $n_D^{20} = 1.4240$ [9]. Dibutylphosphite can remain constant in second stage of process (obtaining of dibutyl ester of trichloromethylphosphine acid) and will be an undesirable impurity in additive Chloreth-40. Dialkylphosphite as a substance of acid character causes corrosion of metals.

In the opinion of one of the above-indicated authors [8], during rhe reaction of trimethylphosphite and tetrachloride of carbon acid chloride of dimethylphosphoric acid can be formed. It is possible that also during synthesis of dibutyl ester of trichloromethylphosphine acid analogous side reactions are observed:

$$(C_4H_9O)_3P+2CCl_4 \rightarrow (C_4H_9O)_2POCl+CCl_3{-}CCl_3+C_4H_9Cl$$
$$CCl_3PO(OC_4H_9)_2+CCl_4 \rightarrow (C_4H_9O)_2POCl+CCl_3{-}CCl_3$$

Formed in these reactions, chlorous butyl and hexachloroethane, will be easily driven off from the basic product, and part of the acid chloride of the dibutylphosphoric acid can remain in the final product. In the presence of moisture the acid chloride will form a substance easily corroding metals, — acid ester of phosphoric acid and hydrochloric acid.

Acid chloride of dibutylphosphoric acid is distilled at 132-133° (15 mm Hg); specific gravity of it $d_4^{20} = 1.0822$, $n_D^{20} = 1.4335$ [9].

It is necessary, however, to note that additive Chloreth-40, obtained according to the above method, by which is anticipated distillation in vacuum of both tributylphosphite, and also dibutyl ester of trichloromethylphosphine acid, is a very active additive, which lowers wear during friction in conditions of high loads. Impurities contained in it do not worsen quality of additive.

Tests of Chloreth-40 as an additive to transmission oils, conducted in stand conditions at the Likhachev automobile plant, gave positive results and served as the base for obtaining experimental lots of additive and further wider tests of it.

During production of experimental lots of additive Cloreth-40 at an installation of the pilot plant type, it was necessary to condiser that initial products — butyl alcohol, triethylamine, and benzene — unconditionally have to be dry. Furthermore, in obtaining additive Cloreth-40, distillation is desirable of both tributylphosphite and also of the final product — dibutyl ester of trichloromethylphosphine acid. Such distillation will decrease content of undesirable impurities in additive — acid

chloride of phosphoric acid and acid ester (dibutylphosphite). In any case one should consider distillation of tributylphosphite necessary.

As was established, the first experimental lots of Cloreth-40, obtained in pilot plant conditions without distillation of tributylphosphite and the final product, contain around 70-75% dibutyl ester of trichloromethylphosphine acid and 20-25% of the above-indicated impurities. Below are the average characteristics of several batches of tributylphosphite and additive Cloreth-40.

Tributylphosphite: $d_4^{20} = 0.9230$, $n_D^{20} = 1.4330$; Cloreth-40: $d_4^{20} = 1.1900$, $n_D^{20} = 1.4545$, content of chlorine 28.30%.

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EFFECTIVENESS OF CERTAIN ORGANO-MOLYBDENUM AND ORGANO-SULFUR COMPOUNDS AS ANTIWEAR ADDITIVES TO LUBRICATING MATERIALS

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VNII NP*

To guarantee normal work of friction units of contemporary complicated mechanisms it is required that lubricating materials remain stable under increased loads and temperatures of 250-350° and above, have a low coefficient of friction, improved lubricating ability, and increased antiwear means.

Mineral and synthetic lubricating oils, however, at increased temperatures are decomposed. Organo silicon liquids are stabler, but they do not possess the obtained lubricating ability [1, 2]. The latter may be significantly improved by application of special thermoresistant antiwear additives. To such additives belong certain organo-molybdenum and organo-sulfur compounds [3-6]. These additives can be successfully applied also for improvement of antiwear properties of different lubricating materials of special purpose.

The mechanism of action of additive on the basis of organo-molybdenum and organo-sulfur compounds, apparently, consists in formation of films which ensure sufficiently good separation of surfaces of friction at high temperatures and large loads [7-9].

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Organo-Molybdenum Antiwear Additive V-15/30

Additive V-15/30 is a complex compound, formed during the reaction of molybdenum, in the form of molybdenum blue, with higher alcohols or esters. Stable complexes are obtained also during combination of molybdenum blue with certain organo-phosphorous compounds, higher amines or amide, such as di- (2-ethylhexyl) phenylphosphate, di-ethylamidodidecylphosphate, di-dodecylamidodidodecylphosphate. Additive V-15/30 is readily soluble in oils and possesses the ability in significant degree to improve antiwear properties of lubricating materials. Action of this additive is especially effective during joint application with organic compounds containing sulfur, chlorine or certain other elements. Apparently, in the presence of the last ones the organo-molybdenum additive will form a more durable antiwear film on rubbing surfaces.

The effectiveness of additive V-15/30 in the pure form and together with other compounds was tested in the composition of different mineral and synthetic lubricating oils, and also silicon liquids. A test was conducted on a four-ball machine and on friction machines with toothed and gear transmissions. Tests on four-ball machine showed that additive V-15/30, taken in quantities in 3-5 times smaller as compared to applied additives, is very effective with respect to antiwear properties in oils of most diverse purposes. Certain results of test of lubricating oils of different origin with additive V-15/30 are represented in Fig. 1.

In Fig. 1 it is clear that in all cases the critical load of seizing in the presence of additive V-15/30, applied separately or together with a sulfurous compound, is significantly increased. Thus, during the addition of additive V-15/30 to di-(2-ethylhexyl) sebacinate (DOS) in a quantity ensuring a content of 0.1% molybdenum in oil, the critical load of seizing is increased from 58 to 148 kg (curves 1 and 2) and in the presence of butyldisulfide from 58 to 154 kg (curves 1 and 3).

A sulfurous compound added in equivalent ratio to molybdenum (calculated on forming MoS_2). With an increase of the quantity of additive V-15/30 to a content of 1% molybdenum in the sebacinate in the presence of butyldisulfide, the seizing was not observed even at a load of 300 kg (curves 1 and 4).

In the composition of silicon liquids additive V-15/30 effectively acts in the presence of sulfurous component, with a 1% molybdenum content. For instance, during a test of initial copolymer-2, seizing of surfaces set in at 50-70 kg, then as in the presence of additive V-15/30, taken together with dibenzyldisulfide, seizing was not marked at loads up to 300 kg (curves 5 and 6).

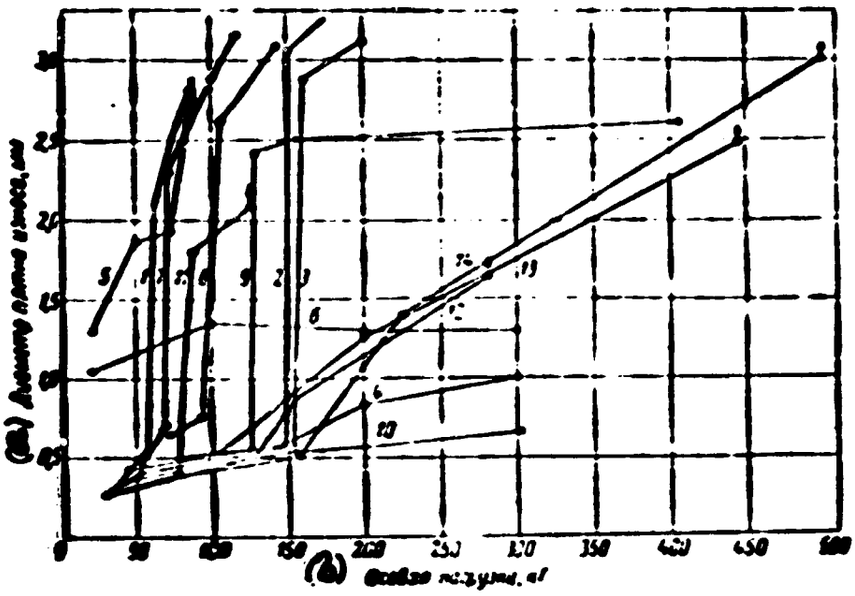


Fig. 1. Effectiveness of action of additive V-15/30 in the composition of different oils.
1—di-(2-ethylhexyl) sebacinate; di(2-ethylhexyl) sebacinate with additive: 2—V-15/30 (0.1% Mo); 3—+ V-15/30 (0.1% Mo) + butyldisulfide; 4—V-15/30 (1% Mo) + butyldisulfide; 5—copolymer-2; 6—the same + V-15/30 (1% Mo) + dibenzyldisulfide; 7—oil MS-20; oil MS-20 with additive: 8—V-15/30 (1% Mo); 9—V-15/30 (0.1% Mo) + butyldisulfide; 10—V-15/30 (0.3% Mo) + butyldisulfide; 11—transmission oil DS-12; oil DS-12 with additive: 12—V-15/30 (0.15% Mo); 13—sulfurous additive LZ-6/9 (3% Mo); 14—V-15/30 (0.15% Mo) + sulfurous additive LZ-6/9 (3% Mo).
KEY: (a) Diameter of spot of wear, mm; (b) Axial load, kg.

In the composition of mineral oils additive V-15/30 was tested at concentrations, calculated on molybdenum, from 0.1 to 0.3%, where its action turned out to be sufficiently effective already at a 0.1% Mo content in oil. During addition of additive to oil MS-20 up to a content of 0.1% Mo the critical load of seizing was increased from 70 to 95 kg (curves 7 and 8) and during joint application with butyldisulfide — from 70 to 125 kg.

Diameter of spot of wear in the last case was increased to 2.5 mm without further change with increase of load to 400 kg (curves 7 and 9).

Increase of quantity of additive to a 0.3% Mo content in oil in the presence of butyldisulfide caused a still sharper improvement of antiwear properties of oil (curves 7 and 10).

During test of additive V-15/30 in the composition of transmission oil DS-12 (mixture of 74% residual and 26% distillate component — industrial 12, 0.15% Mo) as a second component 3% of sulfurous additive LZ-6/9 was used. Results of tests characterize high effectiveness of joint action of additives, especially with respect to critical load of fusing. Thus, in the presence of one additive V-15/30 the load of seizing was increased from 79 to 126 kg and in the presence of one sulfurous additive, from 79 to 100 kg; during joint application of both additives from 79 to 158 kg; the load of fusing was changed from 126 to 282, 447 and 501 kg respectively (curves 11-14).

On the basis of obtained laboratory data was tested oil DS-12 with additives V-15/30 and LZ-6/9 on a Glison (Likhachev Moscow Automobile Factory) stand for tests of rear axles in assembly. The results obtained confirmed laboratory data on effectiveness of action of this combined additive; surface of teeth of gears of spiral-conical transmissions of automobile after testing turned out to be in good condition.

It is necessary to note that, along with very effective antiwear properties additive V-15/30 has certain deficiencies. It is insufficiently thermally stable

in the composition of certain high-temperature synthetic lubricating materials. In mineral oils the stability of solutions depends upon origin of base component and may be improved by means of addition of certain inhibitors.

Effectiveness of Organo-Molybdenum Additive V-15/30 as a Means for Applying Antifriction Film of Hydroxysulfurous Molybdenum on Surface of Friction

Developed in VNII NP, organo-molybdenum additive V-15/1 is readily soluble in mineral and synthetic oils, but upon heating to 150° is decomposed with a yield of a deposit of hydroxysulfurous molybdenum $MoOS_2$, which is deposited on surfaces of metal in the form of a thin film.

This property of the additive was used for application of an antifriction film on different surfaces of friction (ball and roller bearings, gears, and others).

Such a film was applied by means of treatment of metallic parts at given temperatures by concentrated (20-25%) solutions of additive V-15/1 in different organic thermoresistant liquids.

For a more uniform application of film on the surface, processed parts were placed in a metallic vessel, warmed by an electric furnace and secured in a laboratory vibrator. Forward-backward motion of vibrator ensured uniformity of washing of all surface. As solvents of additive, dioctylsebacinate or organo-silicon high-temperature liquids were used.

Temperature of treatment varied within the limits of 200-350°, depending upon thermal stability of processed steels. Optimum duration of treatment constituted 3 hours. Parts with a brilliant polished surface after treatment by additive V-15/1 obtained (depending upon applied temperature) a dark-gray or almost black color, explained by formation of hydroxysulfurous molybdenum on surface of film. This film is so thin that by existing methods its thickness can not as yet be determined. The presence of molybdenum on surface of balls of steel St. 3, treated by additive V-15/1, was proven by spectral analysis.

Tests of friction surfaces, untreated and preliminarily treated by additive V-15/1, were conducted on different friction machines. In Fig. 2 is shown influence of preliminary treatment of balls from silicon-molybdenum steel and thermal steels EI347 on resistance to wear of film forming in conditions of dry friction and friction with lubricant.

From given data it follows that the best effect is attained at a temperature of treatment of 200° for silicon-molybdenum steel and 300° for thermally stable steels EI347.

In Table 1 are given results of tests on stand "M" of bearing No. 8204 before and after treatment by additive V-15/1. The data allow the conclusion that during preliminary treatment of friction surfaces by additive V-15/1, the effect of lubricant during application of different lubricating materials is significantly improved.

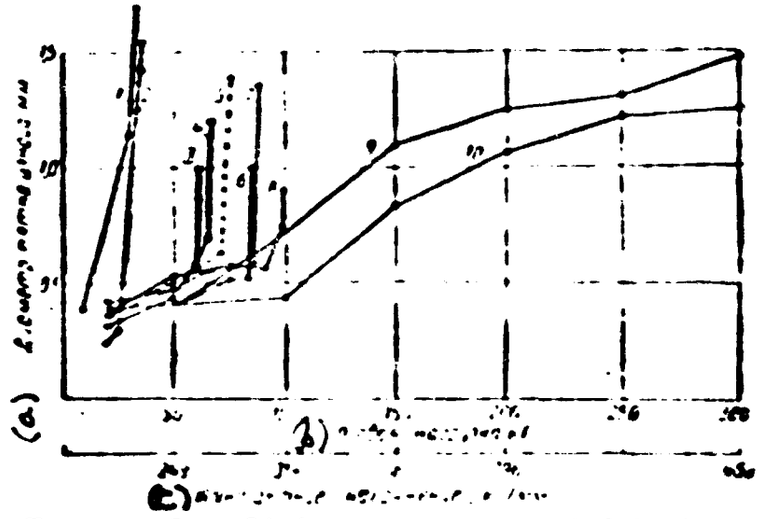


Fig. 2. Influence of preliminary treatment of friction surfaces by additive V-15/1 on effectiveness of lubricant during application of mineral and synthetic lubricating oils.

Conditions of test: four-ball machine; speed of slip 57.5 m/sec; duration of friction under load 60 sec; temperature 200°C; spheres from silicon-molybdenum steel and steel EI347.

Steel EI347: 1—untreated spheres (200°C; oil — dioctylsebacinate); 2—untreated spheres (20°C; oil — dioctylsebacinate); 3—spheres treated at 200° (20°C; oil — dioctylsebacinate); 4—spheres treated at 350° (200°; oil — dioctylsebacinate); 5—spheres treated at 300° (200°C; oil — dioctylsebacinate); 6—the same (20°C); 7—spheres treated at 350° (20°C; oil — dioctylsebacinate); 8—spheres treated at 300° (20°C; oil — dioctylsebacinate); 9—spheres from silicon-molybdenum steel, treated at 200° (200°C; mineral oil V-1); 10—spheres from silicon-molybdenum steel, treated at 300° (200°C; mineral oil V-1).

KEY: (a) Diameter of spot of wear, mm; (b) Axial load, kg; (c) Contact stress, kg/mm.

Table 1. Results of Tests on Vertical Stand "W" of Bearing No. 8204 Before and After Treatment by Additive V-15/1

Condition of treatment: 25% solution of additive V-15/1 in polymethylphenylsiloxane (PMFS-4), temperature 200°, duration of treatment 3 hours.
Conditions of tests: n = 850 rpm, load 15,00 kg/cm^2, temperature 200°.

Bearing No. 8204	Applied lubricant	Length of operation up to scoring*
Untreated.....	Polymethylphenylsiloxane	8 ч. 5 м. -8 ч. 55 м.
After treatment.....	Polymethylphenylsiloxane	21 ч. -28 ч. 30 м.
Untreated.....	Lubricant No. 221	55—58 min.
After treatment.....	Lubricant No. 221	5 ч. 30 м. -10 ч. 15 м.
Untreated.....	Lubricant No. 250	30—32 min.
After treatment.....	Lubricant No. 250	3 ч. -3 ч. 15 м.
Untreated.....	Lubricant No. 210	55—75 min.
After treatment.....	Lubricant No. 210	4 ч. -4 ч. 5 м.

*Ed. Note: The times are in the Russian system Thus 8 ч. = 8 hrs, and 8 ч. 5 м. = 8 hrs 5 min, etc.

Anti-Scoring Organo-Sulfur Additive V-15/2A

Externally additive V-15/2A is a butyrous liquid of light-yellow color, not soluble in water and without limit dissolved in different organic solvents and lubricating oils both mineral, and also in synthetic, and also even in organosilicon liquids (polymethylphenylsiloxanes, methylsiloxanes, tetraoctosiloxane, and others).

Additive V-15/2A differs by a very high stability. During storage over a prolonged time no sign of its decomposition was observed. In solutions of different lubricating oils the additive also can be saved a long time without precipitating, even under conditions of very low temperatures (the order of -50 to -60°).

As can be seen from data in Table 2, basic physico-chemical indices of base liquids practically do not change during the addition of 1.5% additive V-15/2A.

Table 2. Basic Physico-Chemical Characteristics of Additive V-15/2A and its Solutions in Organo-Silicon Liquids

Indices	V-15/2A in pure form	Organo-silicon liquid without additive		Copolymer-2 + + 1.5% V-15/2A	FM-1322 + + 1.5% V-15/2A
		Copolymer-2	FM-1322		
Kinematic viscosity (in cm) at a temperature, °C +					
+ 150	—	—	—	—	4.16
+100	2.13	5.7	7.7	5.49	7.75
+50	5.49	14.5	—	14.13	16.98
+20	—	—	33.7	—	—
0	35.53			82.14	58.62
-20	140			600	130.43
-40	1294	3200	600	5115	497.4
-50	—		1339	—	1298.0
Temperature of thickening, °C	-65 moves	-61 hardens	-70 moves	-60 moves -65 hardens	-60 moves well
Density e_4^{20}	1.137	1.030	—	1.038	—
Coefficient of refraction n_D^{20}	1.5790	—	1.4527	1.4920	—
Flash point (in open crucible), °C	—	—	220	223	—

During the study of thermal and thermo-oxidizing stability of solutions of additive V-15/2A in organo-silicon liquids it was shown that these solutions differ by high stability during heating to 200°. During temperatures of the order of 300-350° heating with intensive supply of air leads to change of color of solutions, not accompanied, however, by loss of hard deposits. During heating of solutions of additive in shown conditions with steel and aluminum plates immersed in them, on the steel plates was observed the formation of a black friable film (apparently, as a result of reaction of products of decomposition of additive with metal), presenting wear and fusing of metals during friction; on aluminum plates films

were not formed. Experiments were set on the study of corrosion aggressiveness of additive V-15/2A. Corrosion was determined in standard conditions at 100° for 3 hours. (All-Union Government Standard 2917-45) and at 150° for 50 hours. (All-Union Government Standard 5162-49).

It turned out that corrosion at 100° and 150° was observed only during reaction of additive with copper or its alloys. On all other tests metals (Al, Mg, Pb and different brands of steel, and also non-stannous bronzes) corrosion was not observed. Experiments showed the possibility of significant reduction of corrosion aggressiveness of additive with respect to copper and copper alloys by means of its passivation in special conditions. Corrosion was able to be reduced on electrolytic copper at a temperature of 150° from 5.7 milligram/cm^2 to 0.05-0.08 milligram/cm^2 during tests in standard conditions.

Effectiveness of Antiscoring Additive V-15/2A in Conditions of Friction at High Temperatures and Large Loads

An evaluation of antiwear and antiscoring properties of lubricating oils with an additive was conducted on a four-ball machine at temperatures of 200° and 250° and on TsIB-5M stand at 350°.

As base oil with these tests, thermally stable organo-silicon liquid.

In Fig. 3 are shown results of tests of organo-silicon liquids: copolymer-2, MF-1322, tetraoctoxylan of lubricant-6 without additive and with additive V-15/2A.

All these liquids are characterized by low lubricating ability and do not prevent fusing of spheres under a load of 150-170 kg.

Addition to these liquids of 1.5% additive V-15/2A eliminates fusing of spheres during testing in a large range of loads up to 300 kg. With such a content of additive, in certain degree a distinction of lubricating ability of base liquids still shows up. For instance, 1.5% additive to tetraoctoxylan does not prevent fusing of spheres under a load of 250 kg.

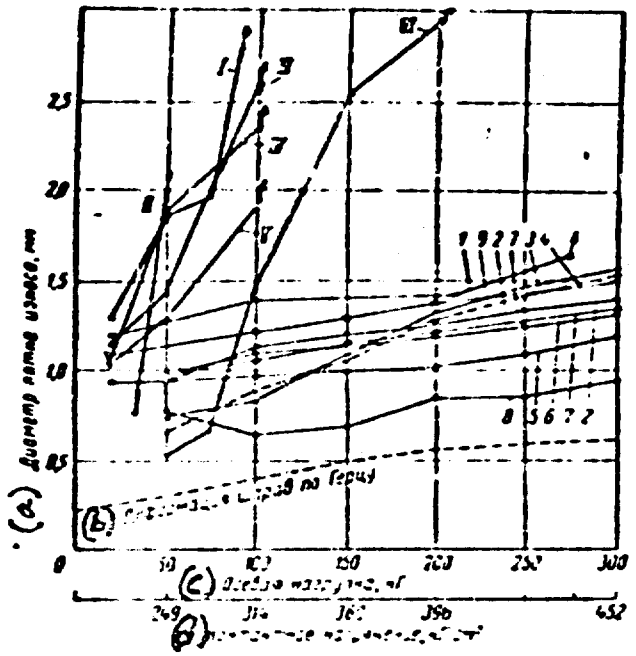


Fig. 3. Results of tests on four-ball machine of different organo-silicon liquids in pure form and with additive V-15/2A.

Condition of tests: length of friction under load, 60 sec; speed of slip, 57.5 cm/sec; temperature, 250° for copolymer-2, lubricant-6, MF-1322/30. Speed of slip, 19.2 cm/sec; temperature, 130° for PMS_{ya}.

I—copolymer-2 (100 fused spheres); II—tetraoctoxylan (100 fused spheres); III—PMFS-4 (d_{150} = 3.5 mm); IV—lubricant-6 (125 fused spheres); V—MF-1322/300; VI—PMS_{ya} (150 fused spheres); VII—275 fused spheres.
copolymer-2, temperature 250°, V-15/2A: 1—1.0%; 2—1.5%; 3—3.0%; 4—6.0%; 5—lubricant-6 + 1.5% V-15/2A, t = 250°; 6—MF1322/300 + + 1.5% V-15/2A, t = 250°; 7—PMFS-4 + 1.5% V-15/2A, t = 250°; 8—PMS_{ya} + 1.5% V-15/2A, t = 130°; 9—Tetraoctoxylan + 1.5% V-15/2A, t = 250°.
KEY: (a) Diameter of spot of wear, mm; (b) Deformation of spheres with respect to cycles per second; (c) Axial load, kg; (d) Contact tension, kg/cm^2.

3% additive V-15/2A smooths distinction in lubrication action of initial organo-silicon liquids, bringing the index of the worst of them to the best, both with respect to values of critical loads of seizing and also with respect to loads of fusing.

The bundle of wear — load curves for a 3% concentration of additive is somewhat lower than for a 1.5% concentration for loads up to 100 kg, but practically on the same level for higher loads (250–300 kg).

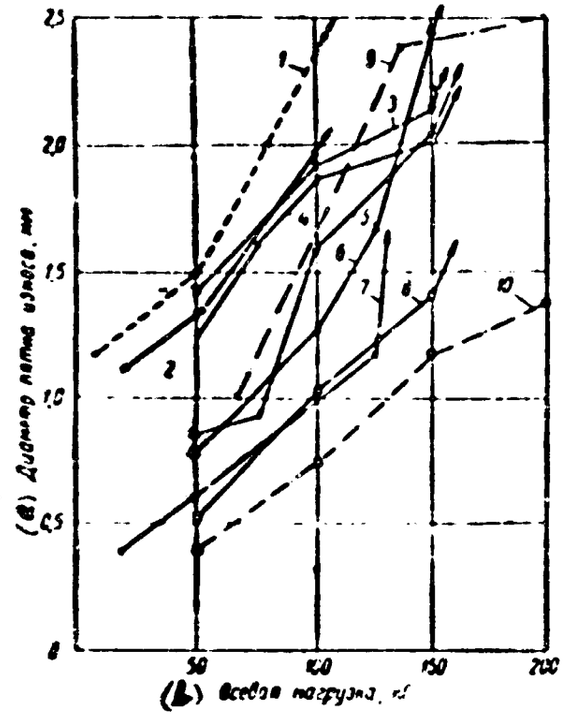


Fig. 4. Influence of preliminary treatment of friction surfaces by additive V-15/2A on effectiveness of the lubricant.
Conditions of tests: n = 500 rpm; temperature, 250° for lubricant PMFS-4, PM-1322/300 and DOS.* n = 1500 rpm, temperature 20° for mineral oil V-1. Silicon-molybdenum spheres d = 12.7 mm.
1—PMFS-4 (untreated spheres; 125 fused spheres); 2—PM 1322/300 (untreated spheres, 150 fused spheres); 3—PMFS-4 (spheres, treated by a 50% solution V-15/2A in PMFS-4 at 250°C; d_{200} = 3.41 mm); 4—PMFS-4 (spheres treated as in 3, at 200°C; d_{200} = 4.5 mm); 5—PM 1322/300 (spheres treated as in 3 at 250°C; d_{200} = 3.74 mm); 6—PM1322/300 (spheres treated as in 3 at 200°C; d_{200} = 4.5 mm); 7—dioctylsebacinate (spheres treated as in 3 at 250°C; d_{150} = 3.1 mm); 8—dioctylsebacinate (spheres treated as in 3 at 200°C; d_{175} = 4.5 mm); 9—mineral oil V-1 (untreated spheres); 10—mineral oil in V-1 (spheres, treated as in 3 at 200°C).
KEY: (a) Diameter of spot of wear, mm; (b) Axial load, kg.
Ed. Note: DOS = Dioctylsebacinate.

With an increase of concentration of additive to 6% improved further antiwear characteristics of applied base oils practically are not improved.

Additive V-15/2A was tested also as a means for application of antifriction sulfide film on different surfaces of friction. The film was applied under conditions similar to these described above for additive V-15/1.

Results of tests, shown in Fig. 4, show that sulfide film obtained during treatment of friction surfaces by additive V-15/2A, significantly improves effectiveness of lubricant during application of different lubricating materials at increased temperatures.

For tests of additive V-15/2A in conditions of rolling friction stand TsKB-54M was used. 1.5% of additive was added to polymethylphenylsiloxane. Tests were conducted under the following conditions.

Number of turns of shaft per minute..... 16000
Radial load of bearing TsKB-1082, kg..... 50
Quantity of oil in system, ml:
in beginning of first stage of tests..... 2500
in beginning of second stage of tests..... 1750
Temperature conditions, °C:
temperature of oil tank.....252—286
temperature of preheater.....435—443
temperature on entrance of oil in bearing....384—386
temperature of external ring..... 350
temperature on getting out of bearing.....356—366
Duration of work of stand on a given regime, hours. 10

Change of physico-chemical characteristics of oil during the time of testing is shown in Table 3.

Table 3. Change of Physico-Chemical Characteristics of Oil During the Time of Testing

Oil	Viscosity kinematic (cs) at a temperature, °C					Pour point, °C	Flash point, °C	Acid number, milligram KOH/g	Specific gravity
	100	50	0	-20	-40				
Fresh.....	5.49	14.14	82.4	311	5115	-65	223	0.1	1.038
After tests.....	7.26	19.8	133.4	890.3	14599	-53	242	0.23	1.492

After 10-hour tests of oil (in 2 stages of 5 hours each) the internal surface of the thermochamber, and also the external surface of the working head turned out to be covered with a film of cobweb-like mass, from white to dark-gray color, easily blown by a flow of air. Both bearings after first and second stages of tests had good mobility, revolved smoothly, without seizings and were useful for further use. After washing the noise in the bearings turned out to be not greater than in new ones. Hardness of rings after tests was within limits of allowance (58-62 Rockwell units). Increase of diameter of balls of bearing (on the average by 2.5 μ), apparently, should be explained by formation of sulfide film during reaction of additive with steel.

The races, external and internal ring turned out to be light, brilliant, without traces of wear.

The balls had a dark color with brilliant and smooth surface. Film on the balls was durable, externally resembling the film obtained at sulfidation.

Given data allow consideration that copolymer-2 with 1.5% additive V-15/2A completely ensures work of rolling bearings at a temperature of 350°.

Conclusions

1. Additive V-15/30, containing a complex compound of molybdenum, possesses the ability to sharply improve antiwear properties of mineral and synthetic lubricating materials.

Its action is especially effective during joint application with compounds containing sulfur, chlorine, or other elements. Deficiency of additive V-15/30 is its unsatisfactory thermo-oxidizing stability in the composition of certain high-temperature lubricating materials.

2. Organo-molybdenum additive V-15/1 may be successfully applied for preliminary application of antifriction noncorroding films on surface of friction. Effectiveness of high-temperature lubricant during application of different lubricating materials significantly increases. This appears in the reduction of wear of metal and prevention of fusing of metallic surfaces under large loads and high temperatures.

3. Organo-sulfur additive V-15/2A is a very effective antiscoring additive to high-temperature lubricating materials. During addition of it from 1.5 to 3.0% to different lubricating materials, including those prepared on the basis organo-silicon liquids, their lubricating ability significantly is improved, and scoring and fusing of metallic surfaces in conditions of high-temperature friction of heavily loaded parts is prevented.

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ANTIOXIDANT ADDITIVES TO LUBRICATING OILS ON A BASE OF PRODUCTS OF REACTION OF PHOSPHORUS PENTASULFIDE AND TERPENES

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To improve useful properties of motor oils two types of additives are usually added to them simultaneously: detergent and antioxidant. As detergent additives, for the most part sulfonates and alkylphenolates of barium and calcium [1, 2] are used. The purpose of the secondary additives is improvement of antioxidant, anti-corrosive, and antiwear properties, which worsen during addition into oil of some primary additives. As secondary additives phosphorous-containing organic compounds are usually used, which it is possible to add independently in lubricating oils to increase durability of butyric film and for work in conditions of super-high pressures [3].

Phosphorous-containing additives react with surface of metal at high temperatures appearing in contact points of surfaces of friction, with formation of phosphides, which form a low-fusible eutectic with the underlying layers of metal (iron or copper). Due to this, microroughnesses of surfaces are easily removed during friction, surfaces are polished, and coefficient of friction is lowered [3, 4].

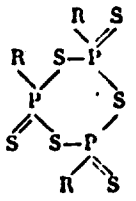
Phosphorous-containing additives delay oxidation of mineral oil in the mass which is attributed to the decomposition by them of peroxides — initiators of oxidation [5, 6], and especially sharply strengthen thermo-oxidizing stability of thin butyric films on steel [7, 8] thanks to passivating action of the phosphide film [9] which is formed.

Protection (anticorrosive action) by phosphorous-containing additives of copper-lead bearings of motors is based on formation of a protective film, containing molecule of additive-[10] or products of reaction of additive and metal [6]. Basic applied phosphorous-containing additives contain also sulfur [6, 11-13], since presence of the latter strengthens action of phosphorus.

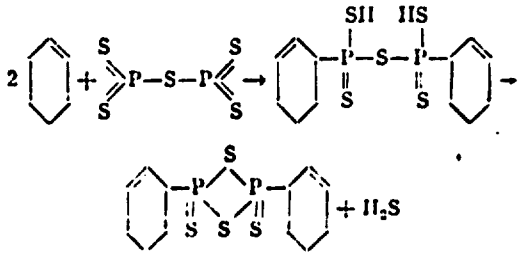
For automobile oils, as additives decreasing wear of pushers and bearings of carburetor motors, dialkyldithiophosphates of zinc and other metals [6, 14] are widely used. For diesel oils, operating at higher temperatures, frequently used are products of reaction of phosphorus pentasulfide with unsaturated hydrocarbons (terpenes and polyolefins) which are stabler at high temperatures than dialkyl-dithiophosphate.

The obtaining of products of the reaction of phosphorus pentasulfide with terpenes is given in a number of patents [15]. Usually 1 mole of powdery P_2S_5 is added at 100-130° to 4 moles of terpene (for instance, pinene, dipentene, or turpentine); an exothermic reaction occurs, and the mixture must be cooled in order to avoid formation of oil-insoluble products. After addition of P_2S_5 the mixture is heated for some hours at 140-150°, and hydrocarbons and more low-boiling substances not entering in the reaction are driven off, and the remainder filtered. Viscous liquids from yellow to brown in color are obtained. To carry out the reaction in smoother conditions, terpene is introduced into the inert solvent (usually in hydrocarbon fraction) which then is driven off, or in mineral oil, which is left in the additive.

The composition of products of reaction of terpene and P_2S_5 at present is not studied. G. M. Kosolapov [16] assumes that with this reaction a mixture of products is formed, in number of which are thiophosphine acids $R_2P(S)SH$ and $RP(S)(SH)_2$ (R — radical of terpene RH) and thiophosphoric esters $(RS)_3PS$ and $RSPS_2$. According to D. P. Dodgson [12] there are formed $(RS)_3PS$ and



The flow of the following main reaction between P_2S_5 and cyclohexene [17] is established:



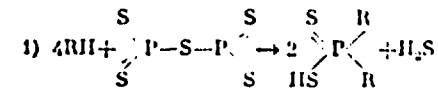
In this reaction atom P is joined to the unsaturated hydrocarbon not by a double bond, but to atom C, which is in position to double bond. The results given below of our experiments show that products of reaction of P_2S_5 with terpenes contain double bonds approximately 2 times less than they should when primary double bonds of terpene are kept constant.

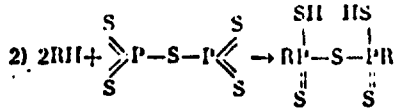
Part of the terpenes during reaction with P_2S_5 is polymerized in view of polymerizing action of the P_2S_5; polyterpene also enters in the product of reaction along with phosphorous-containing compounds. Thus we obtained products of reaction of P_2S_5 with pinene and dipentene fractions of turpentine, containing 2-3% P at a molecular weight of product of 300-350, whereas in the presence of 1 atom P in molecule of product its content had to be around 10%. Obtained also are samples of products containing 5-6% P at a molecular weight of 400-500, for which the content of P had to be 6-8% in the presence of 1 atom P in the molecule. However,

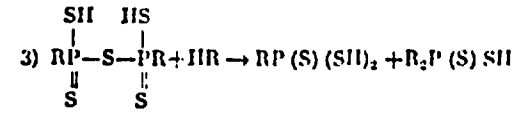
products with increased content of phosphorus, obtained by the usual method, turn out to be not soluble in mineral oils or incompletely soluble, and during storage of their butyric solutions deposits are formed.

We consider that the reaction of terpene with P_2S_5 in the beginning in known measure is analogous to the reaction of P_2S_5 with alcohols, where role of hydroxyl hydrogen of alcohol is executed by an atom of hydrogen of terpene in a-position to double bond, as is observed in the reaction with cyclohexene. A molecule of monocyclic terpene (dipentene) has two double bonds and, consequently, two active atoms of hydrogen; molecule of bicyclic terpene (pinene) has one double bond but its four-member ring easily breaks and it is isomerized into monocyclic which occurs during action of acids and heating, i.e., in conditions of reaction of terpene with P_2S_5. Nonetheless it is shown [24] that bicyclic terpenes as compared to monocyclic during reaction with P_2S_5 give an oil-soluble additive with a large content of phosphorus and best yield with a smaller yield of oil insolube substances.

Analogous to reactions of P_2S_5 with alcohols and cyclohexene, the following initial reactions between P_2S_5 and monocyclis terpene RH are possible:





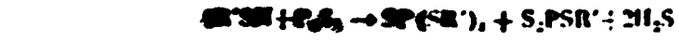


Formed in these reactions, thiophosphine acids are easily polymerized with liberation of H_2S and formation of insoluble polymers. Formation of given compounds also is observed during storage of usual products of reaction of P_2S_5 with terpenes in butyric solutions or in pure form.

H_2S is easily joined to double bond of olefins, giving mercaptans [18] which should occur also during the reaction of P_2S_5 with terpenes:



Mercaptans react then in P_2S_5 with formation of tetrathioorthophosphates and trithiometaphosphates [19]:



For stabilization of products of reaction of P_2S_5 in a number of patents it is proposed to process their aliphatic alcohol [20], by alkylphenol [21] or urea [22], to add in them butyric solution alcohol or carbonaceous acid [24], product of condensation of aldehyde with ammonia [25], or to neutralize their bases. However, these proposals, checked by us, turn out to be insufficient, and for obtaining a stabler product of reaction by given methods it is necessary to reduce the content of phosphorus which decreases the effectiveness of its action.

We found [26] that the reaction of P_2S_5 with terpenes takes place significantly better in the presence of $AlCl_3$; it takes place at a lower temperature (70-90°), less insoluble waste will be formed, yield of additive is higher and it is obtained as stable with a high content of phosphorus. Product of reaction for best stability and effectiveness of action is neutralized by a base of metal.

To carry out such a reaction, turpentine (it is possible in a mixture with gasoline, benzene or other inert solvent) is mixed with ~3% $AlCl_3$ at 40-60° ($AlCl_3$ dissolves with liberation of HCl); the mixture is heated to 70-90° and with this temperature and mixing powdered P_2S_5 in quantity 1 mole per 4-6 moles of terpene is gradually added over 2-5 hours; shown temperature is maintained by external cooling of vessel. After addition of all P_2S_5, temperature of mixture is increased to 130-150°; at this temperature the mixture is mixed 1-3 hours cooled somewhat and filtered or centrifuged for removal of insoluble substances. For removal of $AlCl_3$ the product is washed with 50-70% H_2SO_4 (5-10% on product) and

then water. From purified product unreacting hydrocarbons (and solvent) are driven off in the beginning under atmospheric pressure to temperature of the remainder ~ 200° and then at a pressure of 2-20 mm Hg to a temperature of the remainder of 130-180°. The remainder (acid additive) is mixed with a surplus of hydroxide or oxide of metal (for instance, with 25% milk of lime) 3-5 hours at 80-90°, then temperature is increased to 130-140° for evaporation of water, it is diluted by a hydrocarbon solvent (gasoline), they filter or centrifuge it and drive off the solvent. In Table 1 are given results of obtaining additives by the usual method and in the presence of $AlCl_3$. Raw material in all cases was pinene fraction of turpentine (turpentine oil according to the All-Union Government Standard 1571-54), containing 60% terpene; on experiment it took ~500 g turpentine.

Neutralized products of reaction in the presence of $AlCl_3$ turned out to be sufficiently stable during storage, in spite of having around 5% P in them, and had a significantly less sharp odor than additives obtained without $AlCl_3$.

During neutralization by $Ca(OH)_2$ salts of organophosphorous acids are obtained remaining in the ready additive, giving it a high ash content. During neutralization by ZnO a significant part of the formed salts of organophosphorous acids is not soluble in hydrocarbon solvent and precipitates.

During determination of bromine number, pinene acts like dipentine, i.e., joins to 1 molecule 4 atoms of bromine due to breaking of four-member ring. Bromine number of pinene 265, and products of reaction of P_2S_5 with pinene had to have bromine numbers of 210-225 under the condition of constant double bonds and taking into account composition of products of reaction. Actual bromine numbers of the additives are less than half of the shown magnitude due to the addition of H_2S and partial polymerization.

Table 1. Additives — Products of Reaction of P_2S_5 with Terpenes

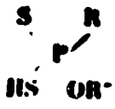
Property	Method of obtaining			
	Usual, without neutralization	In presence of $AlCl_3$		
		Without neutralization	Neutralization by $Ca(OH)_2$	Neutralization by ZnO
Yield, % on terpene + P_2S_5	69.3	81.9	79.4	77.2
Specific gravity d_4^{20}	0.977	—	—	1.035
Index of refraction n_D^{20}	1.5041	1.5559	1.5601	1.5579
Average molecular weight	308	352	475	355
Viscosity at 100°, cs	8.1	16.2	18.3	29.9
Content of phosphorus, %	2.0	5.1	4.9	4.3
Content of sulfur, %	4.9	11.8	9.9	9.5
Ash content, %	0.0	0.0	15.1	0.47
Acid number:				
indicator bromophenol blue	5.9	14.6	9.9	0
indicator phenolphthalein	14.4	61	67	10.3
Bromine number according to Francis	63	80	78	77
Thermo-oxidizing stability according to All-Union Government Standard 4953-49 1% solution of additive in oil MT-16 at 250°, minutes*	40	55	65	65
The same, in plate-evaporator	55	80	95	90
Deposit after a 32-hour heating at 180° a 1% solution of additive in oil AC-5, g/100 g oil	0.21	—	0.01	0.008
Transparency of 1% solution in oil AC-5:				
after dissolution	Transparent	—	Transparent	
after 1 month of storage at ~ 20	Turbid	—	The same	

*Thermooxidizing stability of oil MT-16 base (without additive) according to standard method in a plate-evaporator 20 minutes.

During standard determination of thermo-oxidizing stability according to All-Union Government Standard 4953-49, oil with phosphorous additives, having a high thermo-oxidizing stability, are spread along a significant area of disk, forming a layer of oil significantly thinner than for oils with a low thermo-oxidizing stability. Since speed of oxidation of film of oil increases with decrease of its thickness, then for determination of comparative action of additives in a layer of identical thickness we used a plate evaporator according to All-Union Government Standard 5737-53 having an internal diameter of 21.4 mm, in which was placed a weighed portion of oil (0.05 g) and ring according to All-Union Government Standard 4953-49. From given data it is clear that action of phosphorous additives on thermo-oxidizing stability during identical thickness of layer of oil in plate evaporators shows significantly stronger than during the standard method according to All-Union Government Standard 4953-49.

With the action of P_2S_5 on a mixture of terpene or turpentine and aliphatic alcohol, we obtained additives with a high content of phosphorous and stable during storage. This reaction takes place easily in presence of a catalyst of 1-5% of sulfuric acid on terpene. In Table 2 are given some of the obtained products of the reaction of P_2S_5 with a mixture of pinene fraction of turpentine (turpentine oil according to All-Union Government Standard 1571-54) and n-butanol, prepared in the following manner. To a mixture consisting of 1 mole terpene in the form of turpentine (contains 60% terpenes), 1 mole n-butanol and 2% (on terpenes) 100% H_2SO_4, over 1.5-2 hours at 80-90° 0.3 mole P_2S_5 is added to the mixture, maintaining temperature of mixture by external cooling. After addition of P_2S_5 the mixture is heated to 120-130° and mixes at this temperature for 2 hours, washed from the H_2SO_4 by water at 50-60°, filtered and distilled under atmospheric pressure to a temperature of the remainder of 200°, then under a pressure of 2-20 mm Hg to a temperature of the remainder of 130-180°. The obtained acid additive is neutralized just as the product of reaction of P_2S_5 with one terpene.

The formula of mixed additives (terpene + alcohol) can be presented analogously to the formula of dialkyldithiophosphates:



where R" — radical of alcohol R" OH.

The presence in mixed additive of OR" group facilitates the introduction of metal in the molecule. Thus, neutralized by zinc, the product of the reaction of P_2S_5 with terpene (see Table 1) had a 0.47% ash content, and the mixed additive, neutralized by zinc [Table 2, experiment 135], had a content of 15.5%.

Table 2. Additives — Products of Reaction of P_2S_5 with Equimolecular Mixture of Terpene and n-Butanol

Characteristics	No. experiment		
	128	134	135
Yield, % on terpene + n-butanol + P_2S_5	84.3	83.8	83.6
Specific gravity d_4^{20}	1.017	1.110	1.210
Index of a refraction n_D^{20}	1.5012	1.5261	1.5236
Average molecular weight	292	498	470
Viscosity at 100°, cs	2.97	20.8	17.3
Content of phosphorus, %	6.6	6.2	6.0
Content of sulfur, %	13.0	12.9	11.5
Ash content, %	0	15.3	15.5
Bromine number according to Francis	—	49	52
Acid number:			
Indicator bromophenol blue	25.1	0	0
Indicator phenolphthalein	42.4	36.3	39.2
Potentiometric to pH-4	—	-15.9	-2.6
Potentiometric to pH-9	—	-3.1	7.7
Thermo-oxidizing stability according to All-Union Government Standard 4953-49 of 1% solution of additive in oil MT-16 at 250°, minutes*	45	60	55
The same, in a plate-evaporator	51	85	80
Transparency of 1% solution in oil AS-5 after 1 month of storage at ~20°		Transparent	

*See footnote to Table 1.

Tests of obtained additives in combination with additive MG-102u (contains 20% basic calcium sulfonate, 10% calcium salt of product of condensation of alkylphenol with formaldehyde, 70% mineral oil) in oil MS-20 showed that a calcium-containing additive is the best antioxidant (see Table 1).

Conclusions

1. The reaction of phosphorus pentasulfide with terpenes takes place in the presence of aluminum chloride at a lower temperature and with a smaller formation of high-polymer insoluble substances than in the usual method in the absence of aluminum chloride; neutralized by bases of metals, the products of reaction in the presence of aluminum chloride as compared to those obtained by the usual method, possess best stability, higher content of phosphorus and sulfur, best solubility in oil and give a higher thermo-oxidizing stability to mineral oils in thin film.

2. A new type of organo-phosphorous compounds has been obtained by means of reaction of phosphorus pentasulfide with a mixture is terpene and alcohols in the presence of sulfuric acid as a catalyst. The obtained products of reaction form salts with bases of metals, which are applicable as additives to lubricating oils.

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METAL DIALKYLDITHIOPHOSPHATES AS ANTIOXIDANTS OF LUBRICATING OILS

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Dialkyldithiophosphates are polyfunctional additives to lubricating oils. As was established, certain additives of this type possess washing, anticorrosive, and antiwear properties and are, furthermore, antioxidants, and certain are depressors and demulsifiers [1].

Dialkyldithiophosphates of metals, as antioxidants of lubricating oils, were briefly characterized by us earlier [2, 3]. It was established that they increase thermo-oxidizing stability of oils (All-Union Government Standard, 4953-49) and delay formation of tarry products not soluble in oil in conditions of standard tests on PZV motor. Oils containing dialkyldithiophosphates of metals, as a rule, differed by smaller content of acid products (smaller acid and number) than oil without additives [3].

In literature there are also other data about antioxidant action of dialkyldithiophosphates. Prutton [4] investigated mechanism of action of anticorrosive additives — inhibitors of corrosion of copper-lead alloys of bearings — and found that corrosion in significant degree depends on stability of oil. In connection with this a number of additives of the antioxidant type was tested.

Tests were conducted in presence of catalysts of oxidation -- metallic copper and organic salts of copper soluble in oil, for instance copper oleate. As was shown, certain additives, also including zinc dialkyldithiophosphate delay process of oxidation of oil. The action of inhibitors in this case the author connects with their ability to decompose hydrogen peroxide forming during oxidation of hydrocarbons of oil. Larson [5] gave general characteristics of zinc dialkyldithiophosphates as additives to lubricating oils and also established that they essentially delay oxidation of high-purified (white) oil by atmospheric oxygen. He also confirmed influence of zinc dialkyldithiophosphate on speed of decomposition of peroxides.

In this work is studied the antioxidant activity of dialkyldithiophosphate of metals of different structure and the influence of certain factors on process of oxidation of hydrocarbons of oil in presence of these additives is shown.

For investigation technical additives which have following structure were taken*.

$[(RO)_2PSS]_2Ba$; R $C_{20}-C_{24}$ ДФ-1

$[(RO)_2PSS]_2Ba$; R $C_{16}-C_{20}$ ДФ-2

$[(CH_3(CH_2)_3CH(C_2H_5)CH_2O)_2PSS]_2Ba$ ДФ-12

$[(RO)_2PSS]_2Zn$; R $C_{20}-C_{24}$ ДФ-5

$[(CH_3(CH_2)_3CHO)_2PSS]_2Zn$ ДФ-8

$[(CH_3(CH_2)_3CH(C_2H_5)CH_2O)_2PSS]_2Zn$ ДФ-9

$[CH_3(CH_2)_3CHO]_2PSSZnSSP[OCH_2CH(CH_3)_2]_2$ . . . ДФ-10

$[CH_3(CH_2)_3CH(C_2H_5)CH_2O]_2PSSZnSSP[OCH_2CH(CH_3)_2]_2$ . . ДФ-11

The influence of additives on oxidation of oil DS-8 and fractions separated from this by chromatographic means was studied.

Oil DS-8 -- distillate obtained from sulfurous oils. It was distilled within the limits of 330-420° and had the following characteristics:

*Ed. Note: ДФ = DF.

viscosity at 100°, cs..... 7.98
flash point, °C..... 186
temperature of thickening, °C..... -32
content of sulfur in oil, %..... 1.04

Oil DS-8 was divided by chromatographic method (silica gel of brand ASK, desorbent — isooctane, benzene, alcoholbenzene) into a fraction, characteristics of which are given in the table.

Chemical Composition of Oil DS-8

Separated fractions	Yield, %	n_D^{20}	Content of sulfur, %
Paraffin and naphthenic hydrocarbons.....	50.8	1.4740	0
Monocyclic aromatic hydrocarbons and sulfurous compounds.	31.5	1.5090	1.26
Bicyclic aromatic hydrocarbons and sulfurous compounds.....	13.6	1.5408	3.11
Resins.....	3.9	—	—

Average-molecular weight of fraction of paraffin and naphthenic hydrocarbons constituted 404, $d_4^{20} = 0.8027$, $n_D^{20} = 1.4740$. According to data of structural-group analysis an average molecule of this fraction contained two naphthenic rings; share of carbon in naphthenic structures constituted 35.2%, in paraffin structures 64.8%.

The majority of experiments of oxidation were conducted with fraction of naphtheneparaffin hydrocarbons separated from oil DS-8. This fraction does not contain natural inhibitors of oxidation, is very unstable and, therefore, is the most receptive to action of additives of the antioxidant type.

Oxidation of oil was determined with respect to absorption of oxygen by oil in a closed system, and the quantity of absorbed oxygen was established with respect to the drop of barometric pressure. This principle of determination of oxidizability of hydrocarbons and other substances was for the first time applied by Mourev and Dufraisse [6]. We used the somewhat modified method of O. G. Popik [7],

according to whom the quantity of absorbed oxygen was determined by the rise of water in barometric tube. In all experiments, by the drop of barometric pressure was determined the volume of absorbed oxygen, and results of oxidation were presented in the form of curves of dependence of the quantity of absorbed oxygen on the length of oxidation. The weighed sample of oil constituted 2 g.

Comparative Activity of Antioxidants of the Metal Dialkyldithiophosphates Type

In Fig. 1 are given results of oxidation of paraffin-naphthenic fraction in presence of different dialkyldithiophosphates of metals at a temperature of 180°. Concentration of additives in oil in first series of experiments constituted 3.5% (Fig. 1a) and in second series 2 mmole/100 g oil (Fig. 1b).

From given data it is clear that the paraffin-naphthenic fraction itself is extremely unstable — absorption of oxygen in the assumed conditions is finished in six minutes. All dialkyldithiophosphates in one or another measure delay speed of oxidation of hydrocarbons and are, consequently, antioxidants. However, their activity as antioxidants is not identical and depends in the first place on structure of hydrocarbon radicals. Least active are additives DF-9, DF-11, and DF-12, containing primary hydrocarbon radicals, i.e., obtained on the basis of primary alcohols — isobutyl and 2-ethylhexyl. All remaining additives contain secondary hydrocarbon radicals (secondary octyl radicals in additives DF-8 and DF-10 or secondary radicals of technical alcohols in additives DF-1, DF-2, DF-5) and correspondingly differ by increased and almost identical activity. This may especially graphically be seen in Fig. 1b, on which are shown results of oxidation of fraction containing an equimolecular quantity of additives.

Obtained data about influence of structure of hydrocarbon radicals on antioxidant properties of dialkyldithiophosphates are in accordance with source material [5].

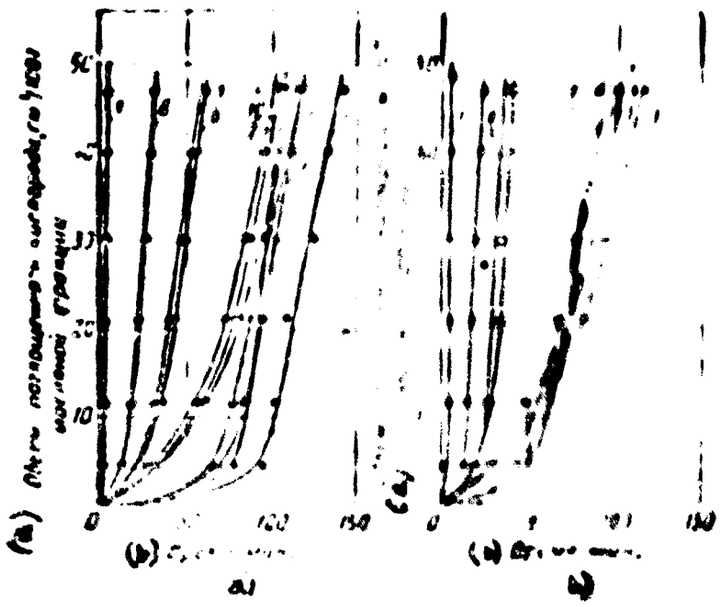


Fig. 1. Influence of antioxidants of the metal dialkyldithiophosphate type on oxidation of paraffin-naphthenic fraction.
a —concentration of additives 3.5%; 1—paraffin-naphthenic fraction; paraffin-naphthenic fraction with additives: 2—DF-1; 3—DF-2; 4—DF-5; 5—DF-8; 6—DF-9; 7—DF-10; 8—DF-11; 9—DF-12; 10—lyubrisol 1060; 11—santolube 393; b—concentration of additives 2 mmole/100 g fraction; 1—paraffin-naphthenic fraction; paraffin-naphthenic fraction with additive: 2—3.5% DF-1; 3—3.0% DF-2; 4—3.3% DF-5; 5—1.7% DF-8; 6—1.7% DF-9; 7—1.4% DF-10; 8—1.4% DF-11; 9—1.8% DF-12; 10—0.8% lyubrisol 1060; 11—0.8% santolube 393.
KEY: (a) Volume of absorbed oxygen, $cm^3/100$ g butyric fraction; (b) Time, minutes.

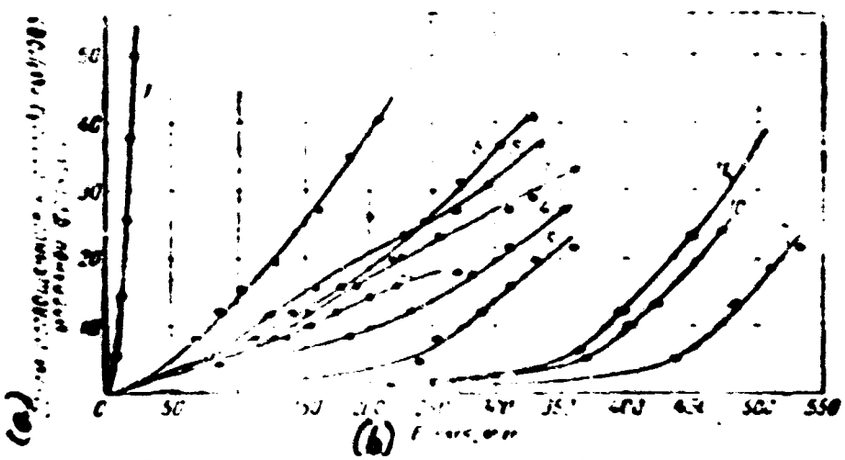


Fig. 2. Influence of antioxidants of the type dialkyldithiophosphates of metals on oxidation of paraffin-naphthenic fraction.
1—paraffin-naphthenic fraction; paraffin-naphthenic fraction with additive: 2—DF-1; 3—DF-2; 4—DF-5; 5—DF-8; 6—DF-9; 7—DF-10; 8—DF-11; 9—DF-12; 10—Lyubrisol 1060; 11—Santolube 393.
KEY: (a) Volume of absorbed oxygen, $cm^3/100$ g butyric fraction; (b) Time, minutes.

In Fig. 2 are given results of oxidation of paraffin-naphthenic fraction of hydrocarbons in the presence of the same additives (concentration 3.5%), but at a temperature of 150°.

The basic conclusion which was made earlier about the influence of hydrocarbon radicals (secondary and primary hydrocarbon radicals) on antioxidant activity of dialkyldithiophosphates is also verified in this series of experiments of oxidation, conducted at a lower temperature. It is essential also to note that with decrease of temperature of oxidation, activity of antioxidants of the dialkyldithiophosphates type sharply increases. For instance, the time of oxidation of fraction (22 minutes) in the presence of additive DF-10 increased more than 25 times (over 9 hours).

Temperature of Oxidation

The influence of temperature on oxidation of paraffin-naphthenic fraction in the presence of additives DF-1 and DF-11 was studied at temperatures of 120°, 130°, 140°, 150°, 160°, 180° and 200°.

Stability of the fraction itself with decrease of temperature from 200° to 120° is increased in a very insignificant degree (Fig. 3).

The action of additives DF-1 and DF-11 as antioxidants directly depends on temperature. At a temperature of 200° both additives practically do not increase stability of butyric fraction. With degrease of temperature of oxidation from 200° to 120° activity of additives as antioxidants continuously increases and at a temperature of 120° both additives almost completely delay oxidation of hydrocarbons of butyric fraction. In the whole investigated interval of temperatures, additive DF-1 (high-molecular barium dialkyldithiophosphate) turned out to be a more active antioxidant than additive DF-11 (comparatively low-molecular zinc dialkyldithiophosphate).

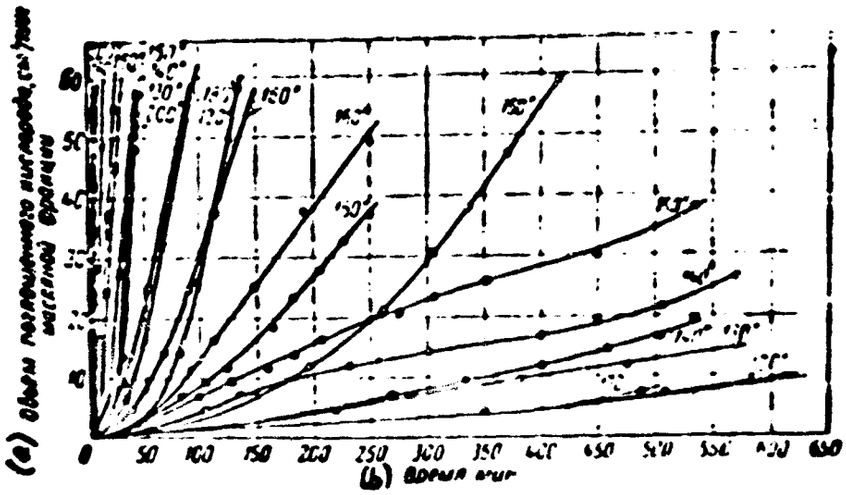


Fig. 3. Influence of temperature on oxidation of paraffin-naphthenic fraction, containing additives DP-1 and DP-11. x — paraffin-naphthenic fraction; paraffin-naphthenic fraction with additive: ● — 2% DP-1; ○ — 2% DP-11; ◐ — 5% DP-11.
KEY: (a) Volume of absorbed oxygen, $cm^3/100$ g butyric fraction; (b) Time, minutes.

The lowering of activity of additives at high temperatures, it seems to us, is connected with partial decomposition of additives.

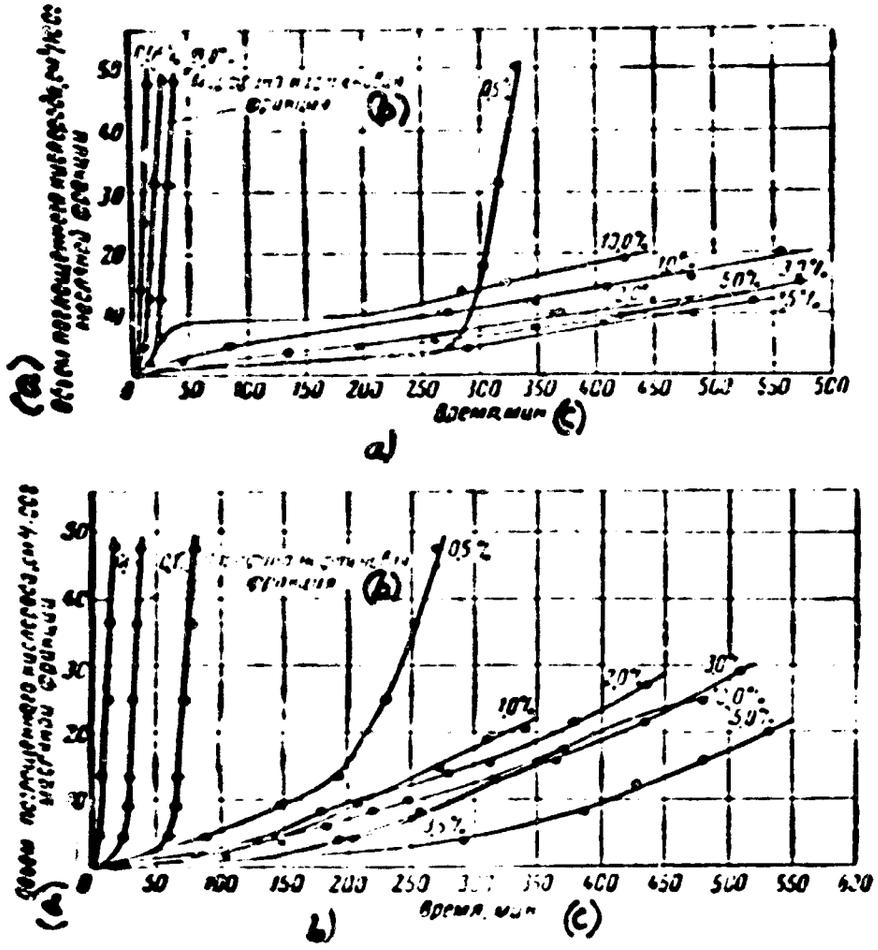
Concentration of Additives

Influence of concentration of additives on oxidation of oil was studied on the example of additives DP-1 and DP-11 (Fig. 4a, b).

Antioxidant action of additive DP-1 with increase of concentration from 0.05 to 1.5% increases, then during concentrations of the order of 1.5-5.0% remains approximately on an identical level; after further increase of concentration, the antioxidant action of the additive is somewhat lowered. With very small concentrations (0.05-0.1%), action of the additive on oxidation of butyric fraction is very insignificant. Consequently, optimum concentration of additive DP-17 in assumed conditions of oxidation should be considered 1.5% (or 0.75% barium dialkyl-dithiophosphate proper).

The general character of influence of concentration of additive DP-11 on oxidation of butyric fraction (see Fig. 4b) is analogous for additive DP-1, but

optimum concentration of additive DF-11 constituted 5% instead of 1.5% for additive DF-1. This distinction in optimum concentrations of both additives, which will be still more significant in the list on molar concentrations, once again points to higher antioxidant activity of additive DF-1 as compared to additive DF-11.



a)

b)

Fig. 4.
a—influence of concentration of additive DF-1 on oxidation of paraffin-naphthenic fraction (temperature of oxidation 150°).
b—influence of concentration of additive DF-11 on oxidation of paraffin-naphthenic fraction (temperature of oxidation 150°).
KEY: (a) Volume of absorbed oxygen, $cm^3/100$ g butyric fraction; (b) Paraffin-naphthenic fraction; (c) Time, minutes.

Influence of Technical Additives On Oxidation of Butyric Fraction

In Fig. 5 are represented results of oxidation of paraffin-naphthenic fraction in the presence of different technical additives.

The following additives were tested: known antioxidants diphenylamin and Ionol (2.6-di-tert-butyl-4-methylphenol), additive of the alkylphenolates type --

Paranolx 56A (disulfide of barium diisobutylphenolate), barium alkylphenolate ("washing" component of additive tsiatim*-339), tsiatim-339 (contains disulfide of barium alkylphenolate) vnii np-350 (barium alkylphenolate with high content of barium); vnii np-360 (contains vnii np-350 and vnii np-354--dialkyldithiophosphate --dialkylphenyldithiophosphate); additive of sulfonate type -- (sulfonate of barium) washing component of additive aznii-5), aznii-4 (contains sulfonate of calcium and sulphurized oil), PMS_{ya} (sulfonate of calcium); additive of metal dithiophosphates type -- IP-22k (disulfide of calcium dialkylphenylidthiophosphate), DF-1 (high-molecular dialkyldithiophosphate of barium).

As one should have been led to expect, additives of the sulfonates type only in insignificant degree affect oxidation of oils. Little active also are additives of the alkylphenolates type (barium alkylphenolate, vnii np-350), although they also possess a certain antioxidant action. Significantly more active are additives of the alkylphenolate type, containing sulfur or phosphorus in the form of sulfide or dithiophosphates (tsiatim-339, vnii np-360, vnii np-361, paranox 56A). The most active antioxidants in the assumed conditions of oxidation turned out to be additive DF-1 (high-molecular dialkyldithiophosphate of barium) and the well-known antioxidant Ionol.

Given data once again confirm expediency of application of mixed additives, for instance, consisting of sulfonates not possessing an antioxidant action, antioxidants of the type of additive DF.

*Ed. Note: Additive is named for research institute TsNIAT-M or tsiatim = Central Scientific Research Institute of Aviation Fuels and Lubricants.

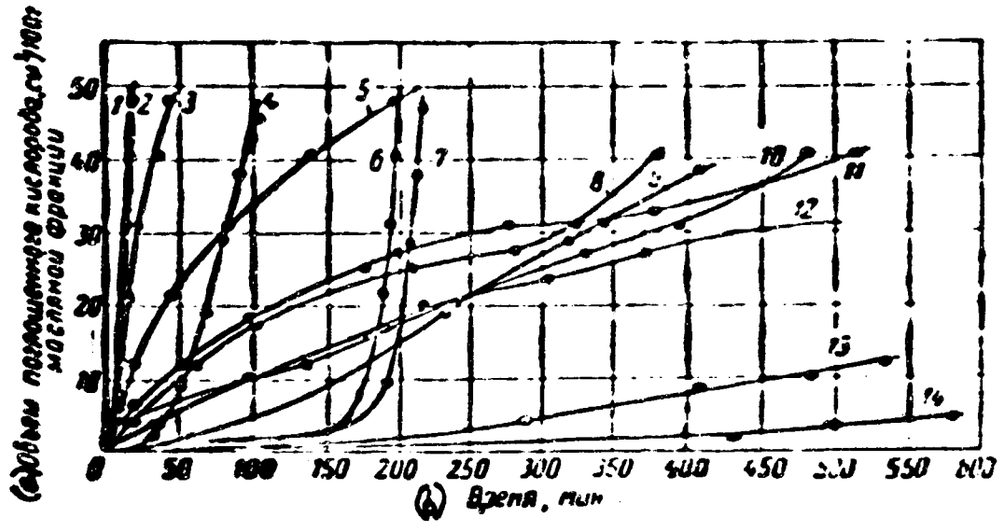


Fig. 5. Influence of different technical additives on oxidation of paraffin-naphthenic fraction.

Conditions of oxidation: temperature 150°; concentration of additives 2%; concentration of diphenylamin and Ionol 0.3%.
1—paraffin-naphthenic fraction; 2—low-ash sulfonate; 3—aznii-4; 4—diphenylamin; 5—vnii np-350; 6—PMS$_{ya}$; 7—alkylphenolate; 8—tsiatim-339; 9—IP-22k; 10—vnii np-361; 11—vnii np-360; 12—Paranox 56A; 13—DF-1; 14—Ionol.
KEY: (a) Volume of absorbed oxygen, cm^3/100 g butyric fraction; (b) Time, minutes.

Influence of Chemical Composition of Fractions Separated from Oil, on their Oxidation in the Presence of Additive DF-1

As was said above, oil DS-8 was divided into fractions: paraffin-naphthenic hydrocarbons, monocyclic aromatic hydrocarbons containing sulfurous compounds, and bicyclic aromatic hydrocarbons containing sulfurous compounds. From fractions of aromatic hydrocarbons sulfurous compounds were removed by oxidation by hydrogen peroxide and subsequent yield of sulfoxides formed by adsorption on silica gel.

In Fig. 6 it is clear that monocyclic hydrocarbons, separated from oil and not containing sulfurous compounds, are unstable the same way as paraffin-naphthenic hydrocarbons.

Significantly stabler are bicyclic hydrocarbons. Sulfurous compounds, contained in fraction of monocyclic aromatic hydrocarbons, sharply increase stability of this fraction, nearing it in this respect to the ability of the oil itself. The high stability of oil DS-8, consequently, is explained by content

in it of certain aromatic fractions and, especially, sulfurous compounds, which are natural antioxidants with respect to unstable hydrocarbons of oil.

The antioxidant action of certain sulfurous compounds of oil, and also individual organic compounds of sulfur was noted in literature [8, 9, p. 286].

From given data it is also clear that presence in oil DS-8 of natural antioxidants paralyzes action of synthetic additive — antioxidant DF-1. If additive DF-1 is an active antioxidant in regard to paraffin-naphthenic hydrocarbons and monocyclic hydrocarbons of oil not containing sulfurous compounds, then the same additive does not render antioxidant action on monocyclic and bicyclic hydrocarbons containing sulfurous compounds. The speed of oxidation of fraction of monocyclic hydrocarbons containing sulfurous compounds, the same as oil DS-8 itself, in presence of additive DF-1 even increases somewhat.

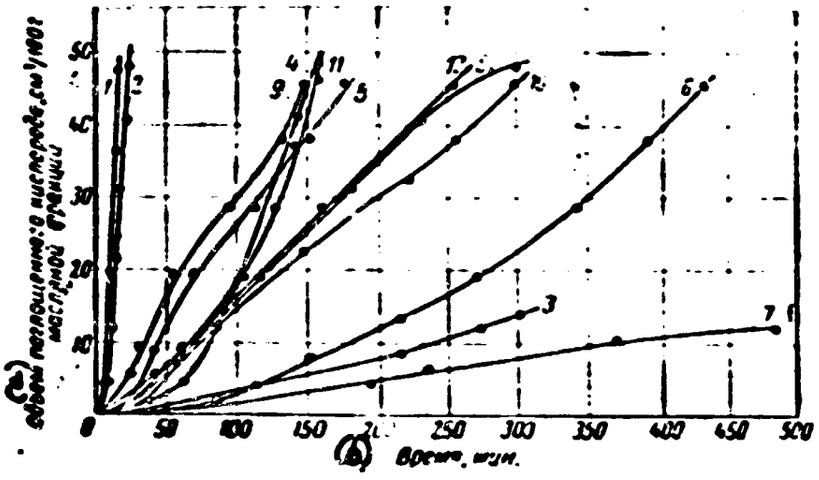


Fig. 6. Influence of chemical composition of fractions separated from oil DS-8, on their oxidation in the presence of additive DF-1.

Conditions of oxidation: temperature 150°; concentration of additive DF-1 2%.
1—paraffin-naphthenic hydrocarbons; 2—monocyclic aromatic hydrocarbons; 3—monocyclic aromatic hydrocarbons containing sulfur; 4—bicyclic aromatic hydrocarbons containing sulfur; 5—bicyclic aromatic hydrocarbons; 6—DS-8; 7—paraffin-naphthenic hydrocarbons + DF-1; 8—monocyclic aromatic hydrocarbons + DF-1; 9—bicyclic aromatic hydrocarbons + DF-1; 10—monocyclic aromatic hydrocarbons containing sulfur + DF-1; 11—bicyclic aromatic hydrocarbons containing sulfur + DF-1; 12— DS-8 + DF-1.
KEY: (a) Volume of absorbed oxygen, $cm^3/100$ g butyric fraction; (b) Time, minutes.

Obtained data about influence of chemical composition of hydrocarbons fractions on their oxidizability in the presence of antioxidant DF-1, naturally, provide a basis for the following question: can additives of this type be antioxidants of lubricating oils in actual conditions of their use. In connection with this question, first of all it is necessary to consider data about catalytic action of metals on oxidation of hydrocarbons. Our earlier examples of antioxidant action of metals alkyldithiophosphates on different oils (determination of thermooxidizing stability, accumulation of tarry and acid products in process of test on motor PZV) pertain to experiments in which oil was in contact with metals. The very same occurs also in actual conditions of using the oils.

Influence of Metals and their Oxides on Oxidation of Oil in Presence of Additive DF-1

In Fig. 7 is given the dependence of speed of oxidation (asorption of oxygen) on time for oil DS-8 in the presence of metals — copper and iron, and also oxide of copper. Reduced metals — copper and iron and oxide of copper were applied in a powdery form.

Oil DS-8 in presence of metals or oxides becomes weakly stable and with a large content of metal (Cu, 5% of weight of oil; 1:1) practically absolutely unstable (see Fig. 7). Consequently, metals in these conditions are strong catalysts of oxidation of hydrocarbons and absolutely paralyze action of natural inhibitors of oil (sulfurous compounds).

Additive DF-1 in presence of metals and oxides increases stability of oil DS-8, in this or that measure nearing it to the stability of oil in the absence of metals and oxides. Additive DF-1, as a surface-active material, apparently is adsorbed onto the metallic surface and passivates this surface, rendering thus an indirect positive influence on stability of oil. Passivation of metals was noted in literature in connection with investigation of mechanism of action of anticorrosive additives [9].

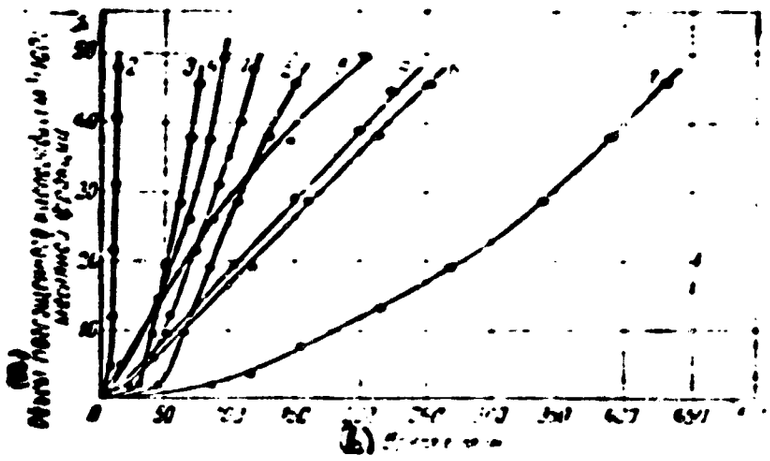


Fig. 7. Influence of metals (copper and iron) and their oxides (oxide of copper) on oxidation of oil DS-8 in the presence of addition DF-1.

Condition of oxidation: temperature 150°; concentration of additive DF-1 2%.
1—DS-8; 2—DS-8 + Cu (1:1); 3—DS-8 + Cu; 4—DS-8 + Fe; 5—DS-8 + CuO; 6—DS-8 + DF-1; 7—DS-8 + Cu + DF-1; 8—DS-8 + Fe + DF-8 + Fe; 9— DS-8 + CuO + DF-1.
KEY: (a) Volume of absorbed oxygen, $cm^3/100$ g butyric fraction; (b) Time, minutes.

At present it is not possible to resolve whether the action of alkyldithiophosphates in the conditions we considered leads only to passivation of metals. This question will be subjected to still further study.

Independently of character of action of additives of the type dialkyldithiophosphates of metals in conditions of use under increased temperatures and contact with metals these additions will increase stability of lubricating oils.

Conclusions

1. Antioxidant action of metal dialkyldithiophosphates depends on their structure. Dialkyldithiophosphates containing secondary hydrocarbon radicals, are more active than dialkyldithiophosphates containing primary hydrocarbon radicals. The strongest antioxidant turned out to be additive DF-1.

2. Dialkyldithiophosphates possess the greatest activity at temperatures not exceeding 150°. At a significant increase of temperature of oxidation, actions

of additives as antioxidants weakens, apparently, due to thermal decomposition of additives.

3. Additives of the sulfonates type only in insignificant degree affect oxidation of oils. Little active are also additives of the alkylphenolates type. Significantly more active are additives of the alkylphenolate type containing sulfur or phosphorus in the form of sulfide or dithiophosphates. The most active antioxidants in assumed conditions were additives DF-1 and Ionol.

4. The investigated oil (DS-8) contains natural inhibitors - certain aromatic hydrocarbons and sulfurous compounds, in the presence of which additive DP-1 does not delay process of oxidation of hydrocarbons of oil.

5. Meals and their oxides are catalysts of oxidation of hydrocarbons of oil. In the presence of metals natural inhibitors are insufficiently active, and oil becomes unstable.

Metal dialkyldithiophosphates (DF-1) passivate metals and correspondingly increase stability of hydrocarbons of oil with respect to oxidation by atmospheric oxygen.

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SYNTHESIS OF NEW ANTIOXIDANT ADDITIVES TYPE OF SHIELDED PHENOLS

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MINKh i GP*

For stabilization of power engineering oils and motor fuels at present in the USSR two additives are use: n-oxydiphenylamine and Ionol.

In distinction from Ionol, n-oxydiphenylamine is not very acceptable in view of bad solubility in oil products.

The most long-term antioxidant additive at present is the additive Ionol (2.6-di-tert-butyl-4-methylphenol), the production of which will be carried out in the next few years.

According to the assumed technology of the process of production of Ionol, simultaneously with its obtaining will be formed around 50% byproducts, constituting derivatives of m-cresol, which as yet has not found an efficient use. The problem of present investigation to develop synthesis of new additives on the basis of use of these byproducts.

Synthesis of new antioxidant additives is combined with development of production of insulating oils and motor fuels. The effectiveness of the action

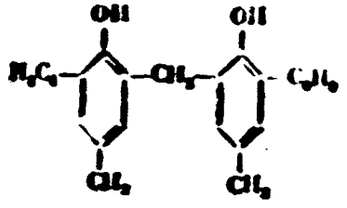
*Moscow Order of Labor of the Red Banner Institute of the Petroleum Chemical and Gas Industry named for Academician I. M. Gubkin.

of different antioxidant additives in certain degree can be judged by antioxidant properties of different alkylphenolates, entering in the composition of one or another additive.

In the work of Nixon and others [1] is given a table of antioxidant effectiveness of different alkylphenolates. The table is composed not only on the basis of the work of the authors themselves, but also on other works published in literature [2]. The value of effectiveness was determined on the basis of induction periods (at 100° with excess pressure of oxygen 7 kg/cm^2) and speed of formation of acids in turbine oil.

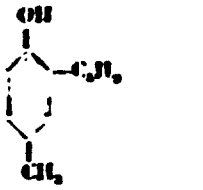
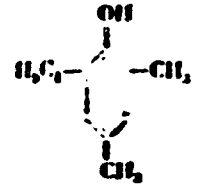
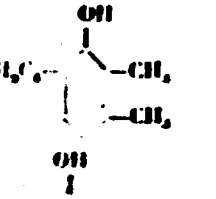
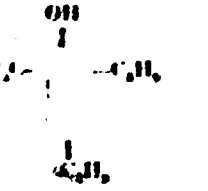
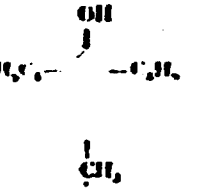
In Table 1 is given antioxidant effectiveness of certain alkylphenols, having a large value for synthesis of a number of additives. The most effective are shielded trialkylphenols, as, for instance, Ionol (standard addition).

If one were to judge by the induction period, then still more effective should be trialkylphenol, for which in position 2 and 4 stand methyl groups and in position 6 tertiary-butyl group. It was established that induction period of this alkylphenol is higher than that of Ionol; however, with respect to speed of formation of acids in turbine oil Ionol is almost 2 times faster. It is possible to improve properties of this trialkylphenol by synthesis of a biphenol compound of the following structure:

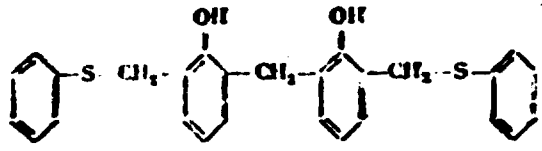


i.e., 2,2'-methylene-bis (6-tert-butyl-4-methylphenol), which it is possible to consider as a compound of two molecules of 2,4-dimethyl-6-tert-butylphenol, having a common methylene group.

Table 1. Effectiveness of Alkylphenols as Antioxidants

Alkylphenols	Structural formula	Relative effectiveness (Ionol-1) according to the data of			
		authors of article	Cosgrove and Waters [5]	Rosenwald and others [4]	Wasson and Smith [2]
2-tert-butyl-4-methylphenol		0.8	—	0.71	0.21
2,4-dimethyl-6-tert-butylphenol		1.38	2.00	1.60	0.51
2,3-dimethyl-6-tert-butylphenol		0.75	—	—	—
2,4-di-tert-butyl-6-methylphenol		0.56	0.75	0.47	0.21
2,6-di-tert-butyl-4-methylphenol (standard Ionol)		1.00	1.00	1.00	1.00

In the work of Mikeska and others [3] for stabilization of lubricating oils sulfur-containing additives of the following type were used:



and others with a large quantity of rings connected with different sulfur-containing compounds.

150

From given literary material the following conclusions can be made.

1. Alkylphenol additives with methylene cross-links possess a higher antioxidant effectiveness than alkylphenols.

2. Alkylphenol additives containing sulfur in the form of sulfide and disulfides, and other sulfur-containing additives are also effective antioxidants.

The obtained and investigated certain additives constituting bis-phenols and disulfides of bis-phenols.

Synthesis of additives constituting bis-phenols, consists of two basic stages.

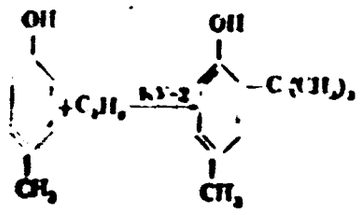
1. Alkylation of phenols by olefins in the presence of different catalysts.

2. Condensation of alkylphenols with formaldehyde in the presence of hydrochloric acid.

A. Synthesis of Additive 2,2'Methylene-Bis (6-Tert-Butyl-4-Methylpheonl) on a Base of n-Cresol

First Stage

Alkylation of n-cresol by isobutylene (in presence of cationite KU-2)



Description of Reaction of Alkylation

In reactor, supplied by a reflux condensor, a gas inlet tube, hermetically sealed mixer, and a thermometer, is placed 62 g crystal n-cresol (0.2 mole) and 22 g cationite KU-2 (37% on n-cresol).

Into the reaction mixture, heated to 70-80°, is passed isobutylene for 4 hours. End of the reaction is established according to the increase in weight of the isobutylene, which should be higher than theoretical by several percent. Yield of alkylate constituted 95.5 g.

The obtained alkylate was subjected to fractionation in vacuum at 20 mm Hg (Table 2).

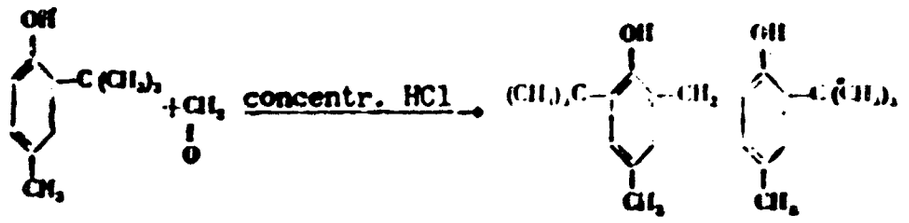
Table 2. Results of Fractionation of Alkylate

No. fraction	Boiling range of fraction at 20 mm Hg, °C	Weight of fraction, g	Yield of fraction, % on alkylate
1	90—120	34.7	37.3
2	120—130	56.3	60.5
Remainder	—	2.0	2.1
Altogether.....	—	93.0	99.9

Yield of alkylphenols was significantly increased, when in the reaction of alkylation more cationite (70% on n-cresol) was taken. Degree of purity of 2-tert-butyl-4-methylphenol was determined with respect to content of hydroxyl groups (theoretical content 10.35% OH). The found percent of hydroxyl groups was near the theoretical value and constituted 10.8%. Such a purity of the product is ensured by application of cationite KU-2 as catalyst, at which side reactions and polyalkylation are excluded.

Second Stage

Condensation of 2-tert-butyl-4-methylphenol with formaldehyde



Description of Reaction of Condensation

In a retort, supplied by a reflux condenser, mixer, thermometer and liquid-drop funnel, is placed 32.8 g of 2-tert-butyl-4-methylphenol (0.2 mole) and 6.7 g concentrated hydrochloric acid of specific gravity 1.19 (near 20% on alkylphenol).

To reaction mixture, heated on water bath to 50-70°, while being mixed from the liquid-drop funnel is poured 7.5 g (0.1 mole) formaldehyde in the form of a 40% aqueous solution. The reaction took place with evolution of heat up to 90°. Heating during mixing was done for 2 hours on a boiling water bath; toward the end of the reaction the temperature of the reaction mixture was raised to 100-105° and heating with this temperature continued for 30 minutes longer. The obtained white hard crystal mass was liberated from the acid catalyst by a solution of calcinated soda. After extraction of the additive by a gasoline "Galosha", the solution was poured into a dividing funnel. The aqueous layer was separated. Upper gasoline layer was left for crystallization. The separated crystals constituted additive 2.2'-methylene-bis (6-tert-butyl-methylphenol). The yield constituted 26 g, or 7% of the theoretical.

The additive had a melting point of 130-131°. The obtained molecular weight (322) was near to theoretical (340). Quantity of hydroxyl groups was equal to 10.6% (instead of 10% theoretical) which indicated a sufficient degree of purity of product.

Period of stability of additive 2.2'-methylene'bis (6-tert-butyl-4-methylphenol) was somewhat higher than standard (Table 3).

It was established that bis-phenol, constituting dialkylphenol (2-tert-butyl-4-methylphenol), connected by a methylene cross-link, had a higher antioxidant effectiveness than initial dialkylphenol. These data served as a basis for synthesis of an additive of such type from 4.6-di-tert-butyl-3-methylphenol. The last one is obtained in significant quantities as by-product in obtaining Ionol; use of it as raw material for obtaining a new antioxidant additive is desirable.

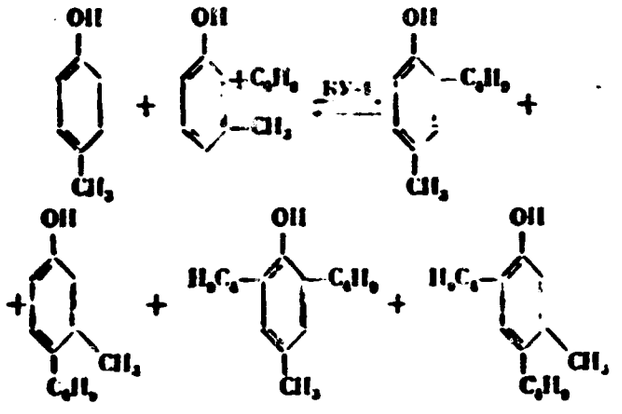
Table 3. Test of Antioxidant Effectiveness of Additives on Ethylated Gasoline B-70 According to All-Union Government Standard 6667-56

No. sample	Additive	Concentration of additive, %	Period of stability, hours
1	4 ml TES (brand 1-TS).....	—	2
2	2.2'-methylene-bis (6-tert-butyl-4-methyl-phenol)	0.05	40
3	Ionol (standard).....	0.05	38

B. Synthesis of Additive 2.2'Methylene-Bis (4.6-di-tert-Butyl-3-Methylphenol) on a Base of Dicresols Containing 60.7% m-Cresol

First Stage

Alkylation of dicresols by isobutylene in presence of cationite KU-1



Description of Process of Alkylation

In reactor is placed 235.5 g dicresols and 90.0 g cationite KU-1 (38% on dicresols).

In reaction mixture, heated to 70-80°, during energetic mixing isobutylene is passed for 19 hours, up to an increase of weight of reaction mixture by 244.0 g. Then alkylate is poured from settled catalyst by decantation. The cationite is

washed from the residue of alkylate by an equal volume of gasoline during mixing and heating on a water bath. After cooling the cationite is filtered from gasoline solution on a Buechner funnel. The remainder of alkylate after distillate of gasoline is combined with the main mass of alkylate. Ionol was separated from alkylate by extraction by a methanol-alkali solution of alkylate in the following manner.

A Claisen solution (400 ml) is mixed with alkylate and twice extracted by 600 ml cumene. The combined extracts are washed by a fresh Claisen solution (500 ml), after which the extract is distilled in a vacuum with selection of three fractions.

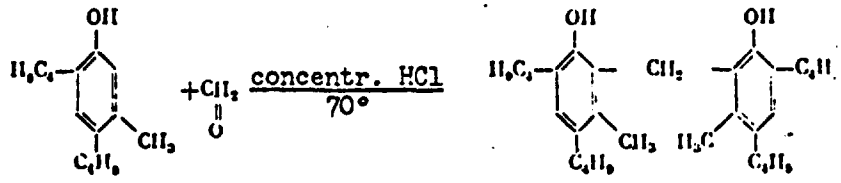
Fractions.....	1	2	3
Boiling range of fractions, °C.	Up to 120	144—160	160—170
Pressure, mm Hg.....	50--50	.0	20

The second fraction crystallized while it stood. The obtained crystals were filtered on a Buechner funnel. Yield of Ionol constituted 43.0 g, or 45.6% on n-cresol contained in raw material.

4.6-di-tert-butyl-3-methylphenol was separated from methanolbutakaline solution by 20% hydrochloric acid (2 [illegible]. Mixture alkylcresols was washed by a weak solution of bicarbonate until there was no longer an acid reaction of the washing waters. The obtained mixture of alkylcresols was fractionated in a vacuum with selection of three fractions. As a result of two distillations a fraction was separated which crystallized while it stood. Filtered on Buechner funnel, crystals of a light yellow color melted at 59-60°. Yield of 4.6-di-tert-butyl-3-methylphenol constituted 68.0 g, or 50% on m-cresol contained in raw material.

Second Stage

Condensation of 4.6-di-tert-butyl-3-methylphenol with formaldehyde



Description of Reaction of Condensation

In a retort for condensation is placed 14.0 g 4.6-di-tert-butyl-3-methylphenol (0.06 mole) and 2.8 g hydrochloric acid of specific gravity 1.19.

During mixture, to the reaction mixture heated to 70°, they added 2.2 g (0.03 mole) formaldehyde in the form of a 40% solution.

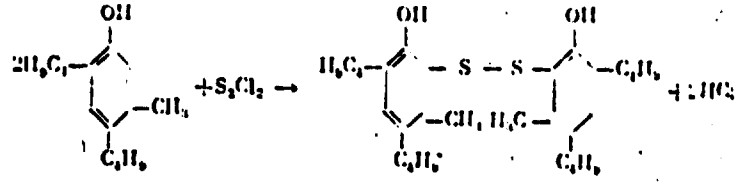
The reaction took place with little evolution of heat. As a result 14.0 g syrupy liquid of dark-red color is obtained. While standing, this liquid crystallized. After recrystallization from xylene are obtained colorless big prisms of a substance having a melting point of 203.5-204.5° and a molecular weight of 449 (theoretical 452).

The yield constituted 8.0 g and from the mother liquor was separated 3.7 g. In all 11.7 g is obtained, or 81% of the theoretical value.

C. Obtaining Antioxidant Additive of the Disulfide of Bis-Phenol--Disulfide-(4.6-Di-Tert-Butyl-3-Methylphenol) Type

The initial product for synthesis of additive 4.6-di-tert-butyl-3-methylphenol is a by-product during production of Ionol.

Disulfide-4.6-di-tert-butyl-3-methylphenol was obtained in a single-stage process according to the following diagram:



Description of Process of Sulfurization

In a three-necked retort, supplied by mixer, liquid-drop funnel, and reflux condenser with a funnel joined to it and a reflux condenser with a phial connected to it for absorption of gasiform hydrogen chloride, is placed 9.0 g 4.6-di-tert-butyl-3-methylphenol and 20.0 g benzene.

The retort is heated on a water bath to 40-50° and from the liquid-drop funnel chlorous sulfur is slowly added by drops; then the contents of the retort are energetically mixed. Temperature of water bath is gradually increased to 60°. Upon completion of addition of chlorous sulfur the reaction mixture is heated on boiling water bath 30 minutes and then cooled. In the dividing funnel the cooled reaction mixture is washed from the gaseous hydrogen chloride by a solution of bicarbonate until there is no acid reaction of the washing waters. After distillation of solvent a dark-brown, very viscous liquid was obtained. Yield of disulfide-4.6-di-tert-butyl-3-methylphenol constituted 8 g, or 89% on initial trialkylphenol. Content of sulfur in additive was equal to 13.1% (theoretical 12.7%).

Effectiveness of obtained antioxidant additives of the shielded phenols type is given in Tables 4 and 5.

From Table 4 it is clear that the disulfide additive, obtained from 4.6-di-tert-butyl-3-methylphenol, is a satisfactory antioxidant for transformer oil; it somewhat yields in effectiveness to Ionol.

From Table 5 it is clear that disulfide additive, obtained from 4.6-di-tert-butyl-3-methylphenol, is a good antioxidant for gasoline containing unsaturated hydrocarbons. In effectiveness it is equivalent to Ionol 2.2'-methylene-bis (4.6-di-tert-butyl-3-methylphenol) is also a good antioxidant additive for gasoline containing unsaturated hydrocarbons; but it yields somewhat to Ionol in its effectiveness.

Table 4. Effectiveness of Antioxidant Additives of the Shielded Phenols Type

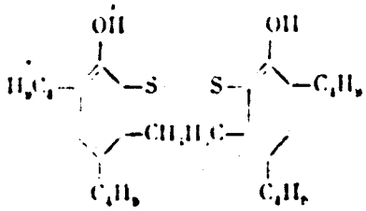
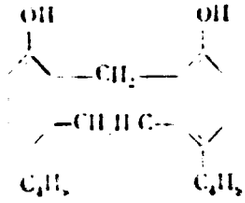
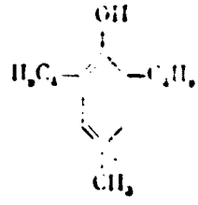
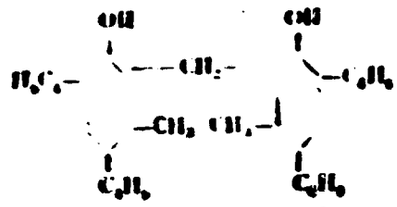
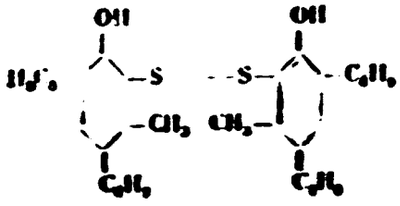
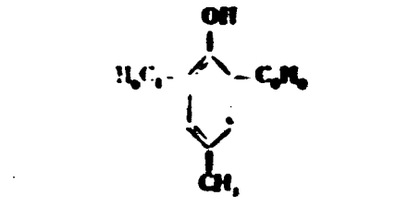
Sample	Structural formula of additive	Concentration of additive, %	Acid number, milligram KOH	Precipitate, %	Low-molecular acids	
					Nonvolatile	Volatile
Eastern oil	—	—	0.56	0.04	0.018	0.044
The same + disulfide-4.6-di-tert-butyl-3-methylphenol		0.3	0.17	traces	0.013	0.041
Eastern oil + 2.2'-methylene-bis (4.6-di-tert-butyl-3-methylphenol		0.3	0.78-0.09	0.07	0.034	0.10
Eastern oil + 2.6-di-tert-butyl-4-methylphenol-(Ionol)		0.2	0.028	None	0.01	0.014

Table 5. Effectiveness of Antioxidant Additives of the Shielded Phenols* Type

Sample	Structural formula of additive	Concentration of additive, %	Induction period, minutes
Synthol (fraction 150-220°C) with content of unsaturated hydrocarbons 8%	—	—	80
The same + 2.2'-methylene-bis (4.6-di-tert-butyl-3-methylphenol)		0.005	120
Synthol + disulfide-4.6-di-tert-butyl-3-methylphenol		0.005	140
Synthol + 2.6-di-tert-butyl-4-methylphenol (Ionol)		0.005	140

*Tests of effectiveness of additives are carried out in laboratories of professor Kl. I. Ivanov and Dr. of tech. sciences I. V. Rozhkov.

Conclusions

1. 2.2'-methylene-bis (6-tert-butyl-4-methylphenol) as an antioxidant additive (0.005%) to ethylated gasoline in effectiveness exceeds the well-known additive Ionol.

2. Disulfide-4.6-di-tert-butyl-3-methylphenol as an antioxidant additive (0.005%) to synthol, evaporating within limits of temperatures 150-220° and

containing 8% unsaturated hydrocarbons is very effective; it is equivalent to Ionol.

This additive, tested in transformer oil, in its effectiveness approximates Ionol.

3. 2.2'methylene-bis (4.6-di-tert-butyl-3-methylphenol) as an antioxidant additive (0.005%) to synthol, is sufficiently effective even in small concentration; the additive approximates Ionol in effectiveness. Tested in transformer oil, the additive in a 3% concentration gave negative results.

4. Developed methods of obtaining two additives: 2.2' methylene-bis (4.6-di-tert-butyl-3-methylphenol) and disulfide-4.6-di-tert-butyl-3-methylphenol allow use of by-product during production of Ionol, i.e., 4.6-di-tert-butyl-3-methylphenol, which up to now is an unused waste.

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SYNTHESIS AND INVESTIGATION OF ANTIOXIDIZING ADDITIVES FOR POWER ENGINEERING AND OTHER OILS

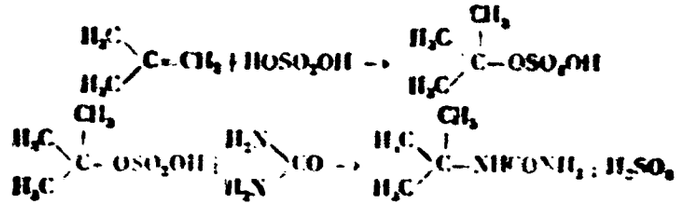
A. M. Kuliyev, G. A. Zeynalova,
and A. B. Abdinova
INKhP AN*

To obtain antioxidizing additives, a number of nitrogen-, hydroxyl-, and phosphorous-containing compounds were synthesized.

Nitrogen- and hydroxyl-containing compounds were synthesized on a base of urea, by direct reaction of urea with olefins and joint condensation of alkyl-phenols and urea with formaldehyde.

Tertiary alkyl-derivative ureas were obtained by reaction of urea with olefins in the presence of sulfuric acid as a catalyst.

During alkylation of urea of olefins are obtained mono- and dialkyl-derivative ureas:



As the primary olefins were taken isobulylene, asymmetric methylethyl ethylene, trimethyl ethylene, butylenes, and isopropyl ethylene. It was established that urea is not alkylated by secondary olefins.

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During alkylation of urea by asymmetric methylethyl ethylene and trimethyl ethylene the very same reaction products were obtained.

The following tertiary alkyl-derivative ureas were obtained: mono-tert-butyl-, di-tert-butyl-, and amylurea.

Tertiary alkyl-derivative ureas are white circular crystals with a high melting point. Physico-chemical constants of synthesized tertiary alkylated ureas are presented in Table 1.

To establish the structures of the obtained compounds their hydrolysis was carried out in an alkaline medium in the presence of a monoethyl ester of ethylene glycol:

$$(CH_3)_3C\text{-}NHCONH_2 + 2NaOH \rightarrow (CH_3)_3C\text{-}NH_2 + Na_2CO_3 + NH_3$$

$$(CH_3)_3C\text{-}NHCONH\text{-}C(CH_3)_3 + 2NaOH \rightarrow 2(CH_3)_3C\text{-}NH_2 + Na_2CO_3$$

During hydrolysis of dialkyl-derivative ureas monoamyls were also obtained, which indicates that the tertiary dialkyl-derivative ureas which we synthesized, are symmetrical. The physio-chemical constants of the obtained alkylamines are presented in Table 2.

Tertiary alkyl-derivative ureas are poorly soluble in oils, therefore, they cannot be used as anti-oxidizing additives.

Since the synthesis of tertiary alkyl-derivative does not present particular difficulties, their hydrolysis can fully be used to obtain tertiary alkylamines.

We carried out the joint condensation of alkylphenols and urea with formaldehyde in a weak acid medium at a temperature of 96-98°. For this there were synthesized alkylphenols with different length of side chain, different degree of branching, and different arrangement of side chain.

There were obtained alkylphenols with side chains C_3, C_4, C_5, C_6, C_7, C_8, C_9, and C_{16}.

We obtained alkylphenols by reaction of phenol with corresponding alcohols in the presence of concentrated sulfuric acid. Cetylphenol was obtained by alkylation of phenol by cetyl chloride in the presence of aluminum chloride.

Table 1. Physico-Chemical Constants of Tertiary Alkyl-Derived Ureas

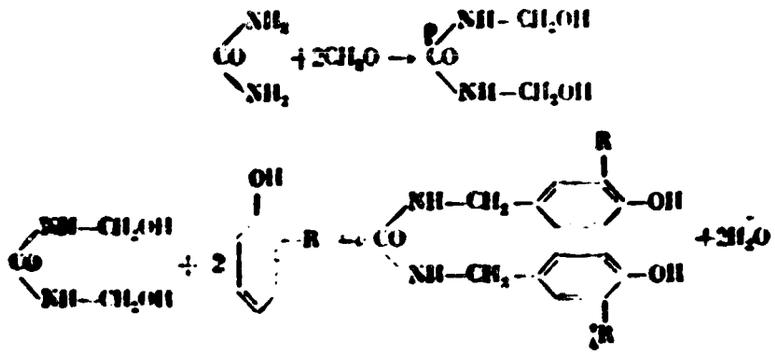
Product	Structural formula	Yield, %	Molecular weight		Melting point, °C		Content					
							C		H		N	
			Found	Calculated	Found	Reference data	Found	Calculated	Found	Calculated	Found	Calculated
tert-Butyl urea.....	$(CH_3)_3C-NHCONH_2$	41.0	116.8	116.0	171-172	172.0	51.60	51.72	10.4	10.36	24.70	24.52
Di-tert-butyl urea.....	$(CH_3)_3C-NHCONH-C(CH_3)_3$	85.5	170.9	172.0	248.0	250.0	62.77	62.79	11.65	11.62	15.88	16.27
tert-Amyl urea.....	$C_2H_5-C(CH_3)_2-NHCONH_2$	42.7	131.1	130.0	152.5	152.5	55.32	55.46	10.82	10.77	21.39	21.54
Di-tert-amyl urea.....	$C_2H_5-C(CH_3)_2-NHCONH-C(CH_3)_2-C_2H_5$	37.2	200.8	200.0	205.0	—	66.04	66.0	12.02	12.0	13.87	14.0

Table 2. Physico-Chemical Constants of Tertiary Alkylamines

Products	Structural formula	Yield, %	Boiling point, °C		Specific weight d_4^{20}		Coefficient of refraction n_D^{20}	
			Found	Reference data	Found	Reference data	Found	Reference data
tert-Butylamine....	$(CH_3)_3-C-NH_2$	71* 63**	44-46	45.2	0.6980	0.7004	1.3794	1.3794
tert-Amylamine....	$(CH_3)_2-C(C_2H_5)-NH_2$	72.1*** 65.3****	77-79	77.8	0.7320	0.731	1.3953	—

*On tert-butyl ureas
**On di-tert-butyl ureas
***On tert-amyl ureas
****On di-tert-amyl ureas

The condensation reaction of alkylphenols and urea with formaldehyde takes place according to the probable diagram:



The synthesized products of the condensation were tested as antioxidizing additives. Stability against oxidation was determined by the VTI [F. Dzerzhinskiy All-Union Heat Engineering Institute] method.

Commercial transformer oil was used as primary oil. As a result of investigation, it was established that the products of condensation of tertiary alkylphenols are more effective antioxidants than the products of condensation of secondary alkylphenols (Table 3).

Among the products of condensation of tert-alkylphenols, the antioxidizing properties improve with increase of molecular weight of the product. The most effective product of condensation is para-tert-octylphenol. Upon addition of this product of condensation to transformer oil, the acid number of the oil after oxidation decreases from 0.24 to 0.030 mg KOH.

Subsequently the products of condensation were synthesized using an alkylphenol produced by the chemical industry and an alkylphenol obtained by alkylation of phenol in a 100-180° fraction of thermal cracking; the approximate structural formula of the synthesized compounds is

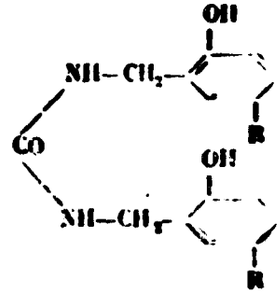


Table 3. Results of Tests of Products of Condensation of Alkylphenols and Urea with Formaldehyde

Additive	Quantity of additive, wt %	Characteristics of transformer oil, oxidized according to VTI method	
		Precipitate, insoluble in light benzene, wt %	Acid number, mg KOH
Product of condensation of para-isopropyl phenol	0.05	0.016	0.06
	0.1	0.012	0.05
	0.3	0.028	0.06
Product of condensation of para-tert-butyl phenol	0.05	0.044	0.1
	0.1	0.024	0.09
	0.3	0.044	0.09
Product of condensation of para-tert amyl phenol	0.05	0.044	0.08
	0.1	0.021	0.05
	0.3	0.062	0.06
Product of condensation of:			
para-sec-butyl phenol	0.1	0.036	0.06
sec-hexyl phenol	0.1	0.07	0.1
sec-octyl phenol (fraction II)	0.1	0.027	0.17
sec-octylphenol (fraction III)	0.1	0.076	0.1
para-tert-octylphenol	0.1	0.015	0.03
nonyl phenol	0.1	0.022	0.12
cetyl phenol	0.1	0.056	0.17
Without additive	0.0	0.07	0.24

Data on the analysis of these products of condensation, called additive aznii-11* is presented in Table 4.

In Table 5, 6, and 7 are data on the tested additive aznii-11 in a mixture with transformer oils MK-8 and MK-6 at temperatures of 120°, 150°, and 170°. In these same tables are data on the antioxidizing activity of other known additives.

*Ed. Note: The additive is named for a research institute; aznii = AzNII = Azerbaydzhan Scientific Research Institute.

The optimal quantity of additive aznii-11 which effectively acts on the stability of oil is 0.1%.

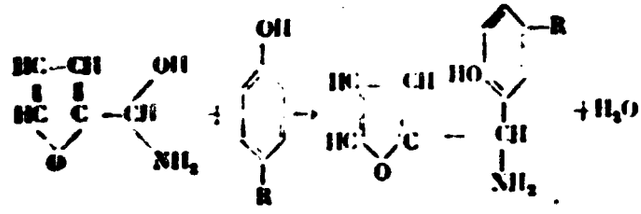
With the use of additive aznii-11, precipitate and acid number after oxidation are lowered almost half. The additive possesses antioxidizing activity equal to the activity of the additives Ionol and para-oxydiphenylamine during testing according to VTI method under standard oxidation conditions at a temperature of 120°. At higher temperatures of oxidation (150° and 170°) aznii-11 proved to be significantly more effective than Ionol.

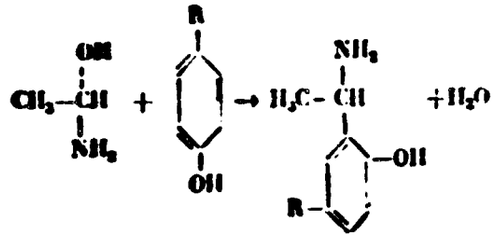
There is particular interest in products of condensation of alkylphenols with certain derivative aldehydes. As primary alkylphenols were taken para-tert-butyl-, para-tert-amyl-, and para-tert-octylphenols, and also alkylphenol obtained by alkylation of phenol by unsaturated hydrocarbons contained in 100°-180° fraction of distillate of thermally cracked paraffin, and alkylphenol produced by the chemical industry.

The last two alkylphenols of molecular weight 200-225 approximately correspond to the alkylphenol which has a $C_8 - C_9$ radical in a side chain.

As aldehydes there were taken furfurol and acetaldehyde ammonia.

The reaction goes according to the diagram





Analysis of condensation products is in Table 8.

The synthesized compounds were tested as antioxidizing additives to oil MK-8, turbine oil, and transformer oil. For comparison in these conditions, oil

Table 4. Results of Analysis of Additive aznii-11

Product of condensation (additive)	Analysis of product of condensation		
	Molecular weight	Nitrogen content, %	Content of hydroxyl group
Additive synthesized using alkylphenol obtained by alkylation of phenol by products of thermal cracking of paraffin....	501	3.9	5.6
Additive obtained using industrial alkylphenol.....	500	3.6	5.8

Table 5. Influence of Additive aznii-11 on Stability of Oils

Product	Quantity of precipitate, %	Acid number, mg KOH
Oil MK-8.....	0.052	0.25
Oil MK-8 with additive:		
0.05% aznii-11.....	0.024	0.10
0.1% aznii-11.....	0.050	0.15
0.5% aznii-11, synthesized on a base of industrial alkylphenol.....	0.038	0.08
0.1% aznii-11, synthesized on a base of industrial alkylphenol.....	0.025	0.09
Transformer oil.....	0.050	0.18
Transformer oil with additive:		
0.05% aznii-11.....	0.030	0.07
0.1% aznii-11.....	0.035	0.09

Table 6. Results of Determination of Stability of Oils in a Mixture with Different Antioxidizing Additives According to the VTI Method at a Temperature of 120°

Product	Quantity of precipitate %	Acid number, mg KOH
Oil MK-8	0.052	0.25
Oil MK-8 with additive:		
0.05% Ionol	0.045	0.52
0.1% Ionol	0.036	0.31
0.3% Ionol	0.021	0.06
0.05% para-oxydiphenylamine	0.025	0.06
0.05% aznii-11	0.024	0.10
Transformer oil	0.050	0.18
Transformer oil with additive:		
0.05% Ionol	0.054	0.21
0.1% Ionol	0.028	0.15
0.03% Ionol	0.022	0.04
0.05% para-oxydiphenylamine	0.031	0.06
0.1% para-oxydiphenylamine	0.064	0.47
0.05% aznii-11	0.030	0.07

Table 7. Results of Determination of Stability of Oils in a Mixture with Antioxidizing Additives According to VTI Method at Temperatures of 150° and 170°

Product	Quantity of precipitate, %	Acid number, mg KOH
Temperature of oxidation 150°C		
Oil MK-8	2.40	3.20
Oil MK-8 with additive:		
0.05% aznii-11	0.35	0.65
0.1% aznii-11	0.25	0.45
0.05% Ionol	0.70	1.20
0.1% Ionol	1.00	1.75
Temperature of oxidation 170°C		
Oil MK-8	3.20	4.00
Oil MK-8 with additive:		
0.05% aznii-11	1.50	2.80
0.1% aznii-11	1.53	2.00
0.05% additive ionol	2.30	3.70
0.1% additive ionol	2.30	5.60
Oil MK-6	1.52	2.20
Oil MK-6 with additive:		
0.5% aznii-11	0.41	0.84
0.5% Ionol	0.61	1.21

Table 8. Results of Analysis of Products of Condensation

Assumed structural formula	Molecular weight		Content, %							
			C		H		N		OH	
	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated
$C_6H_3(OH)C_9H_9$ C_6H_3OCH NH_2	259	256	72.3	73.1	7.2	7.7	5.6	5.69	6.7	6.9
$C_6H_3(OH)C_{11}H_{13}$ C_6H_3OCH NH_2	263	269	74.7	74.1	7.9	8.0	5.2	5.20	6.2	6.5
$C_6H_3(OH)C_{13}H_{17}$ C_6H_3OCH NH_2	301	302	76.0	75.7	8.7	8.8	4.6	4.63	5.0	5.8
$C_6H_3(OH)R$ * C_6H_3OCH NH_2	330	—	—	—	—	—	4.2	—	—	—
$C_6H_3(OH)R'$ ** C_6H_3OCH NH_2	334	—	—	—	—	—	4.0	—	—	—
$C_6H_3(OH)C_9H_9$ CH_2CH NH_2	191	191	75.0	76.0	9.2	9.2	6.9	7.30	8.6	8.7
$C_6H_3(OH)C_{11}H_{13}$ CH_2CH NH_2	245	247	76.0	75.3	9.7	10.1	5.9	6.10	8.0	8.2
$C_6H_3(OH)C_{13}H_{17}$ CH_2CH NH_2	255	254	77.0	76.5	10.0	10.7	5.0	5.70	6.0	6.7

*Product of condensation of alkylphenol obtained by alkylation of phenol in a 100°-180° fraction of thermally cracked paraffin with furfuramide.

**Product of condensation of industrial alkylphenol with furfuramide (aznii-11 F).

MK-8 was also tested in mixture with antioxidizing additives: para-oxydiphenylamine, α -naphthylamine, and the imported additive, Santolube.

Test results showed that the highest antioxidizing effectiveness is possessed by the product of condensation of para-tert-octylphenol with furfuramide, and also by the product of condensation of industrial alkylphenol with furfuramide (aznii-11F).

In Table 9 are data on the antioxidizing capactities of additive aznii-11F at temperatures of 120° and 150°.

Test results showed that Ionol at a high temperature of oxidation of 150° does not influence the stability of oil MK-8, whereas the use of aznii-11F very significantly reduces the quantity of precipitate and the acid number of the oil.

The greatest effect from this additive is attained with its addition to oil in a 1% quantity.

Broad testing of additives aznii-11 and aznii-11F, carried out in other scientific research institutes, makes it possible to recommend them for practical use.

Table 9. Influence of Antioxidants on Stability of Oil MK-8

Product	Quantity of additive, %	Quantity of precipitate, %	Acid number, mg KOH
Temperature of oxidation 120°			
Oil MK-8	—	0.070	0.24
Oil MK-8 with additive:			
Aznii-11 F	0.10	0.018	0.03
Ionol	0.10	0.036	0.31
para-oxydiphenylamine	0.05	0.040	0.03
phenyl-α -naphthylamine	0.05	0.012	0.22
Santolube	0.05	0.072	0.18
Temperature of oxidation 150°			
Oil MK-8	—	1.01	3.6
Oil MK-8 with additive aznii-11F	0.1	0.21	0.8
	0.3	0.24	0.6
	0.5	0.20	0.4
	0.7	0.17	0.2
	1.0	0.18	0.1
Oil MK-8 + Ionol	0.1	1.01	3.8

SYNTHESIS OF HIGHLY EFFECTIVE DEPRESSOR TO LUBRICATING OILS ON A BASE CHLORINE OF DERIVATIVES OF CEREZINE

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By recent work* it has been established that a molecule of depressor should be certainly represented by a paraffin chain of normal structure, i.e., include group which has the same structure as oil hydrocarbons which form the structure in oils during their cooling. Depressors also act on the formation of these structures.

It is natural and logical, therefore, to assume that action of the usual depressors does not spread to structures which form in oils cerezine hydrocarbons, namely because in molecules of usual depressors there are no hydrocarbons having the same structure as cerezine. A result of this is the fact that a molecule of depressor, containing cerezine should prevent the formation of structures in which cerezine hydrocarbons participate. This assumption indicates that it is necessary to conduct certain investigations on the use of cerezine as raw material for synthesis of depressors, all the more so since in all works on synthesis cerezine and paraffin were considered as absolutely equivalent.

Proceeding from the position that the additive should contain those hydrocarbons which form structure in oils, additives were synthesized on a base of cerezine.

*P. I. Sanin, A. V. Il'yanova and V. V. Sher. Chemistry and Technology of Fuel Oils, No. 8, 1956.

As initial raw material for synthesis of depressors the following products were taken.

1. Cerezine of molecular weight 600, with a melting point of 73° and penetration 18, obtained by the usual acid contact purification of natural ozocerite of Stanislav and Dagadzhik deposits.

2. Cerezine of molecular weight 650, with a melting point of 83° and penetration 10, obtained by the usual method from ozocerite of deposit ShorSu and Surakhany plug.

3. Synthetic cerezine of molecular weight 550, with a melting point of 93° and penetration 9 (cerezine is obtained by the Orlov-Fisher Tropsch method at a combine of artificial liquid fuel. Comparatively low molecular weight and high melting point indicates that it consists mainly of hydrocarbons of normal structure).

The above samples were subjected in laboratory conditions to usual liquid-phase chlorination by free chlorine. Chlorination was conducted in glass equipment at temperatures of 90-100°. It was conducted until products were obtained containing chlorine from 120 to 250%, calculated on monochlorderivatives.

Chlorine derivatives further were used for normal alkylation of hapthalene in the presence of a catalyst — aluminum chloride. Napthalene was alkylated with a view to obtaining in separate cases, mono-, di- and tri-derivatives.

The depressor action of synthesized additives was studied on artificial mixtures. In particular, a 3% solution was taken of cerezine with melting point 83° in Emba residual oil MT-16 viscosity 16.0 cs at 100° and pour point +16°, to which depressors were added in quantity 0.5%.

Data on synthesis and tests of depressors are given in Table 1.

Table 1. Conditions of Synthesis of Depressors

No. additive	Chlorine in chlorocerezine, %	Quantity of napthalene, on 100 g chlorocerezine, g	Melting point of chlorocerezine, °C	$AlCl_3$ %	No. additive	Chlorine in chlorocerezine, %	Quantity of naphtalene, on 100 g chlorocerezine, g	Melting point of chlorocerezine, °C	$AlCl_3$ %
Natural cerezine with melting point 73°, Dagadzhik site					Natural cerezine with melting point 83° from Surakhany plug and ozocerite from Shor-Su				
1	7.6	14.0	65	1.5	9	6.2	75	17	3.0
2	8.8	15.5	62	1.5	10	6.2	75	20	1.5
3	9.9	18.0	60	1.5	11	8.6	70	24	3.0
4	11.2	21.0	59	1.5	12	8.6	70	24	1.5
7	9.9	18.0	60	2.0	13	8.5	70	23	3.0
8	11.2	21.0	59	3.0	14	9.0	65	30	3.0
					15	9.0	65	20	1.5
					16	13.0	6[illegible]	25	3.0

Below are presented data about action of obtained additives on pour point (in °C) 3% solution of cerezine in oil MT-16.

Oil MT-16 + 3% cerezine with melting point 83°..... +35

Oil MT-16 + 3% cerezine with melting point 83° + 0.5% additive:

1% depressor AzNII*..... +32
No. 1..... +20
No. 2..... +14
No. 3..... -20
No. 4..... -28
No. 5..... —
No. 6..... —
No. 7..... -18
No. 8..... -24
No. 9..... 32
No. 10..... 30
No. 11..... -4
No. 12..... -24 to -26
No. 13..... -14
No. 15..... -28
No. 16..... +35
No. 17..... -20

*Ed. Note: Depressor is named for research institute AzNII or aznii = Azerbaydzhan Scientific Research Institute.

No. 18	+20
No. 19	-20 to -22
No. 20	-20 to -24
No. 21	Is insoluble
No. 22	+30
No. 23	-20
No. 24	-16
No. 25	-18 Suspen.
No. 26	-18 Suspen.
No. 27	-12
No. 28	-8
No. 29	-24
No. 30	-2

Positive results are given by additives prepared by alkylation of napthalene with chlorocerezine, containing not less than 9.9% chlorine. Considereing that the molecular weight of cerezine equals 600, one should consider that during chlorination are formed chiefly dichlorderivatives of cerezine. A lowering to 1.5% of the quantity of catalyst also renders a certain positive influence on properties of additive.

Best results of synthesis of additives are obtained when 1.5% of catalyst is used.

Chlorine content in chlorocerezine should be not less than 8.5-9.0% and not more than 12%.

In the manufacture of additives on synthetic cerezine the quantity of chlorine in the chlorocerzine can vary within rather wide limits (from 7 to 12%). But with increase of content of chlorine above 12% during subsequent alkylation of napthalene, the quantity of which is calculated on obtaining of derivative with two radicals, is obtained an additive, not soluble in oils (additive No. 21); in obtaining a compound with one lateral chain, the additive becomes solutle in oils, but loses its depressor properties (additive No. 22).

Calculation of quantity of napthalene during synthesis of additive should be conducted proceeding from the fact that to its molecule are joined two radicals. Increase of quantity of napthalene, even a small one leads to a sharp reduction of depressor properties of arylcerezines.

Data on synthesis of depressors on the basis of synthetic cerezine with a melting point of 93° and investigation of their action on pour point of oils are given in Table 2.

Table 2. Conditions of Synthesis of Depressors on the Basis of Synthetic Cerezine

No. addition	Chlorine in chlorocerezine %	Melting point of chloro-cerezine, °C	Quantity of napthalene per 100 g chloro-cerezine, g	$AlCl_3$, %	No. addition	Chlorine in chlorocerezine, %	Melting point of chloro-cerezine, °C	Quantity of napthalene per 100 g chloro-cerezine, g	$AlCl_3$, %
17	8.1	78	21	1.5	24	9.2	78	18	1.5
18	8.1	78	21	3.0	25	10.2	73	20	1.5
19	11.9	71	31	1.5	26	11.2	71	23	1.5
20	11.9	71	31	3.0	27	7.5	80	15	3.0
21	12.4	68	30	3.0	28	9.2	78	27	1.5
22	12.9	66	50	3.0	29	10.2	73	20	3.0
23	7.5	80	15	1.5	30	11.2	71	35	3.0

Parallel investigations were conducted on the action of one depressor synthesized from natural cerezine and depressor AzNII on oil MS-20 with different content of Baku petrolatum (artificial mixtures). Data are given in Table 3.

Table 3. Action of Depressors on Pour Point of Oil MS-20 Containing Petrolatum

Product	Quantity of petrolatum in oil, %						
	0	2	4	6	8	10	12
MS-20	-16	+10	+22	+28	+32	+32	+35
The same + 0.5% depressor AzNII	-32	-32	-16	-3	+16	+26	+28
MS-20 with additive No. 4 (see Table 1)	-32	-32	-32	-26	-25	-10	-6

With a content of Baku petrolatum in the mixture higher than 4%, influence on pour point of depressor AzNII is sharply lowered and during further increase of content of petrolatum in oil almost disappears, whereas influence of synthesized additive is apparent even with a 12% content of cerezine in the mixture.

Table 4. Influence of Concentration of Depressor on Pour Point of Oil

Additive	Quantity of additive, %				
	1.0	0.5	0.25	0.1	0
Oil without additive.....	—	—	—	—	+16
Paraflow.....	-22	-12	+1	+11	—
Santopour.....	-25	-18	-4	+3	—
Depressor AzNII.....	-22	-22	-8	+5	—
Additive No. 4 (see Table 1).....	-28	-26	-22	-18	—

Also investigated was the action of this additive and known depressors on a 3% solution of Baku petrolatum in residual Emba oil depending upon concentration of additive (Table 4).

Paraflow and Santopour were added from calculation of content of 50% additive proper.

Table 5. Action of Different Depressors on Pour Point of Oil MT-16

Products	Quantity of additive, %	Pour point, °C
Oil MT-16.....	—	+30
Oil MT-16 with additive:		
Paraflow.....	3.0	+30
Santopour.....	3.0	+30
Depressor AzNII.....	1.5	+30
No. 4 (see Table 1).....	1.5	-26

From given data it is clear that at a 0.1% concentration of additive is the newly synthesized additive most effective. Besides this, was investigated the action of known depressors and one of the synthesized additives on a 5% solution of cerezine with a melting point of 73° in residual Emba oil (Table 5).

Known depressors on oils containing cerezine render no influence. The depression caused by synthesized additive, constitutes 56°.

Simultaneously with the enumerated investigations the following ones were conducted.

1. Action of Depressors on Commercial Oils Obtained from Distillates and Hydrone of Tuymazy Crude by Means of Selective Purification, Deparaffination and Final Rectification by Bleaching Clay by the Contact Method

According to their composition oils are either completely distillates, or a mixture of a distillate product with residual in different proportion. Action of samples of synthesized depressors on pour point of commercial oils was tested parallel with depressor AzNII (Table 6).

Table 6. Action of Depressors on Pour Point of Deparaffinated Commercial Oils of Selective Purification

Oil	Analysis of oil						
	Specific gravity d_4^{20}	Kinematic viscosity at 100°, cs	Flash point (in open crucible), °C	Coke, %	Pour point, °C		
					without depressor	depressor AzNII	additive No. 4
Lubricating oil from reservoir A Raw-Kuibyshev NPZ (petroleum refinery) + 8.8% depressor AzNII	0.897	9.60	224	0.27	-17	-28	-28
Lubricating oil from reservoir B + 0.5% depressor	0.814	9.50	212	0.23	-18	-28	-24
Lubricating oil from reservoir C + 0.5% depressor	0.892	9.50	216	0.25	-17	-22	-24
Lubricating oil from reservoir D + 0.5% depressor	0.892	9.53	210	0.22	-15	-30	-30
Lubricating oil from reservoir E + 0.5% depressor	0.895	9.55	212	0.25	-17	-26	-28

From the table it is clear that the action of both depressors on the shown oils is absolutely similar.

2. Action of Depressors on Pour Point of Oils of Selective Purification of Shallow Deparaffination

Deep deparaffination, as is known, leads to significant lowering of yield of commercial oils from raw material, and also to impairment of index of viscosity of oils. In connection with this it is expedient to deparaffinate oil at higher

temperatures and to obtain final pour point of oils by means of addition of highly effective depressors. Proceeding from this, in laboratory conditions samples were prepared of oils of shallow deparaffination with a pour point higher than 0°C and on them is tested a sample of arylcerezine (Prece. No. 4) and depressor AzNII (Table 7).

From given data it is clear that arylcerezine is significantly more effective than depressor AzNII, especially when the test is conducted on residual oils.

Table 7. Action of Depressors on Pour Point of Oil of Shallow Deparaffination

Oil	Yield from oil-containing paraffin, %	Kinematic viscosity at 100°, cs	Pour point, °C		
			without depressor	depressor AzNII	additive No. 4
Distillate raffinate from reservoir D of New-Kuibyshev NPZ (Petroleum Refining Factory) deparaffinated at -1°, +0.5% depressor.....	75.1	6.1	+8	+6	-10
The same, deparaffinated at -10°, +0.5% depressor...	78.0	6.9	-3	-18	-20
Residual raffinate from reservoir E, deparaffinated at 0°, +0.5% depressor.....	81.2	20.8	+3	+4	-15
The same, deparaffinated at +5°, +0.5% depressor.....	80.9	21.3	+4	-8	-18
The same, deparaffinated at -10°, +5% depressor.....	80.6	21.9	+2	-10	-18
Mixture of residual oil from experiment 4 with distillate oil from experiment 2 in a 35:65 ratio +0.5% depressor	—	9.7	+2	-12	Below -20
The same +0.2% depressor....	—	9.7	+2	0	-19

3. Action of Depressors on Extract of Phenol Rectification of Distilled Raffinates

Obtained results are given in Table 8.

Table 8

Product	Pour point, °C		
	without depressor	depressor AzNII 0.5%	additive No. 4 0.5%
Extract from reservoir Zh....	+6	+5	-2
Extract from reservoir Z in mixture with lubricating oil in a 25:75 ratio.....	+12	+8	0
Filtrate from laboratory oil-free crude paraffin.....	+8	+6	0
Extract in mixture with lubricating oil from reservoir A (cylinder oil)..	+12	+2	-20

In this case the newly synthesized depressor is also more effective.

4. Influence of Synthesized Depressors On Viscosity of Oils At Low Temperatures

Any lubricating oil, acting in flow at increased temperatures as a normal Newton liquid, with a decrease of temperature manifests properties characteristic for colloidal systems. It is known that existing depressors affect appearance of structure in oils, and shift the anomaly of viscosity into region of lower temperatures.

Also investigated was influence of obtained depressors and depressor AzNII on viscosity of oil MT-16, containing 3% cerezine with melting point 83° (Table 9). Tests were conducted on a Volorowich rotary viscosimeter.

Table 9. Influence of Depressors On Viscosity of Oil MT-16, Containing 3% Cerezine

Product	Pour point, °C	Viscosity at a temperature of -11°, poises
Oil MT-16 + 3% cerezine with a melting point of 83°.....	+35	20280
The same + 0.5% depressor AzNII..	+32	18230
Oil MT-16 + 3% cerezine with a melting point of 83° + additive:		
No. 4.....	-28	6050
No. 17.....	-20	6920
No. 19.....	-20 to -22	6030
No. 12.....	-20	6120
No. 15.....	-28	5560
No. 26.....	-18 mobile	6180

From given data it is clear that synthesized additives very significantly affect viscosity of given mixture at temperatures of -11° whereas depressor AzNII has practically no influence.

SYNTHESIS AND PROPERTIES OF POLYGLYCOL ESTERS AND THEIR APPLICATION AS COMPONENTS OF SYNTHETIC OILS AND ADDITIVES

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MINKh i Gp*

A new type of synthetic lubricating oils are reaction products of alcohols and phenols with oxides of alkylene (ethylene, propylene). These oils are widely applied abroad under name of polyglycol esters.

Polyglycol esters possess a number of very valuable properties. They have a low pour point (-55° to -60°), good viscosity-temperature characteristic, and a high index of viscosity. At low temperatures they are more mobile than mineral oils of identical viscosity. One of the interesting properties of these oils is their ability (during operation in motors at increased temperatures) to be decomposed with formation of volatile products and to be volatilized, not leaving resins, varnish, and carbon deposits on motor parts. The oils can obtain the most diverse viscosities, changing the ratios of the initial alcohol and alkylene oxide. Oxides of alkylene are condensed with alcohols and phenols according to a chain mechanism in the following diagram:

$$ROH + (CH_2CH-CH_2)_x \rightarrow RO(CH_2\underset{CH_3}{\underset{|}{C}}HO)_xCH_2-\underset{CH_3}{\underset{|}{C}}H-OH$$

*Moscow Order of Labor of the Red Banner Institute of the Petroleum Chemical and Gas Industry named after Academician I. M. Gubkin.

Consequently, depending upon quar . .y of molecules of olefin oxide and character of initial alcohol or phenol, are obtained compounds of different structures, constituting esters of polyglycols with chains of different length which influences the difference of their properties.

In foreign literature dedicated to this problem, can be found information about properties and results of a test of these oils in motors [1-6]. In Soviet literature the problem of obtaining polyglycol esters as lubricating materials has been treated very little; synthesis is described of polyglycol esters on the basis of ethylene oxide and certain alcohols in the presence of iron sulfate [7]. Certain catalysts were studied in reactions of condensation of alkylene oxides with alcohols [8, 9]. This work is dedicated to the synthesis of different polyglycol esters and study of their low-temperature properties.

Below is a description of synthesis of different polyglycol esters, which according to their character can be divided into two groups: 1) polyglycol esters on the basis of phenol and propylene oxide and 2) polyglycol esters on the basis of alcohols and propylene oxide.

Synthesis of Polyglycol Esters on Basis of Phenol and Propylene Oxide

Parent substances for synthesis of polyglycol esters of first group were phenol with a boiling point of 181° para-tert-butylphenol with a melting point of 99°; para-tert-octylphenol with a melting point of 68-70°; propylene oxide with a boiling point of 35° and hard caustic soda. In all cases were used the equipment and method described during synthesis of polyglycol ester on the basis of phenol and propylene oxide; only the ratio of components of phenol and propylene oxide changed.

The reaction goes according to the diagram

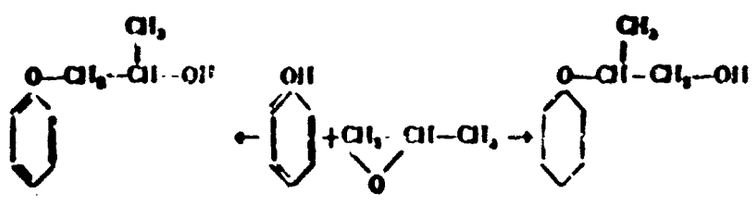


Table 1. Physico-chemical Properties of Polyglycol Esters on the Basis of Propylene Oxide and Phenol

No. п/п	No. experiment	Taken in reaction of phenol and oxide of propylene in ratio	Boiling range, °C	Pressure, mm Hg	Molecular weight	OH, %	d_{20}^{20}	n_D^{20}	Four Point, °C	Viscosity, cs		Index of viscosity	$\frac{\nu_{50}}{\nu_{100}}$
										at 50°	at 100°		
1	1	1:1	118-119	18	153.5	11.6	1.07	1.5239	-36	5.96	1.596	—	3.7
2			125-126	17	154	11.4	1.065	1.5210	-36.5	5.98	1.56	—	3.8
3	2	1:2	132-140	17	—	—	—	—	-34	6.25	1.633	—	3.8
4			159-165	16	—	—	—	—	-42	7.10	1.90	—	3.7
5	3	1:3	145-155	14	—	—	—	—	-38	6.76	1.758	—	3.8
6			155-165	14	—	—	—	—	-43	7.31	2.07	—	3.5
7	4	1:4	—	—	—	—	—	—	-40	11.09	2.63	—	4.2
8	5	1:5	170-3[illegible]	20	300	5.67	—	—	-45	10.65	2.68	—	3.9
9	6	1:15	180-340	4	421	4.25	1.021	1.684	-43	21.3	5.02	125	4.2
10	7	tert-Butylphenol and propylene oxide 1:15	155-325	13	431	3.58	1.006	1.6893	-32	27.7	5.14	160	5.4
11	8	tert-Octylphenol and propylene oxide 1:10	170-305	13	475	3.13	0.978	1.5888	-28	46.2	7.515	101	6.14

Two isomers are obtained: α-phenyl ester and β-phenyl ester of propylene glycol.

Into a 250 cm^3 three-necked retort, supplied by mechanical mixer, condenser, thermometer, and liquid-drop funnel, was loaded phenol (0.5 mole) and 1% hard caustic soda (as catalyst) calculated on taken sample. Mixer and heater were turned on and gradually temperature of reaction mixture rose to 130°. After achievement of this temperature, from the liquid-drop funnel was added the necessary quantity of propylene oxide by drops, with such a speed that it all entered into the reaction.

Upon completion of reaction, which continued 4 hours, the product is washed 3-4 times from residues of phenol by hot water. After that it was subjected to distillation in a vacuum into fractions, which then were characterized basically by their low-temperature properties. Physico-chemical properties of polyglycol esters are shown in Table 1. From analysis of data of table are revealed the following regularities.

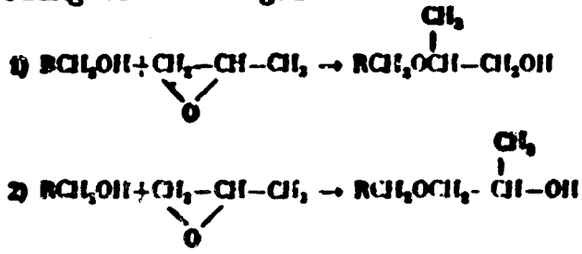
1. Increase of quantity of groups of propylene oxide in molecule leads to increase of viscosity of polyglycol ester and simultaneously to a lowering of its pour point.

2. Increase of molecular weight of initial substituted phenol leads to increase of viscosity of obtained oil; viscosity-temperature properties and pour point worsen somewhat.

Synthesis of Polyglycol Esters on the Basis of Alcohols and Propylene Oxide

The following products with temperatures of boiling served as initial raw material: n-propyl alcohol 97.2°; n-heptyl alcohol 176.3°; n-octyl alcohol 195.2°; isopropyl alcohol 79.5-85.4°; isoamyl alcohol 132°; 2-ethylhexanol 184°; oxide of propylene 36-38°; hard caustic soda; hard caustic alkali.

The reaction goes according to the diagram:



i.e., two isomeric esters of propylene glycol are formed.

Two series of experiments on condensation of oxide of propylene with alcohols were conducted: 1) at atmospheric pressure, 2) at increased pressure (from 3 to 43 atm (tech)). In the first series of experiments, synthesis of polyglycol esters took place in equipment and conditions described during synthesis of polyglycol esters on the basis of acid propylene and phenol. An exception was temperature, which in reaction with heptyl, octyl, and 2-ethylhexyl alcohols was maintained on a level of 170-180°; furthermore, length of reaction was increased 1.5-2 times. Yield of condensate constituted from 92 to 96%. Results of physico-chemical investigation of fractions separated during vacuum distillation of condensate obtained with isoamyl, heptyl, octyl, and 2-ethylhexyl alcohols, are presented in Table 2.

Data of Table 2 show that with increase of groups of propylene oxide in the molecule, viscosity is increased of polyglycol ester (such dependence was observed during condensation of propylene oxide with phenol) and also that polyglycol esters on the basis of propylene oxide and alcohols have a low pour point (of the order of -60°) and a sloping viscosity-temperature curve.

Insignificant impairment of low-temperature properties — pour point and viscosity-temperature constant for polyglycol esters with increase of their molecular weight may be explained by the formation of polymers of propylene oxide, which can be obtained by prolonged heating at a high temperature. In connection with this, a number of experiments on condensation of great quantities of propylene oxide with alcohols (in 1:4 to 1:16 ratios) prevent polymerization of propylene oxide were conducted in an autoclave at increased pressure (from 3 to 43 atm (tech)).

Table 2. Physico-chemical Properties of Polyglycol Esters on the Basis of Propylene Oxide and Alcohols (polyalkylene glycols are obtained at atmospheric pressure)

No. п/п	Number of experiment	Name of alcohol	Taken in reaction of phenol and oxide of propylene in the ratio	Boiling range, °C	Pressure, mm Hg	Molecular weight (found)	OH, %	d_4^{20}	n_D^{20}	MR	Pour point, °C	Viscosity, cs at 50°	Viscosity, cs at 100°	$\frac{\nu_{50}}{\nu_{100}}$
1	1	Isoamyl	1:1	63-71	12	133	12.7	0.856	1.4147	38.3	—	—	—	—
2				71-110	12	166	10.8	0.880	1.4204	48.0	—	—	—	—
3				64-65	4-5	146.5	11.6	0.877	1.4180	42.1	—	—	—	—
4	2	"	1:2	52-6[illegible]	4	146	11.9	0.875	1.4188	42.2	—	—	—	—
5				1[illegible]-137	4	210	8.8	0.9340	1.4295	58.3	—	—	—	—
6	3	"	1:2.86	52-74	3-4	142	12.3	0.872	1.4251	41.2	—	—	—	—
7				10[illegible]-137	3-4	218	8.35	0.941	1.4298	59.5	-60	4	1.5	2.66
8				137-210	3-4	300	5.82	0.975	1.4384	81.3	—	7.62	2.34	3.25
9	4	Heptyl	1:2	100-176	8	216	7.8	0.9044	1.4301	62	-62	4.04	1.54	2.62
10	5	"	1:4	150-200	4	314	5.37	0.9575	1.4421	85.7	-60	7.45	2.28	3.26
11				200-240	4	438	3.8	0.9575	1.4463	120	-54	12.4	3.47	3.86
12	6	2-ethylhexyl	1:4	150-200	4-5	298	—	0.965	1.4420	82	-56	7.7	2.22	3.46
13		"		202-230	4-5	367	—	0.984	1.4455	100	-53	11.9	3.2	3.7
14	7	Octyl	1:4	110-190	3-4	245	—	0.9500	1.4375	—	-60	5.92	1.93	3.06
15		"		190-228	3-4	325	—	0.9750	1.4431	—	-54	10.1	2.84	3.55

Polyglycol esters were obtained on the basis of propyl, isopropyl, isoamyl, n-octyl and 2-ethylhexyl alcohols and propylene oxide. As catalyst of reaction caustic soda or caustic alkali was used.

Obtaining Polyglycol Esters by Condensation of Propylene Oxide with Different Alcohols in an Autoclave at Increased Pressure

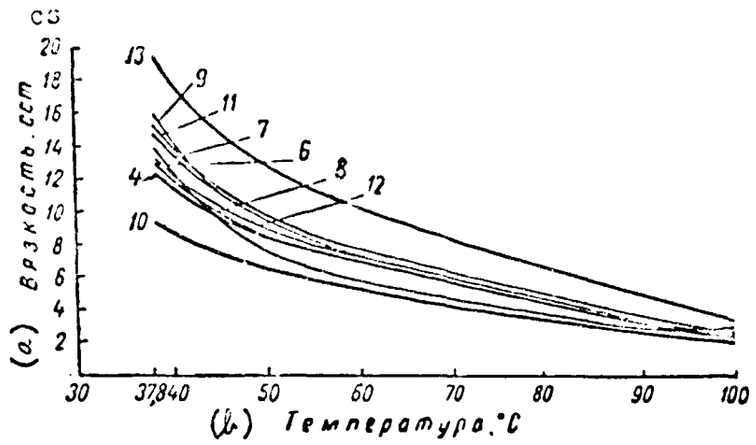
The reaction took place in a steel revolving autoclave 0.5 l in capacity externally heated by electricity.. In the autoclave was loaded alcohol (0.5 mole) and caustic soda or caustic alkali amounting to 1% of total sum of reagents. At a temperature of 60° valve of autoclave was opened to the atmosphere for removal of air from zone of reaction. After that, at a temperature of 130° into the autoclave gradually moved propylene oxide. Temperature of reaction was regulated by decrease or increase of heating, taking into account the heat given off during the reaction. Pressure in separate experiments varied within the limits of 3-43 atm (tech). Duration of experiment was 3 hours. Contents of autoclave was mixed periodically. Ratio of alcohol and propylene oxide in the separate experiments varied from 1:4 to 1:16.

The yield of condensate in almost all experiments constituted 95-96%. Product of reaction was filtered from suspended mechanical impurities and in a number of experiments was subjected to distillation in vacuum. Results of physical chemistry research of fractions separated during distillation of condensate are presented in Table 3 and in the figure (number of curves on figure correspond to ordinal numbers in Table 3). As a result of conducted research the following regularities are established.

Table 3. Physico-chemical Properties of Polyglycol Esters on the Basis of Propylene Oxide and Alcohols
(Polyalkylene glycols are obtained in autoclave)

No. п/п	No. experiment	Alcohol	Taken in reaction of phenol and propylene oxide in the ratio	Boiling range, °C	Pressure, mm Hg	Molecular weight (found)	d_{20}^{20}	n_D^{20}	Pour point, °C	Viscosity (cs) at a temperature, °C					Index of viscosity	$\frac{\nu_{50}}{\nu_{100}}$
										-40	0	37.8	50	100		
1	1	Octyl	1:6	100-140	6	197	0.908	1.4350	-60	—	—	6.5	4.58	1.59	—	2.88
2				140-168	6	245	0.924	1.4380	-60	—	—	7.8	5.3	1.88	—	2.82
3				168-187	6	302	0.936	1.4396	-60	—	—	9.13	6.3	2.14	196	2.94
4				187-220	6	360	0.955	1.4427	-60	—	—	12.4	8.25	2.56	175	3.23
5	2	Isoamyl*	1:8	88-230	2-3	260	—	1.4429	-55	—	—	12.48	8.07	2.42	—	3.4
6	3	"	1:8	—	—	—	0.972	1.4401	-60	—	112	13.9	7.8	2.57	198	3.63
7	4	2-ethylhexyl	1:8	—	—	262	0.976	1.4459	-57	—	156	14.7	9.4	2.6	160	3.6
8	5	n-propyl	1:8	—	—	—	0.987	1.4410	-58	—	94.4	13.0	8.35	2.6	180	3.2
9	6	Isopropyl	1:8	—	—	—	0.987	1.4431	-60	20050	121.69	16.1	9.46	2.66	170	3.56
10	7	"	1:4	—	—	—	—	1.4289	-60	—	—	9.52	6.25	2.05	198	3.04
11	8	"	1:16	—	—	—	0.9960	1.4498	-52	—	172.88	15.42	9.8	2.71	160	3.61
12	9	"	1:4	—	—	—	0.982	1.4374	-60	—	—	13.37	9.07	3.09	202	2.94
13	10	"	1:8	—	—	—	0.991	1.4408	-	—	—	19.35	12.9	3.73	174	3.45

*Polyglycol esters, obtained on the basis of isoamyl, 2-ethylhexyl and isopropyl and isopropyl alcohols, were investigated without preliminary fractionation.



Dependence of viscosity on temperature for oils obtained on the basis of different alcohols and propylene oxide.
KEY: (a) Viscosity, cs; (b) Temperature, °C.

1. Viscosity of polyglycol ester increases with increase of quantity of propylene oxide combined with alcohol.

2. With increase of viscosity of polyglycol ester is increased its pour point, and also value of ν_{50}/ν_{100} ratio.

3. With an increase of number of carbon atoms in molecule of alcohol is increased the absolute value of viscosity and is somewhat increased the pour point of polyglycol ester. Value of ν_{50}/ν_{100} ratio almost does not change.

4. Polyglycol esters obtained from alcohols of normal structure have a higher pour point as compared to polyglycol esters obtained from alcohols of isostructure.

Polyglycol ester (experiment 10) was oxidized by air (0.25 l/min; 12 hours) according to method of VTI [F. Dzerzhinskiy All-Union Heat Engineering Institute], while initial acidity of it was increased by 0.005 which testifies to stability of it to oxygen.

Conclusions

1. Polyglycol esters obtained on the basis of propylene oxide with alcohols possess higher low-temperature properties than polyglycol esters obtained on the basis of phenols.

2. With a change of ratio of initial components (propylene oxide and alcohol) are obtained polyglycol esters of different viscosity with high low-temperature properties.

3. Easily obtainable alcohols, for instance isopropyl, can be used for synthesis of polyglycol esters with high low-temperature characteristics.

4. On a base of alcohols produced in industrial scale, can be obtained synthetic lubricating oils of the polyglycol ester type, possessing good low-temperature properties.

5. Certain polyglycol esters upon addition to mineral oils improve their dispersive and washing properties and, therefore, can be used during preparation of multifunctional mixed compositional additives.

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SYNTHESIS AND INVESTIGATION OF ADDITIVES INCREASING LUBRICATING PROPERTIES OF OILS

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When organic compounds containing chlorine and sulfur are added to lubricating oils, strength of butyric film is increased and lubricating ability of oils is improved. As additives to oils used at super-high pressures, are applied also exters of carbonaceous acids and alcohols, vegetable and animals fats, forming on surface of metal adsorbed layers of molecules due to the polar groups in them. Sulfonated fats, and certain sulfide and thio ethers not only lower wear of motor parts, but also improve anticorrosive properties of lubricating oils.

Chlorinated compounds, prepared on a base of aromatic hydrocarbons are more thermally stable than compounds prepared on a base of aliphatic hydrocarbons. Stability of these additives depends mainly on content of sulfur and chlorine.

Synthesis of additives to oils for transmission and hypoid gears was conducted in the direction of synthesis of chlorine- and sulfur-containing compounds from petroleum products containing a significant quantity of aromatic hydrocarbons, and also in the direction of obtaining esters of naphthenic acids and polyatomic alcohols.

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Initial raw material for obtaining chlorinated compounds was high-aromatic products of pyrolysis, and namely a napthalene squeezing containing condensed aromatic hydrocarbons, solvent and 160-300° fraction, separated from light oil of pyrolysis. Later for synthesis of chlorine derivative, naptha of catalytic cracking was used, evaporating at a temperature of 160-270°. The shown products contain up to 60-80% aromatic hydrocarbons.

In products of pyrolysis, furthermore, is contained up to 25-30% unsaturated hydrocarbons, which, during chlorination will be resinified, are polymerized and worsen quality of additives obtained on their base. To remove them, the products of pyrolysis are subjected to purification by sulfuric acid. Content of olefins in naphtha of catalytic cracking does not exceed 2-3%.

Products of pyrolysis and cracking are subjected to chlorination by electrolytic chlorine at 70-80°.

To accelerate the reaction, chlorination is conducted in the light or in the presence of a catalyst -- powdered iron, while chlorine heads for the aromatic nucleus. After chlorination the obtained products are processed by a solution of caustic soda during heating for decomposition of unstable chlorine-derivatives and neutralization of hydrochloric acid dissolved in them.

Prepared thus, chlorinated products of pyrolysis and catalytic cracking upon addition to lubricating oils increase their antiwear properties.

A second series of additives -- complex esters -- was synthesized from naphthenic and stearic acids and ethylene glycol or phenol.

Esters obtained from unchlorinated acids, almost do not increase antiwear properties of oils. At the same time esters from chlorinated acids with alcohols increase antiwear properties of oils.

The esterification of chlorinated naphthenic acids by ethylene glycol, taken in equimolecular ratios, went according to the following equation:

$$2C_nH_{2n-2}ClCOOH + \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} \rightarrow \begin{matrix} C_nH_{2n-2}ClCOOCH_2 \\ | \\ C_nH_{2n-2}ClCOOCH_2 \end{matrix} + 2H_2O$$

In the reaction with formation of ester the acid number of the initial mixture is lowered from 140-150 milligrams KOH to 8-10 milligrams KOH.

Esters from chlorinated naphthenic acids and phenol were synthesized through acid chlorides of acids:

$$3C_nH_{2n-2}ClCOOH + PCl_3 \rightarrow 3C_nH_{2n-2}ClCOCl + H_3PO_3$$

$$C_nH_{2n-2}ClCOCl + C_6H_5OH \rightarrow C_nH_{2n-2}ClCOOC_6H_5 + HCl$$

The remaining free acids after treatment by a weak solution of caustic soda were washed by water.

Tests on a four-ball machine showed that esters of chlorinated naphthenic acids and phenol increase durability of butyric film to a larger degree than do esters of their chloronaphthenic acids and ethylene glycol.

It is necessary to note that additives obtained from the above esters, in the presence of a small quantity of free acids sharply increase corrosive aggressiveness of oil. Therefore, our research in subsequent years continued mainly in the direction of obtaining chlorine and sulfur-containing compounds.

A basic criterion for judgement on possibility of application of synthesized compounds as additives for oils used in hypoid and transmission gears, was testing on a four-ball machine.

As base oil was used airplane oil MK-22, which in viscosity-temperature properties most approximates transmission oils.

As a result of laboratory research and tests on a four-ball machine were developed optimum conditions for synthesis of the most effective additive aznii-9*, prepared on a base of products of catalytic cracking and products of pyrolysis. During development of conditions of synthesis of additive the influence of different factors, and namely of diffused light, catalyst, and others was clarified.

*Ed. Note: Additive named after research institute. aznii = Azerbaydzhan Scientific Research Institute: also written AzNII.

In Table 1 are given results of test on four-ball machine of different oils with 3% additive aznii-9.

With increase of concentration of additive, antiwear properties of oils increase and attain maximum with an addition of 7-10% additive.

Depending upon quality of initial raw material for chlorination, and also upon applied anticorrosive component, it is possible to prepare additive aznii-9 in five variants.

1-st variant.

Purified from unsaturated hydrocarbons, napthalene squeezing or fraction of light oil is chlorinated to a content of 15-20% chlorine, then is sulphurized by elementary sulfur to a content of 1-1.5% sulfur.

Table 1. Results of Test on Four-Ball Machine of Different Oils with 3% Additive aznii-9

No. sample	Product	Diameter of spot of wear, mm	Critical load P_k, kg
8	Airplane oil MK-22.....	0.38	52
3	The same + 3% additive.....	0.51	103
5	AK-15.....	0.38	52
6	The same + 3% additive.....	0.45	78
14	Transformer oil, thickened by polyisobutylene.....	0.36	39
27	The same + 3% additive.....	0.45	78
24	Bright stock.....	0.38	52
25	The same + 3% additive.....	0.55	116

The sulfurization of chlorinated products of pyrolysis can be excluded if effective anticorrosive additive aznii-7 is added to the additive.

2-nd variant

Naphthan of catalytic cracking is chlorinated to a content of 30-35% chlorine, after which to it is added anticorrosive additive aznii-7 with an ash content of 10-11%, containing 3-4% sulfur.

3-rd variant

1. Chlorinated naphtha (content of chlorine 30-35%).
2. Oxidized petrolatum (acid number 25-30 milligram KOH).

4-th variant

1. Chlorinated naphtha.

2. Additive aznii-7.

3. Oxidized petrolatum (as such or washed by hydrate barium oxide).

5-th variant

1. Chlorinated naphtha.

2. Additive BFK-1.

Ratio of chlorinated products and anticorrosive components corresponds to 80:20 or 70:30, and in 4-th variant 70:20:10.

In Table 2 are given results of tests of oils with additives and without additives on a four-ball machine.

As can be seen from the table, additives of the type aznii-9, synthesized with respect to all five variants, sharply increase indices of antiwear properties of oils and durability of butyric film. Antiwear properties of additive aznii-9, judging by results of tests on four-ball machine, are analogous to antiwear properties of imported additives. It is necessary to note that the additive acts especially well at increased temperatures (80-100°) and pressures (indices σ_{200} and σ_{300}).

A test was conducted of airplane oil MK-22 without additive and with additive aznii-9 (prepared according to 1-st variant) on reducing gears of trolley busses. On the basis of results of tests during a trolley run of 40-45,000 km on an oil with additive and 20-23,000 km on an oil without additive the following conclusions were made.

1. Wear of teeth of gear when it operates on an oil with additive is twice less than when it operates on an oil without additive (Figs. 1 and 2).

2. When trolley busses operate on an oil with additive aznii-9 corrosion of surface of teeth of worm gear and worm was not observed.

One of the basic shortcomings of additive aznii-9 is its corrosive aggressiveness, especially in the presence of water. The addition of anticorrosive additive aznii-9 and oxidized petrolatum sharply lowers corrosion of steel and copper plates when oil

contains 3% water. Corrosion was determined according to methods of the ASTM and All-Union Government Standard 2917-45.

Table 2. Results of Test of Transmission Oils on Four-Ball Machine

No. sample	Oil	Content, %		Critical load P_k, kg
		Chlorine	Sulfur	
1	Airplane oil MK-22 with additive	—	—	52
2	Transmission motor and tractor (nigrol cylinder oil)	—	—	39
3	Fumigating resin, prepared from extract	—	1.5	49
4	MK-22 + 3% chlorinated and sulfurized naphthalene squeezing	16.4	1.0	83
5	MK-22 + 5% chlorinated and sulfurized naphthalene squeezing	16.4	1.0	95
6	MK-22 + 3% chlorinated and sulfurized naphtha of catalytic cracking	20.0	1.0	95
7	MK-22 + 3% chlorinated and sulfurized gas oil of catalytic cracking	16.5	1.5	85
8-12	MK-22 + 3-5% additive aznii-9 in all five variants	—	—	98—108
13	MK-22 + 3% santopoil	—	—	103
14	MK-22 + 3% Lubrisol-70	—	—	132
15	MK-15 without additive	—	—	55
16	MK-15 + 7% aznii-9 (5th variant)	—	—	95

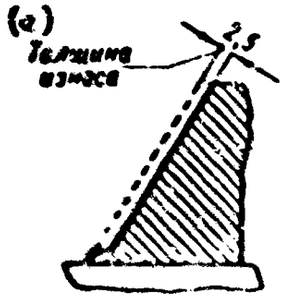


Fig. 1. Wear of tooth of worm wheel on oil without additive.
KEY: (а) Thickness of wear.

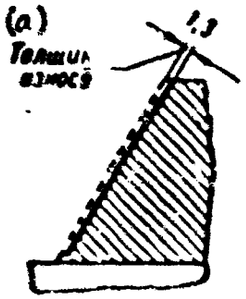


Fig. 2. Wear of tooth of worm wheel on oil with additive.
KEY: (а) Thickness of wear.

During testing on a Gliesson stand at the Likhachev factory and in NATI [Automobile and Tractor Scientific Research Institute] the additive gave unsatisfactory results (3 and 4-th variants).

Good results were shown by an additive, prepared according to the 5-th variant, at the Baku tire factory. Bright stock served as base oil during the tests.

ADDITIVES ENSURING UNIFORMITY OF SLOW MOVEMENT OF UNITS OF METAL-CUTTING MACHINES

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In connection with increasing requirements for cleanness of treated surfaces and accuracy of treatment of articles, special urgency belongs to the guarantee of uniformity of slow shifts of supports, platforms, and other units of metal-cutting machines, including automatic machine tools equipped by program control.

Guarantee of stability of slow shifts of units of machines in general is a complex problem, combined with influence on characteristics of friction in guides, on rigidity of mechanism of supplies and on characteristics of drive of machine. Influence on characteristics of friction in many cases is the most effective.

Slide guides of metal-working machines (usually a cast iron — cast iron pair) during shift of supports with feed speeds operate in conditions of mixed friction due to low speeds, waviness of surface and presence of significant macro-unevennesses, entering of oil at low pressure, contamination by its abrasive and lubricating-liquid coolant, frequent stops and reversing during work.

In these conditions the usual industrial oils cause an intermittentness of movement.

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In process of joint work of VNII MP and ENIMS [Experimental Scientific Research Institute of Metal-Cutting Lathes] as an anti-skip additive to industrial oils for the first time were used different salts of high-molecular fatty acids (soap), including stearate and oleostearate of aluminum (in concentration 1.6-2.7%) which showed optimum results. The last one was used by us in the form of a consistent lubricant AMS-3, containing 18% oleostearate of aluminum, in whose composition as basis enters high-viscous residual steam engine cylinder oil.

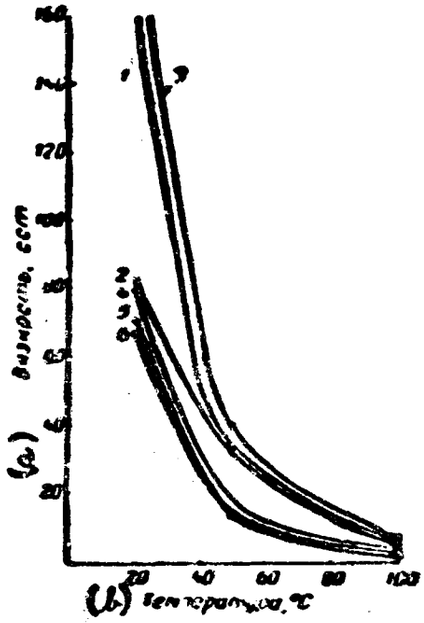


Fig. 1. Characteristics of viscosity of standard oils ES3 and CS3 and developed types of oils for machine tool guides.
1) oil ES3; 2) oil CS3; 3) industrial 45NKZ + 3% olein acid; 4) industrial 12 NKZ + 1.9% stearate of aluminum + 0.015 polymethylsiloxane liquid; 5) industrial 12 NKZ; 6) industrial 12 NKZ + 3% chlorostearine.
KEY: (a) Viscosity, cs; (b) Temperature, °C.

Being easily adsorbed on metallic surfaces, soaps decrease influence of defects of surface and quickly to a change of form of sliding surface.

Aluminum stearate (oleostearate of aluminum) improves antiwear and anticorrosive properties of oil, since high viscosity of soaps promotes formation of lubricating layers of sufficient thickness which is essential for reduction of wear, and also lowers pour point of paraffinaceous oils; thanks to these properties, it can be used as an additive of complex action.

In distinction from other soaps, in particular calcium base, stearate and oleostearate of aluminum readily dissolve in mineral oils in any concentrations. Therefore, samples of oils tested by us constituted stable solutions of high degree of dispersiveness.

Oils with an additive of aluminum stearate (2%) have high anticorrosive properties as compared to special oils of foreign production, containing as an anti-skip additive olein acid or chlorinated stearin (in concentration 3%). During prolonged storage the last ones partially precipitated (Fig. 1).

B. G. Lur'ye investigated the influence of different additives on uniformity of slow shifts and friction in guides on a specially developed ENIMS stand, simulating operational conditions of work of guides.

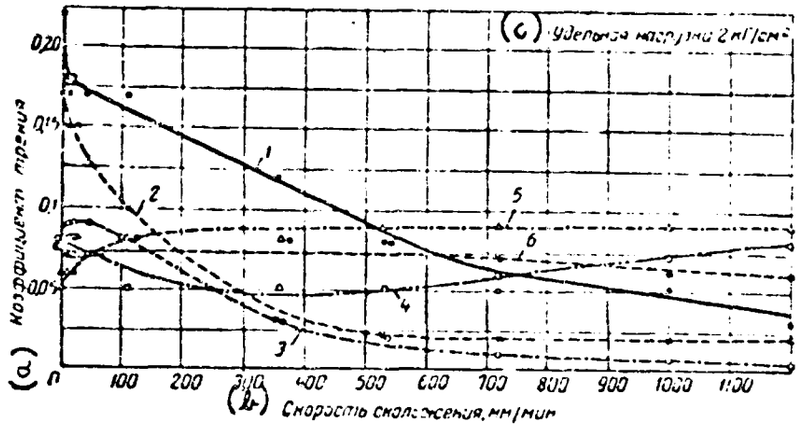


Fig. 2. Dependence of coefficient of friction (f) on speed of slip (cast iron - cast iron friction pair).
Oils: 1) industrial 45; 2) industrial 45 + 10% chlorinated paraffin; 3) industrial 45 + 3% olein acid; 4) AMS-3; 5) industrial 20 + 10% AMS-3; 6) industrial 12 + 1.6% aluminum stearate.
KEY: (a) Coefficient of friction; (b) Speed of slip, mm/min; (c) Specific load 2 kg/cm^2.

When industrial oil 45 (Fig. 2) is used a jump of coefficient of friction is observed during transition from rest to motion and a sharp drop of it with increase of speed prior to beginning of transition to liquid friction (100 mm/min).

Oils of increased viscosity, for instance steam engine cylinder oil and a mixture of cylinder 6 with motor oil (1:4) do not ensure smooth movement at low feed speeds (Table 1).

Table 1. Magnitude of Skips During Friction Depending Upon Sort of Lubricant and Speed of Slip

Conditions of tests on ENIMS stand: cast iron -- cast iron friction pair; specific load 2 kg/cm^2; rigidity of drive 37 kg/mm^2

Oil	Magnitude of jumps at speed, mm/min					
	0.8	5	20	110	530	1200
Industrial 12.....	0.29	0.14	0.05	0.08	0.19	0.35
Industrial 45.....	0.07	0.03	0.03	0.12	0.38	0.01
Cylinder 6 (20%) + + motor (80%).....	0.24	0.12	0.04	0.08	0.01	0.01
Steam engine cylinder oil.....	0.005	0.005	0.006	0.005	0.004	0.005
Lubricant AMS-3	Movement uniform					
Industrial 45 + 3% olein acid.....	0.00	0.00	0.005	0.005	0.01-0.12	0.01
Industrial 12 + 10% AMS-3.....	Movement uniform					
Industrial 20 + 10% AMS-3.....	Movement uniform					
Vnii np-401.....	Movement uniform					

Table 2. Accuracy of Manual Vertical Feed of Polishing Circle in Surface Grinding Machines

No. machine	Accuracy of vertical feed per 5 mm when the guides are lubricated	
	Oil industrial 20	Oil vnii np-401
1	5^{+16}_{-5}	5 + 2
2	5^{+28}_{-5}	5 ± 2
3	5 ± 5	5 ± 2
4	5 ± 3	5 ± 1.5
5	5 ± 5	5 ± 1.5

Industrial oils with an additive of aluminum salts of high-molecular fatty acids give low, practically constant coefficient of friction (Fig. 2) that ensures smoothness of slow movement in the whole speed range and necessary accuracy of calculated shifts (Table 2). Additives consisting of lithium stearate and calcium salts of cotton oil and hydrogenated fat, turned out to be ineffective.

On the basis of results of work conducted on creation of an oil ensuring smoothness of slow shifts of metal-cutting machines, was developed oil vnii np-401 (TU NP No. 26-60), made up of mineral oil of average viscosity with ~ 2% aluminum stearate and with 0.015% antifoam additive -- liquid pms-200A (VTU No. 16-60).

CHAPTER III

TECHNOLOGY OF PRODUCTION OF ADDITIVES

SYNTHESIS AND TECHNOLOGY OF PRODUCTION OF MULTICOMPONENT ADDITIVE VNII NP-360 TO MOTOR LUBRICATING OILS

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Perel'miter
VNII NP*

Additive vnii np-360** consists of two components. One of components — barium alkylphenolate (vnii np-350) — possesses washing properties, and the other — zinc dialkylphenyldithiophosphate (vnii np-354) — anticorrosive and antioxidant properties.

As antioxidant addition can be used also component vnii np-353 — free dialkylphenyldithiophosphoric acid. This component is used in a number of additives in combination with component vnii np-350 (additive vnii np-361) or sulfonate additives (for instance, additives PVS_{ya}-353).

Initial raw material for synthesis of components is alkylphenol, obtained during alkylation of phenol by olefins containing basically 8-12 atoms of carbon. Such alkylphenol is used for the production of additive tsiatim-339***. In laboratory conditions synthesis of components of additive was conducted on separate narrow fractions of alkylphenol, separated from industrial alkylphenol by rectification in vacuum.

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*All-Union Scientific Research Institute for Oil and Gas Refining and the Production of Synthetic Liquid Fuel.

**Additives designated by number and initials of institute.

***Ed. Note: Additive is designated by the initial standing for the Central Scientific Research Institute of Aviation Fuels and Lubricants, developers of the additive.

In Fig. 1 is given diagram of obtaining of additive vnii np-360.

Component vnii np-350 (barium alkylphenolate) is obtained by interaction of alkylphenol with hydrate of barium oxide. The latter is taken in stoichiometrical quantity or in small surplus, in order to completely replace hydroxyl groups of alkylphenol. Reaction of barium - coating is conducted during dilution of alkylphenol by oil, use of which is connected with necessity of lowering viscosity of reaction mass. Furthermore, during realization of reaction in oil — diluent, the best solubility of barium alkylphenolate is achieved and its mixing with other components is facilitated.

In a number of cases completely substituted barium alkylphenolate will dissolve badly in oil. With increase of molecular weight of initial alkylphenols, the solubility of barium alkylphenolates is increased. Solubility of barium alkylphenolates is changed also depending on structure of alkyl radical of alkylphenol.

It is characteristic that insoluble barium alkylphenolate is completely dissolved in oil with addition to it of up to 20% alkylphenol or component vnii np-354, and also in gasoline, benzene and other solvents. Quantity of barium alkylphenolate, insoluble in oil, drops with increase of temperature of barium coating and duration of mixing of barium alkylphenolate with oil at increased (130-140°) temperatures.

In industry it is expedient to obtain barium alkylphenolate at a temperature of 130-140° with the use of oil - diluent. In case of formation of barium alkylphenolate, not completely soluble in oil, one should dilute the component with gasoline or any other light solvent, remove mechanical impurities by centrifuging and then distill off the solvent. Such a diagram of obtaining high-quality barium alkylphenolate is checked on experimental installation of VNII NP and on industrial installation of Yaroslavskiy Petroleum Processing Factory named after Mendeleyev.

Component vnii np-354, possessing antioxidant, antiwear and anticorrosive properties — zinc salt of dialkylphenyldithiophosphoric acid, — is obtained during interaction of alkylphenol with phosphorus pentasulfide and with subsequent

treatment of obtained product with zinc oxide.

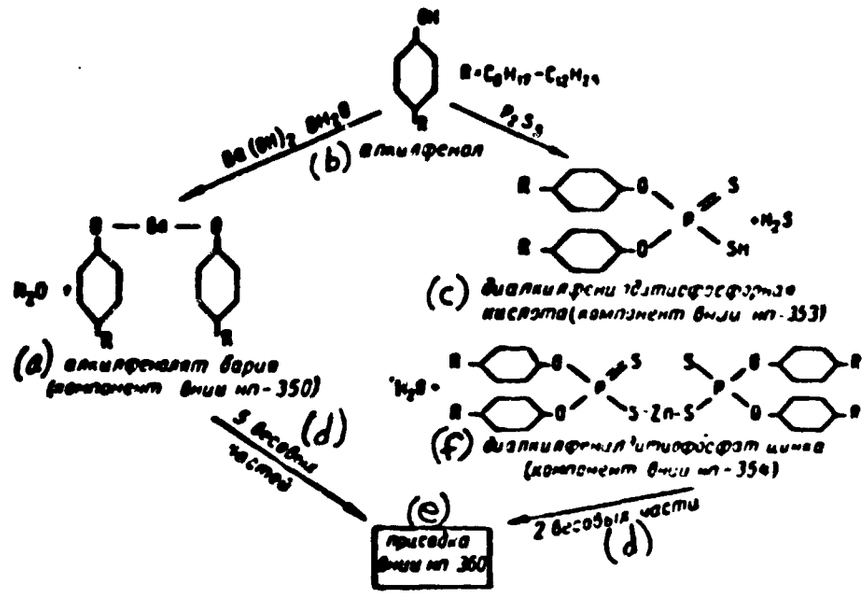
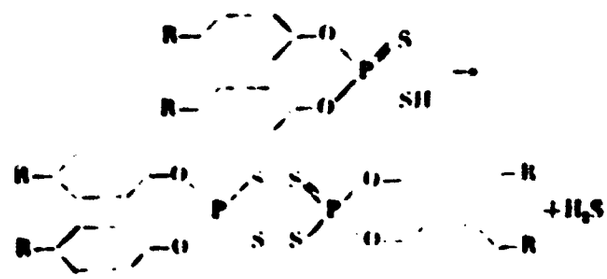


Fig. 1. Diagram of obtaining of additive Vnii np-360. KEY: (a) Barium alkylphenolate (component Vnii np-350); (b) Alkylphenol; (c) Dialkylphenyldithiophosphoric acid (component Vnii np-353); (d) Part: by weight; (e) Additive Vnii np-360; (f) Zinc dialkylphenyldithiophosphate (component Vnii np-354).

During interaction of alkylphenol with phosphorus pentasulfide at a temperature of 80-130°, acid ester of dithiophorphoric acid (component VNII NP-353) will be formed. With this will be formed also small amount of tarry products. Similar reaction has been well studied for aliphatic alcohols [1-5]. At a temperature below 80-90° the process proceeds slowly. At a temperature higher than 130° flow of side processes is observed, connected with further conversion of diester. One of such reactions is formation of thioanhydride of diester of dithiophosphoric acid:



In the course of this process the content of sulfur in product of reaction decreases, molecular weight is increased and acid number (Table 1) is lowered. With decrease of acid number the possible yield of needed zinc salt in turn decreases.

Table 1. Influence of Temperature of Reaction on Properties of Component VNII NP-353. (duration of heating 2 hr)

Index	Content, %		Molecular Weight
	Sulfur	Phosphorus	
Temperature, °C:			
130	9.2	5.3	520
170	7.3	5.6	620
200	6.6	—	890
For $(RC_5H_4O)_2$ PSSH calculated	11.1	5.4	575

To obtain component vnii np-354 diester of dithiophosphoric acid (component vnii np-353) is treated by zinc oxide at a temperature of 80-90°. Process is conducted in oil — diluent for lowering of viscosity of medium and convenience of realisation of technological operations. In the indicated conditions reaction proceeds easily and there will be formed salt of dithiophorphoric acid, soluble in oil, which can be checked by ash content of product.

Increase of temperature during treatment by zinc oxide leads to lowering of ash content of component, which is connected with conversion of dithiophorphoric acid into thioanhydride of acid, as was described above.

Component vnii np-354 after treatment by zinc oxide is subjected to centrifuging for removal of mechanical impurities, and then mixed with component vnii np-350.

Fundamental flow diagram of obtaining of additive vnii np-360 is listed in Fig. 2. Separate assemblies of this diagram were checked during development of

technology of additive in laboratory, on experimental installation of VNII NP and on industrial installation.

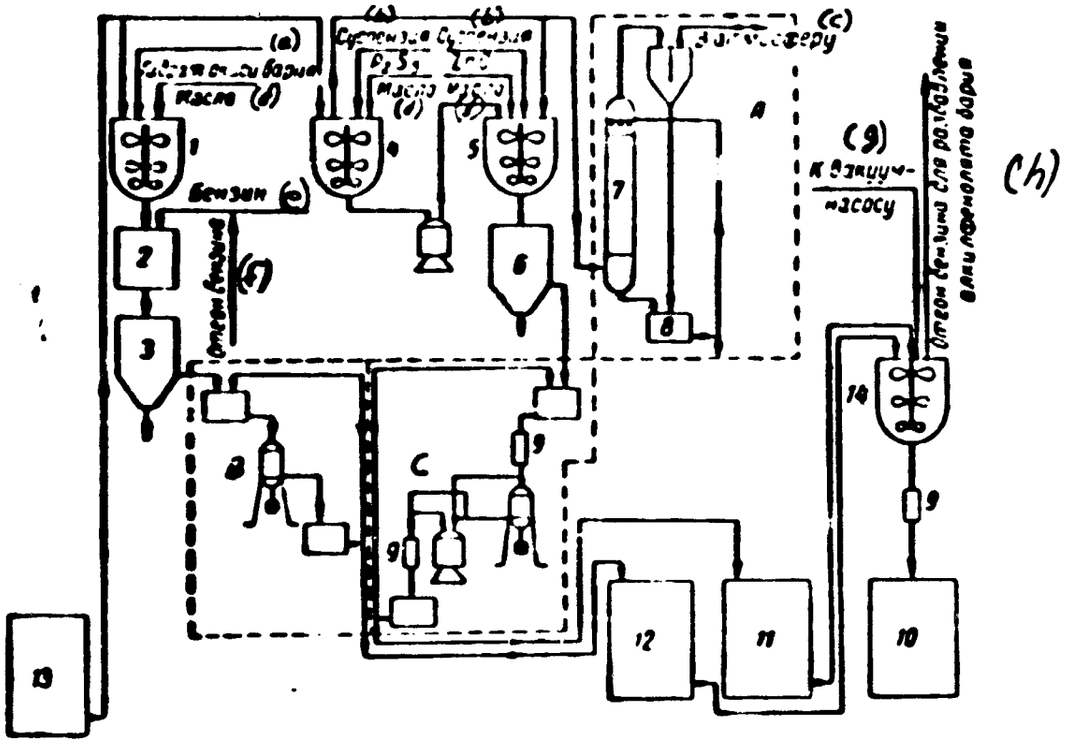


Fig. 2. Fundamental diagram of production of additive vnii np-360.
A—assembly of absorption of hydrogen sulfide; B—block of centrifuging of component vnii np-350; C—block of two-stage centrifuging of component vnii np-304.
1—mixer of barium-coating; 2—vessel of mixing of barium alkylphenolate with gasoline; 3—settling tank; 4—mixer of phosphorous-coating; 5—mixer for treatment by zinc oxide; 6—settling tank; 7—scrubber; 8—vessel for alkali solution; 9—heat exchanger; 10—vessel for additive vnii np-360; 11—vessel for component vnii np-354; 12—vessel for solution of component vnii np-350 in gasoline; 13—vessel for dried alkylphenol or fraction of alkylphenol; 14—mixer.
KEY: (a) Hydrate of barium oxide; (b) Suspension; (c) To atmosphere; (d) Oil; (e) Gasoline; (f) Distillate of gasoline; (g) To vacuum pump; (h) Distillate of gasoline for dilution of barium alkylphenolate.

Main indices with respect to composition of additive vnii np-360 and its components, and also some physicochemical properties are listed in Table 2.

Table 2. Characteristics of Additive VNII NP-360 and its Components.

Properties	Component vnii np-350	Component vnii np-354	Additive vnii np-360
Kinematic viscosity at 100°, cs.....	30—50	19—25	13—20
Content, %.....			
Ashes.....	17—18	7—8	13.5—16.5
Phosphorus.....	—	2.4—2.5	0.75—1.0
Sulfur.....	—	5.0—5.5	1.4—2.0
Zinc.....	—	2.3—2.6	0.8—1.0
Barium.....	10.5—12.0	—	8.0—9.5
Water.....	Absence		
Mechanical impurities.....	Not more than 0.15		

Estimate of operational qualities of components of additive was conducted by different laboratory methods and on various oils, mainly obtained from sulfur-bearing crudes.

One of the factors determining washing action of additive is its neutralizing properties. Below* are given data on effective neutralizing action of components and their compositions (duration of effective neutralization, %), obtained radiometrically on installation RUM-1. As base oil is used lubricating oil AS-9.5 from sulfurous crudes. Component vnii np-353 and vnii np-354, just as base oil without additive, have neutralizing action close to zero.

AC-9.5 + 5% vnii np-350.....180

AC-9.5 + 5% vnii np-350 + additive
1.5% vnii np-353..... 25
4.5% vnii np-353..... 37
9.0% vnii np-353..... 0
1.5% vnii np-354..... 40
4.5% vnii np-354..... 32

*Experimental data were obtained by Yu. S. Zaslavskiy with colleagues.

From the given data it is clear that high neutralizing action of barium alkylphenolate in significant measure is suppressed by addition of components vnii np-353 or vnii np-354, and this suppression depends on concentration of the latter.

During the study of stability of oils AS-5 and AS-9.5 according to method of VTI (All-Union "Order of the Red Banner of Labor" Scientific Research Institute of Heat Engineering im. F. E. Dzerzhinskiy) it was shown that with the use of washing component (barium alkylphenolate), the quantity of deposit and acidity after oxidation significantly is increased, while with the use of components vnii np-353 and vnii np-354 they decrease. Mixtures of barium alkylphenolate with components vnii np-353 or vnii np-354, added to the above-indicated oils, improve characteristics of oils during oxidation according to VTI as compared to oils without additives.

Data obtained during oxidation of oils AS-5 and AS-9.5 at temperatures of 160 and 180° are presented in Table 3.

From data of Table 3 it is clear that in oils with barium alkylphenolate, in spite of its high neutralizing properties, acid number after oxidation is higher than in oil without additive. Such a phenomenon can be explained by the fact that barium alkylphenolate promotes oxidation of oil. In presence of components vnii np-350 and vnii np-354 the acid number after oxidation is lower than samples of oils with each of these components separately.

Character of deposits after oxidation is different for samples of oils with components vnii np-350 and vnii np-354. Here, just as in the case of acid number, there is observed sharper lowering of deposit-formation in the presence in oil simultaneously of two components.

Interesting observations can be made during comparison of results of oxidation at temperatures of 160 and 180°. Acid number of oil without additive after oxidation is increased at 180° almost 4 times as compared with acid number at 160°. In the case of oil with additive vnii np-360, acid number remains practically the same during oxidation at 160° and 180°.

Table 3. Stability of Oils AS-5 and AS-9.5 During Oxidation According to Method of VTI

Oil	Acid number, mg KOH/g*		Deposit after oxidation, %		
	Up to oxidation	After oxidation	Total	Hydroxyacids and asphalteness	Carbenes and Carboids
Temperature of oxidation 160°					
AS-5 base.....	0.02	3.5	2.5	—	—
AS-5 with additive:					
2.5% vnii np-350.....	Alk	10.0	16.5	—	—
5.0% vnii np-350.....	Alk	9.5	25.7	—	—
2.0% vnii np-353.....	0.49	2.1	1.8	—	—
2.0% vnii np-354.....	Alk	2.5	2.3	—	—
2.5% vnii np-350 + 2.0% vnii np-353.....	Residual	1.4	1.2	—	—
AS-9.5 base.....	0.015	2.6	1.2	1.0	0.2
AS-9.5 with additive:					
5.0% vnii np-350.....	Alk	10.8	19.1	19.0	0.1
2.0% vnii np-354.....	0.64	3.7	0.28	0.07	0.21
5.0% vnii np-350 + 2.0% vnii np-354.....	0.04	3.3	0.007	0.007	0
Temperature of oxidation 180°					
AS-9.5 base.....	0.015	10.3	8.0	3.0	5.0
AS-9.5 with additive:					
20.0% vnii np-350.....	Alk	0.84	38.2	38.0	0.2
5.0% vnii np-350 + 2.0% vnii np-354.....	0.04	3.5	7.0	5.5	1.5

*Acid number in samples of oil AS-5 was determined according to All-Union State Standard 5985-51, in oil AS-9.5 by potentiometric titrating up to PH-7.

Thermooxidizing stability of lubricating oil AS-9.5 according to method of Papok practically is not changed during addition of component vnii np-350. Antioxidant components vnii np-353 and vnii np-354 cause sharp increase of thermal stability (from 27 min for pure oil to 80-84 min for oil with component vnii np-353 or vnii np-354). Mixture of components vnii np-350 and vnii np-353 gives oil high stability, which, however, is lower than for components vnii np-353 or vnii np-354. In all cases of addition of indicated components the quantity of varnish is sharply lowered.

On the basis of investigation of operational properties of oils with separate components and their mixtures by laboratory methods, additive vnii np-360 was recommended for further test on full-scale engines. This additive passed short-term and prolonged stand tests on different engines (D-35, YaAZ-204, KDM-46, SMD, GAZ-51, AD100), and also operational tests on 2D100 diesel locomotive engines and tractor motors. Results of tests showed higher effectiveness of additive vnii np-360 as compared to additives issued at present. Additive vnii np-360 was recommended for use in the first place on diesel locomotive engines during their work on sulfurous diesel fuel.

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ALKYLATION OF PHENOL BY DIISOBUTYLENE IN THE PRESENCE OF SOVIET-PRODUCED CATION EXCHANGE RESINS AS CATALYST

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MINKh i GP*

In technical literature methods of alkylation of phenols by olefins with use of such catalysts as sulfuric acid, alumina, phosphoric acid, aluminum chloride, benzosulfonic acid and others have been widely illustrated. However, use for majority of indicated catalysts was not found, and in existing industrial method of obtaining alkylphenol for production of additives and certain detergents only benzosulfonic acid is used.

According to the method, after termination of alkylation benzosulfonic acid is removed from alkylate latter by multiple water washings. Washing waters, containing benzosulfonic acid, phenol and alkylphenol, before emptying into sewerage require special purification, which brings much trouble in industrial conditions.

In 1952 in laboratory of MINKh i GP im. Gubkin one of us showed the possibility of alkylation of phenol by olefins with the use as catalyst of cationite KU-2, representing sulfonated product of copolymerization of styrene with divinylbenzene [1-6].

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*Moscow Order of Labor of the Red Banner Institute of the Petroleum Chemical and Gas Industry named for Academician I.M. Gubkin.

Mechanism of catalytic action of cationite KU-2 in hydrogen form is analogous to the action of acid catalysts. In this case reaction of alkylation proceeds sufficiently rapidly and completely; alkylate is easily separated from catalyst by simple decantation and does not need water washing, which removes formation of liquid waste requiring purification.

Cationite KU-2, as a rule, is issued in sodium form, and for use of it as catalyst of alkylation conversion into hydrogen form is necessary. Ion-exchange and catalytic properties of cationite depend on completeness and speed of its conversion to hydrogen form.

For development of reliable, easy and fast method of preparation of cationite KU-2, the influence of different factors on the catalytic activity of cationite and speed of process of its preparation during conversion of cationite to hydrogen form are studied, namely:

a) concentrations of acids (sulfuric hydrochloric);
b) temperatures of acids;
c) rates of supply of acids;
d) heights of layer of cationite during its preparation;
e) temperatures of washing water;
f) rates of supply of water for washing, etc.

As a result of conducted research, optimum conditions were found of preparation of cationite as catalyst for alkylation of phenol by olefins (diisobutylene or polymer distillate), consisting of the following.

Weighted portion of cationite in layer of 6-7 cm is loaded in dividing funnel and is processed at room temperature by 10% hydrochloric or sulfuric acid (technical or pure) with rate of flow through cationite of 5 ml/hr of acid per 1 m of air-dry cationite.

Treatment by acid is conducted until concentration of acid issuing from funnel is not equal to concentration of fed acid (titrating 0.1N with solution NaOH).

After this cationite is washed in this way by distilled water with speed of 5 ml/hr of water per 1 g of initial cationite up to neutral reaction of water on methyl orange.

By this method in one-liter dividing funnel it is possible to prepare after 2 hr 45 min 500 g of cationite with high catalytic properties. Consumption of hydrochloric acid amounts to 0.65 g and of water 4 ml per 1 g of cationite (Table 1). For treatment of cationite 10% hydrochloric acid was used.

Table 1. Influence of Method of Treatment of Cationite on Time of its Preparation

Method of treatment of cationite	Time of treatment by acid	Quantity of taken KU-2, g	Consumption of acid		Washing by water		General time of preparation of cationite	Synthesis of alkylphenol	
			Assumed concentration ml	100 %, g	Washing time	Consumption of water, ml		Duration of synthesis	Nonreacting phenol
Acid is fed from below through conical tube with KU-2.....	13 hr	156	2050	214.64	9 hr	1490	22 hr	3 hr 40 min	0.98
Acid is fed from above through dividing funnel with KU-2....	1 hr 30 min	200	1500	157.0	1 hr 15 min	1250	2 hr 45 min	3 hr 35 min	0.95

In the course of research we established the following:

1. Cationite can be used in reaction of alkylation both anhydrous, and also moist.

2. On the same catalyst 8-10 operations of synthesis of alkylphenol can be conducted.

3. Cationite easily yields to regeneration, after which it can be used still for 10-12 operations of synthesis; it was found that from 1 g of air-dry cationite up to 155 g of dry alkylphenol can be obtained.

4. Optimum quantity of catalyst in periodic process of alkylation is 4-6.5 wt % of initial mixture of reagents.

Besides this, we established that synthesis of alkylphenol on cationite KU-2 can be conducted in equipment of ferrous metal, since the reaction mixture does not render any noticeable corroding action on steel; in turn walls of steel vessel also do not affect the speed and completeness of reaction of alkylation and the quality of obtained product.

Alkylphenol obtained on cationite KU-2 and detergents OP-7 and OP-10 synthesized on this alkylphenol completely satisfy requirements presented to them.

On this basis we carried out in industrial conditions synthesis of alkylphenol from phenol and diisobutylene on cationite KU-2, and the obtained alkylphenol was processed into detergent OP-10.

Having obtained good results during alkylation of phenol by diisobutylene in the presence of cationite KU-2 as catalyst, we proceeded to study the process on continuous device.

Continuous Method of Alkylation of Phenol by Diisobutylene in the Presence of Cationite KU-2

In the literature is described the use of cation exchange resins as catalysts in processes of obtaining esters on continuous device.

As a result of numerous experiments we developed diagram of installation of alkylation of phenol by diisobutylene in fluidized bed of catalyst KU-2 (Fig. 1).

Into pressure retort 1, placed in water bath 2, is poured initial mixture preliminarily prepared and heated to 60-70° — a solution of phenol in diisobutylene, consisting of 48 parts by weight of phenol and 100 parts by weight of diisobutylene. In neck of pressure retort is inserted spherical reflux condenser, cooled by water for preventing of impoverishment of mixture of low-boiling (to 90°) fractions of hydrocarbons, contained in diisobutylene in amount to 3%, and removal of phenol.

From pressure retort 1 initial mixture by glass tube through regulating cock proceeds by gravity to lower part of reaction column 3.

Reaction column is conical tube 1000 mm in length, with internal diameter of bottom 20 mm and top 35 mm, with spherical expansion on top of column 150 mm in diameter (separator 4). Its volume is 540 ml.

Column has electric heating. In it is loaded 280 g of cationite in hydrogen form, prepared by the above-described method.

Synthesis of alkylphenol on indicated installation was conducted in the following manner.

Initial mixture by gravity moves to bottom of column, filled with catalyst, at a speed of 2.5-5.5 ml/hr per 1 g of catalyst. Temperature in column was maintained within limits of 120-150°. Due to boiling away of part of low-boiling hydrocarbons and rate of flow of mixture from bottom to top the catalyst is in suspension (fluidized bed) and thus works all over its surface.

Reaction mixture together with part of catalyst suspended in it gets into separator 4, where as a result of sharp loss of rate of flow and lowering of temperature completely is liberated from suspension of catalyst and through condenser 5 enters receiver 6.

Alkylate collected in receiver is subjected to distillation. Basically excess diisobutylene only is driven off. Remainder, depending on its assignment, can be used as such or be subjected to distillation for separation of traces of phenol.

Qualitative indices of alkylphenol, obtained by different methods and on different catalysts, are given in Table 2 and 3.

From the tables it is clear that qualitative indices of alkylphenol, obtained on diisobutylene by different methods, are very close.

During investigation of reaction of alkylation of phenol by continuous method in column with pseudofluidized bed of catalyst the influence of different factors is studied on course of process and completeness of reaction and quality of obtained product.

Table 2. Dependence of Quality of Alkylphenol on Method of Obtaining it and Catalyst Used

Method of obtaining alkylphenol	Catalyst used	Nonreacting phenol (determined by bromometeric method), %	Flash point of alkylphenol, °C	Specific gravity of alkylphenol at 25°, g/cm³	Hydroxyl number of alkylphenol, %
Periodic on isobutylene.....	Sulfuric acid	3.68	107	0.935	4.0
Periodic on diisobutylene.....	BSK	0.5	129	0.920	5.1
Periodic on diisobutylene.....	KU-2	1.1	129	0.935	6.3
Continuous on diisobutylene composition of mixture: 100/48....	KU-2	1.5	133	0.940	7.1
90/48....	KU-2	2.0	126.5	0.944	7.9
Periodic on diisobutylene composition of mixture 80/48.....	KU-2	1.1	93	0.941	6.4

Table 3. Indices of Quality of Alkylphenol, Obtained by Different Methods

Method of obtaining alkylphenol	Consumption per 1 kg of alkylphenol, g			Yield of alkylphenol on phenol, %	Temperature of process of alkylation, °C	Duration of alkylation, hr	Yield of alkylphenol (dry) from operation, g	Volume of reactor, cm³	Output of alkylphenol from 1 cm³ of reactor, g/hr
	Phenol	Diisobutylene	Catalyst						
Periodic on BSK	440	810	136	100.0	110	6	120	500	0.04
Periodic on KU-2	418	800	4.4	109.2	135	3	115	500	0.077
Continuous on KU-2	426	830	3.34	107.0	120-135	-	—	540	1.394

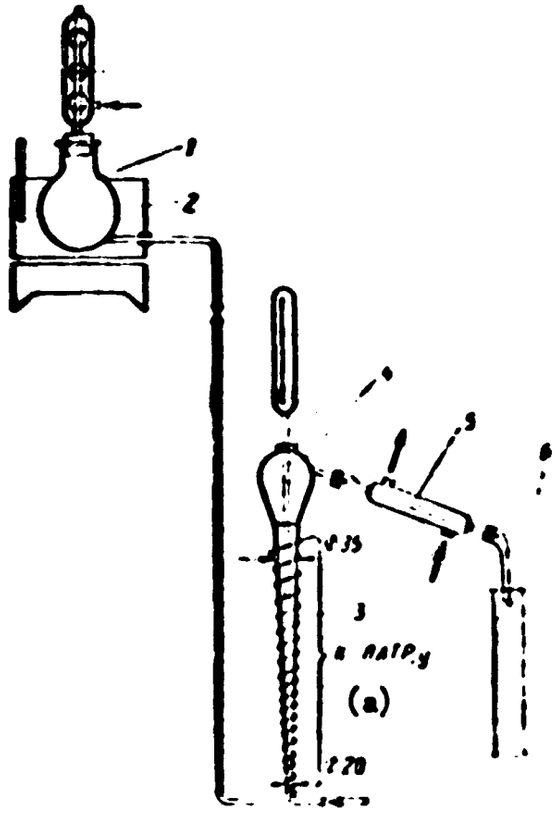


Fig. 1. Diagram of installation of continuous alkylation of phenol on KU-2 in fluidized bed. KEY: (a) To laboratory auto-transformer.

At a temperature up to 120° reaction of alkylation proceeds incompletely and in reaction mixture there remains up to 8-10% of non-reacting phenol. Optimum temperature of process is 120-135°. No noticeable improvements of process with increase of this temperature are noted.

Optimum rate of supply of mixture is 3.5-4.4 ml/hr of catalyst. Smaller rates (to 0.5 ml/g hr) very insignificantly decrease the content of residual phenol in reaction mixture, and high rates (to 5 ml/g hr) do not give reliable separation of alkylate from catalyst and cause splashing over of catalyst in receiver.

With the use of initial mixture, impoverished by diisobutylene, content of non-reacting (residual) phenol in reaction mixture increases as compared with the use of normal mixture of composition — 48 parts by weight of phenol per 100 parts by weight of diisobutylene (or in molar ratios 1: 1.8), and namely 0.4-0.6% with mixture 4[illegible] and 0.5-1.2% with mixture 48/80 (Table 4). Yield of special purpose product on phenol, as was shown in Table 4, decreases. It was determined that optimum molar ratio of phenol to diisobutylene is 1 : 1.8. In conditions of continuous process catalyst can work still 50 hr and more. From 1 g of anhydrous catalyst can be obtained around 300 g of dry alkylphenol. Catalyst can be used both anhydrous, and also without preliminary drying, containing up to 40% moisture.

Table 4. Dependence of Yield of Dry Alkylphenol on Composition of Initial Mixture

Continuous method of obtaining alkylphenol. Catalyst KU-2.

Composition of initial mixture of diisobutylene/phenol, parts by weight	Obtained dry alkylphenol, g	Yield of alkylphenol, % to phenol	Flash point of alkylphenol, °C
100/48	152	107	119.5
90/48	152.5	100.1	116.2
80/48	160.5	97.5	122

Under the above-indicated conditions the productivity of installation with volume of reaction space of 540 mm amounts to 753 g/hr of dry alkylphenol or 1.394 g/hr of alkylphenol with 1 cm^3 of reaction column, which more than 18 times exceeds the yield as compared to periodic process on catalyst KU-2 and almost 35 times on catalyst BSK.

Fitness of obtained alkylphenol for production on basis of it of detergents OP-7 and OP-10 was investigated*.

In examining qualitative indices of detergents OP-7 and OP-10, obtained on alkylphenols by different methods of manufacture, it is clear that they do not essentially differ from each other and completely satisfy requirements of TU (Technical Instructions) for these products. Besides, one should note that moistening properties (determined by coal dust) of OP-7 and OP-10, synthesized on alkylphenols obtained by periodic method on catalyst BSK, are significantly worse than properties

*Successful use of alkylphenols obtained by alkylation of phenol by diisobutylene in the presence of cationite KU-2 for the production of alkylphenol additives is reported in separate work.

of these substances synthesized on alkylphenols obtained on catalyst KU-2. Apparently, here the influence of significant amount of ditertiary aklylderivatives obtained during synthesis of alkylphenol on BSK, shows. Conducted investigations of qualitative indices of final products OP-7 and OP-10 show complete fitness of aklylphenol obtained on catalyst KU-2 both by periodic, and also by continuous methods.

It was determined that consumption coefficients with respect to raw material with continuous method on phenol and catalyst are significantly lower than with periodic method on BSK (Table 3). Consumption of diisobutylene, increased by 10%, cannot be considered with this, since diisobutylene removed during vacuum distillation of alkylate can be completely returned to production for preparation of initial mixture.

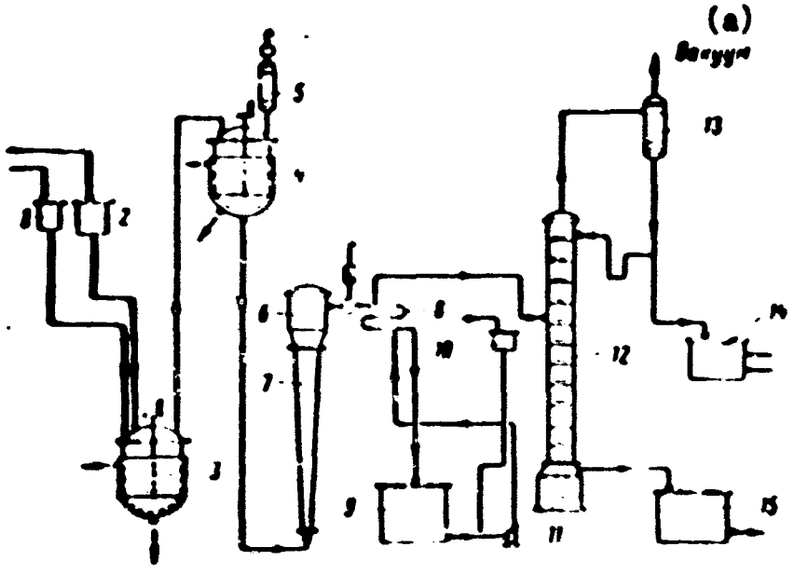


Fig. 2. Diagram of experimental installation for alkylation of phenol by continuous method.
1—measuring device of phenol; 2—measuring device of isooctylene; 3—mixer; 4—pressure tank; 5—reflux condenser; 6—separator; 7—reaction column; 8—heat exchanger; 9—collector of raw alkylphenol; 10—pressure tank of alkali; 11—centrifuge pump; 12—separating column; 13—condenser; 14—separating flask; 15—collector of dry alkylphenol.
KEY: (a) Vacuum.

On the basis of conducted research a diagram of experimental installation for obtaining tert-octylphenol by continuous method was suggested (Fig. 2).

Productivity of new method of obtaining tert-octylphenol by alkylation of phenol by diisobutylene according to continuous system in pseudofluidized bed of

catalyst is 18 times greater during work on the same catalyst in static conditions and 34 times greater as compared to existing industrial process with the use of benzosulfonic acid as catalyst.

New system of obtaining alkylphenol guarantees quantitative conversion of phenol and excludes formation of harmful phenol liquid waste and use of acid-resistant equipment.

Conclusions

1. Alkylphenol obtained by new method is monoalkylphenol (tert-octylphenol), which is fully useful for production of alkylphenol additives and detergent of type OP-7 and OP-10.

2. With respect to moistening properties detergents on a base of alkylphenols obtained by new method exceed corresponding detergents, obtained in industry on a base of catalyst BSK. This is explained by absence of alkylphenol of polyalkylated compounds, since catalyst KU-2 used in new method acts selectively and excludes the possibility of formation of polyalkylated compounds.

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PRODUCTION OF OIL-SOLUBLE SULFONATES BY MEANS OF SULFONATION OF MINERAL OILS BY LIQUID SULFURIC ANHYDRIDE IN SOLVENTS

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Factory "Neftegaz"

Oil-soluble petroleum sulfonates at present are widely used in the following basic directions [1-5]:

1) detergent-dispersive additives to lubricating oils, mainly calcium and barium sulfonates;

2) rust inhibitors for oils, mainly sodium, calcium, barium and zinc sulfonates;

3) emulsifiers of oils, mainly sodium sulfonates.

Moscow factory "Neftegaz" produces oils neftegaz-203, protecting from rusting, which contain as rust inhibitor composition — basic calcium sulfonate (3 parts) and oxidized petrolatum (2 parts). These oils by their own protective action significantly exceed existing liquid preservative lubricants (58", 59, 59ts, K-15, UTI-1, Rujiena and Rujiena liquid). Calcium sulfonate for oils neftegaz-203 is obtained by sulfonation of oils of selective purification from crudes of eastern regions of USSR with viscosity of 5-7 cs at 100° and with molecular weight of 350-400 (for instance, oils AS-5 and industrial 50) by sulfuric anhydride in solution of liquid sulfurous acid anhydride on experimental industrial installation of factory "Neftegaz", which is described below.

For preparation of oil-soluble sulfonates as additives to lubricating oils, initial raw material is mineral oils with molecular weight of 350-700 (for instance, AS-5, AS-9.5, industrial 50, D-11, MK-22, and steam engine cylinder oil), containing significant amount (more than 30% of alkyl- or naphthene - aromatic hydrocarbons, which give during sulfonation alkylarylsulfonates. Hydrocarbons contained in oils, not having aromatic nuclei in molecule (paraffin and naphthenic), do not give sulfonates and are little touched by sulfonating agent. Aromatic hydrocarbons of oil fractions of crude contain one or several aromatic rings, which can be united with naphthene rings and (or) with lateral paraffin chains; aromatic rings can be condensed, as for naphthalene or phenanthrene, or isolated, as for diphenyl methane. In petroleum fractions mixed naphthene aromatic hydrocarbons are frequently met.

To obtain oil-soluble sulfonates mononuclear alkyl aromatic hydrocarbons suit most of all. Polycyclic compounds with short alkyl chains give sulfonates, not soluble or little soluble in oil. Experience of installation of factory "Neftegaz" shows that as raw material for production of sulfonate additives to lubricating oils can serve both distillate and residual oils of selective purification from eastern crudes, and also oils from Baku crudes.

Oil-soluble petroleum sulfonates were obtained basically as byproducts during deep oleum purification of mineral oils — white, transformer and turbine [1-4]. With such purification raw oil (distillate) is mixed at 20-50° with oleum (10-20%) in amount of 5-15% of oil. Acid tar is separated by means of settling or centrifuging: such a treatment is repeated several times. Oil-soluble sulfonates are stored in oil layer and after last treatment by oleum are extracted from it by aqueous ethanol (for instance, 50%) or by another alcohol containing caustic soda. Since sulfo acids during oleum treatment are partially destroyed, then for increase of their yield extraction is conducted of oil layer not only after final portion of oleum, but also after one or several intermediate treatments with oleum. With content in initial raw material of 40-50% sulfonating hydrocarbons the yield of

sulfonates by given method does not exceed 8% (usually it is equal to around 5%).

Recently petroleum sulfonates began to be obtained as special purpose products by means of sulfonation of mineral oils with oleum. In literature start in 1957 of one installation in Canada and three in the United States in the production of sulfonates is reported; reactors with energetic mixing and heat removal (Votator) are used [6, 7].

There is a significant number of patents and works on sulfonation of mineral oils and synthetic alkyl aromatic hydrocarbons with gaseous sulfuric anhydride [8-10]; sulfuric anhydride diluted by inert gas (chiefly nitrogen) is used.

Sulfonation of oils by sulfuric acid, oleum or gaseous sulfuric anhydride occurs in immiscible phases of oil and acid, which significantly lowers the speed of sulfonation (which is determined by speed of dissolution of hydrocarbon in acid [11]). To achieve sufficient depth of sulfonation, significant surplus of acid is taken, contrary to theory (5-15 moles per 1 mole of sulfonated hydrocarbon). Such conditions of sulfonation lead to side reactions (oxidation and resinification of hydrocarbons and sulfonic acids), lowering the yield of sulfonic acids, and formation of significant amount of acid tar — waste requiring significant expenditures for liquidation.

Of the given methods the most absolu[illegible] is sulfonation in Votators, which is carried out during short time of contact of oleum and oil (around 1 min) during cooling, due to which side reactions decrease. However, it is necessary nevertheless to use significant surplus of oleum and with this much acid tar will be formed.

It is significantly more convenient to conduct sulfonation with liquid sulfuric anhydride in solvent — with liquid sulfurous acid anhydride [12-18] or chlorinated hydrocarbons [19, 20]. With such sulfonation homogeneous phase of sulfonated agent and oil will be formed (in case of chlorinated hydrocarbons) or well contacting and partially mixed phases of sulfonated agent and hydrocarbons (in case of liquid sulfurous acid anhydride), thanks to which reaction of sulfonation proceeds

practically instantaneously and yields of oil-soluble sulfonic acids are obtained 3-4 times higher than with the use of sulfuric acid, oleum or gaseous sulfuric anhydride. During sulfonation in presence of solvents acid tar will not be formed, and sulfonic acids are obtained purer. Equipment for sulfonation is highly productive; consumption of sulfuric anhydride amounts to 1.5-2 moles per 1 mole of sulfonating hydrocarbon, which is 3-7 times less than with the use of sulfuric acid or oleum.

Sulfonation by sulfuric anhydride in solution of liquid sulfurous acid anhydride is accomplished by mixing 10-15% indicated solution with oil: adding more solution of sulfuric anhydride to oil, which is in the reactor, or mixing flows of oil and solution of sulfuric anhydride*.

Convenient construction of mixing apparatus was suggested by A. I. Gershenovich [16]; it is used on installation of factory "Neftegaz" (Fig. 1). Into pan 3 there proceed through pipe 2 flow of oil and through pipe 1 flow of solution of sulfuric anhydride in liquid sulfurous acid anhydride. Apparatus works under atmospheric pressure. Cone-mixer 4 open from below, which revolves on axis 3 fastened to bearing 12 with stuffing box seal, with the help of electric motor 14 with speed of 1450 rpm sucks upward liquid from pan 3, mixing it simultaneously. Through holes 16 mixture is thrown out onto wall of cylindrical body 6 and on it flows into discharge branch pipe 8. During mixing of oil with solution of sulfuric anhydride, reaction of sulfonation of aromatic hydrocarbons occurs, with which heat is given off (~42 kcal/mole). Owing to the temperature of oil (~20°) and heat of reaction, part of liquid sulfurous acid anhydride is evaporated, maintaining by this temperature of reaction at -10° (temperature of evaporation of liquid sulfurous acid anhydride). Evaporated sulfurous acid anhydride is taken out through branch pipe 9. With

*Advantage of method of sulfonation with sulfuric anhydride in the presence of liquid sulfurous acid anhydride expounded by author over other known methods of sulfonation is debatable and requires further research. In resolution of conference on additives, the equivalence of all developed methods of sulfonation from the point of view of quality of obtained final product was noted, and the fact that expediency of application of one or another method of sulfonation should be determined by local conditions and economics of production. (Editor' note).

indicated dimensions of body, 400 x 8300 mm, the productivity of apparatus is around 50 kg/hr of oil.

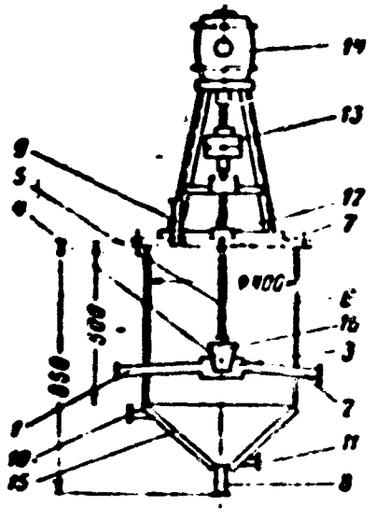


Fig. 1. Sulfonating apparatus. 1—pipe for feed of sulfo mixture; 2—pipe for feed of oil; 3—pan; 4—cone-mixer; 5—axis; 6—body; 7—cover; 8—branch pipe of discharge of sulfo mass; 9—branch pipe of discharge of SO_2; 10,11—branch pipes of intake and discharge of brine; 12—bearing with stuffing box seal; 13—connecting muff; 14—electric motor; 15—casing; 16—hole.

Fundamental flow diagram of installation of factory "Neftegaz" is shown in Fig. 2. Sulfuric anhydride is driven off from 20% oleum and condensed at 32° (on diagram it is not shown). Liquid sulfuric anhydride is gathered in container M_3, whence it along line 1 periodically is passed into mixer A_1 (during work of mixer) on layer of sulfurous acid anhydride already available in it. Liquid sulfuric anhydride in α-form has melting point of 16.8° and boiling point of 44.8°. At a temperature of 25° α-form passes into β-and γ-form; in the latter form it is solid product with sublimation point of 62.5°. To avoid transition of liquid sulfuric anhydride into γ-form and its solidification through condenser of sulfuric anhydride (in diagram it is not shown), casing of container M_3 on lines 17 and 18 and casing of line 1 (not shown on diagram), oil with temperature of 31-33° is circulated. Liquid sulfurous acid anhydride is kept in container M_2, through casing of which on line 19 circulates brine of calcium chloride with temperature of -20°. From container M_2 liquid sulfurous acid anhydride as needed is passed along line 2 into mixer A_1. Through pan of mixer A_1 on lines 20 and 21 cooling brine circulates.

Sulfonating mixture is prepared by mixing 8 volumes of sulfurous acid anhydride

and 1 volume of sulfuric anhydride. Prepared mixture from mixer A_1 along line 3 by gravity joins sulfonating apparatus C. Flow of fed sulfo mixture is regulated by rotameter P_2. Simultaneously into sulfonating apparatus is fed oil from container M_1 along line 4 through rotameter P_1. During sulfonation of oil AS-5 (molecular weight 370) from crudes of eastern regions, the consumption of sulfuric anhydride amounts to around 10% with respect to oil or around 46% molecular with actual content of 40-50% aroratic hydrocarbons in oil. Sulfonated oil in mixture with unevaporated part of sulfurous acid anhydride proceeds by gravity from apparatus C along line 5 into steam-refiner A_2, in which sulfurous acid anhydride is evaporated during work of mixer and circulation of water (with temperature of 50-70°) in casing, passing on lines 22 and 23.

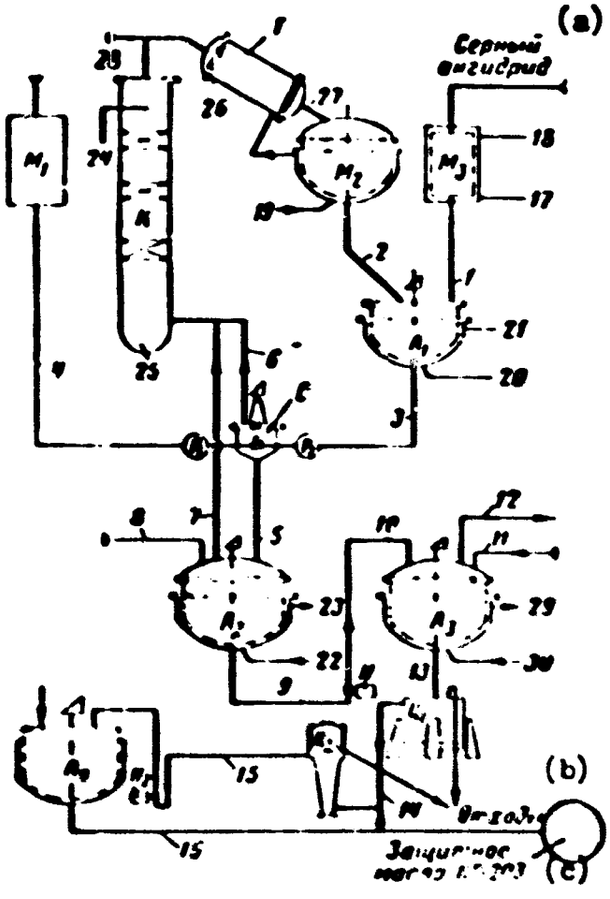


Fig. 2. Fundamental flow diagram of installation of factory "Neftegaz". KY: (a) Sulfuric anhydride; (b) Waste; (c) Protective oil MK-20З.

Vapor of sulfurous acid anhydride from apparatus C along line 6 and from steam-refiner along line 7 go to purification column K, containing packing from Raschig rings for catching drops of oil and products of sulfonation carried away with sulfurous acid anhydride. With necessity column K can be sprinkled with cold low-viscosity oil along line 24, lowering oil along line 25. Purified vapor of sulfurous acid anhydride from column K enters condenser T, through which circulates brine (t = 25°) along line 26. Liquid sulfurous acid anhydride from

condenser T along line 27 enters container $Ж_2$. During starting of installation sulfurous acid anhydride is loaded along line 28 from bottles.

Containers $Ж_2$, $Ж_3$ and mixer A_1 have at the top gas-outlet lines (on diagram they are not shown), proceeding into gas-collecting column. Sulfonated oil, steam-refined in steam-refiner A_2 will divide usually into two layers. Lower layer (for oil AS-5 around 20% of mixture) contains formed disulfoacids, part of monosuloacids, giving during neutralization oil-soluble sulfonates, and small amount of sulfurous acid and sulfuric anhydrides. Upper and lower layers are neutralized together with excess of milk of lime with concentrations around 25% from calculation of 6-8% calcium oxide in initial oil. With neutralization of only the upper oil layer the yield of oil-soluble sulfo acids amounts to around 60% from that obtained during joint neutralization. For possibility of pumping lower thick layer from steam-refiner A_2, in it there is conducted in the beginning partial alkalization of 10-20% of entire quantity of milk of lime, proceeding along line 8. During partial alkalization there will be formed uniform mobile emulsion, which from steam-refiner A_2 is pumped by pump H on lines 9 and 10 into mixer A_3. In mixer along line 11 remaining amount of milk of lime is added and then water is evaporated by heating the mixture to 140-150°. Steam is drawn off along line 12.

Apparatus A_3 is warmed by hot steam ..gine cylinder oil (200-250°), circulating on lines 29 and 30. Dehydrated product with temperature of 130-140° proceeds by gravity along line 13 to centrifuge Ts-1 of basket type (TV-600), where it is centrifuged 5-6 times by means of circulation of product with the help of pump thr.. gh intermediate containers (on diagram they are not shown). Further the product, proceeding along line 14, at the same temperature 3-4 times is centrifuged on supercentrifuge Ts-2 (SGS100 x 750), where finally mechanical impurities are removed and concentrate of basic calcium sulfonate is obtained (see table). In the case of oil AS-5 and AS-9.5 from eastern crudes, the content in concentrate of neutral calcium sulfonate is 20-35%.

To obtain protective oils "Neftegaz-203", concentrate of calcium sulfonate along line 15 by pump H_2 moves to apparatus A_4, in which at 130-150° it is mixed with oxidized petrolatum and oil-diluent, and mixture is passed along line 16 through supercentrifuge Ts_2 1-2 times.

Sulfonation of aromatic hydrocarbons of oil, in spite of surplus of expended sulfuric anhydride, goes only 50-60%, which was calculated both by analysis of concentrates, and also by content of aromatic hydrocarbons in oils (20-25%), obtained from concentrates after extraction from them of sulfonates. During sulfonation part of aromatic hydrocarbons are sulfonated to disulfoacids, which give oil in soluble sulfonates and are removed from concentrate during treatment by lime.

According to the given diagram of work, the process is continuous only in stage of sulfonation; subsequent stages are periodic. Sulfonated mixture is very viscous and is stratified into two layers; therefore it is impossible to steam-refine it from sulfurous acid anhydride continuously by means of circulation in plate column. High viscosity of concentrate also hampers continuous removal from it of water in column. Use of mutual low-viscosity solvent of both layers of sulfonated oil wholly removes these difficulties in realization of continuous process. As mutual solvent xylene fraction of pyrolysis was checked. With dilution by it (for instance, 1 : 1) of sulfonated oil, uniform loose mass is obtained; yield and quality of concentrate with its treatment do not differ from that obtained without diluent.

As mutual solvents can also be used chlorinated hydrocarbons — dichloroethane, trichloroethylene, tetrachloroethylene, carbon tetrachloride, chloroform and others.

Chlorinated hydrocarbons, as mentioned above, are used as diluent of sulfuric anhydride instead of liquid sulfurous acid anhydride. It is possible to use also low-molecular-weight fluorinated hydrocarbons or chlorinated-fluorinated.

We investigated laboratory sulfonation of oils in the following variants:

1) solution of sulfuric anhydride in dichloroethane and solution of oil in dichloroethane;

2) solution of sulfuric anhydride in liquid sulfurous acid anhydride and solution of oil in dichloroethane;

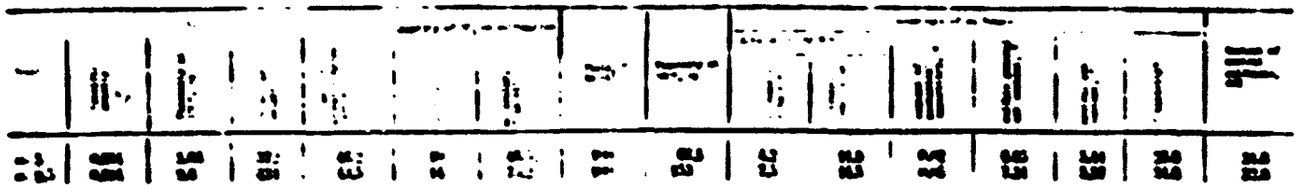
3) solution of sulfuric anhydride in carbon tetrachloride and solution of oil in carbon tetrachloride;

4) solution of sulfuric anhydride in liquid sulfurous acid anhydride and solution of oil in carbon tetrachloride.

With the use of only chlorohydrocarbon solvents during reaction it is necessary to remove heat; this can be done by ordinary water. With the use of 2 parts of solvent per 1 part of oil the reaction is carried out easily even at 20-30°.

Sulfonation in identical conditions in the presence of solvents according to the indicated variants showed that dichloroethane and carbon tetrachloride give approximately identical results (with respect to quality and yield of sulfonates) with those obtained during the use of liquid sulfurous acid anhydride.

Quality of Standard Concentrates of Basic Calcium Sulfonate Obtained on Installation of Factory "Neftegaz" During Sulfonation of Oils AS-5 and AS-9.5 from Eastern Crudes



*Ratio 100 sulfate general ash content — neutral ash content over neutral ash content.

**Calculated with respect to neutral ash content and content of ashes in precipitated sulfonate (17%).

Conclusion

Sulfonation of mineral oils (for the purpose of obtaining oil-soluble sulfonates) with liquid sulfuric anhydride in solvents — liquid sulfurous acid anhydride, dichloroethane or carbon tetrachloride as compared to sulfonation with

oleum or gaseous sulfuric anhydride has the following advantages: high speed of sulfonation, allowing us to use continuous sulfonation in apparatuses of great productivity; absence of acid tar; greater purity of obtained sulfonates; 3-7 times smaller consumption of sulfuric anhydride with respect to obtained sulfonate; 3-4 times greater yield of sulfonates from raw material.

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METHODS OF OBTAINING MULTIASH SULFONATES

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VNII NP*

Main direction of the work set forth is the development of technology of obtaining so-called multiash additives or components of additives on the basis of petroleum oil-soluble sulfo acids, which differ from usual sulfonates by content of metal, several times exceeding stoichiometrical quantity.

It was necessary to clarify properties distinguishing such compounds from the usual sulfonates, possibilities of their use both in pure form, and also as component of additive; for instance, additive vnii np-362 **, suggested in 1958, is mixture of usual calcium sulfonate with barium alkylphenolate and antioxidant.

As detergent components and additives to rotor oils widely are used sulfonates of petroleum origin. Since 1940 [1] sulfonates have been used which contain stoichiometric quantity of metal in molecule and correspond to structural formula $(RSO_3)_2Me$.

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**Designation by number and name of institute.

Activity of such sulfonates, like additives to oils, is increased with increase of molecular weight of organic radical of molecule [2]. With appearance of new, more forced motors, working on fuel with high content of sulfur, requirements for properties of additives are increased. In connection with this there appear sulfonate additives of alkaline action [3] of composition $2SC_3MeOH$.

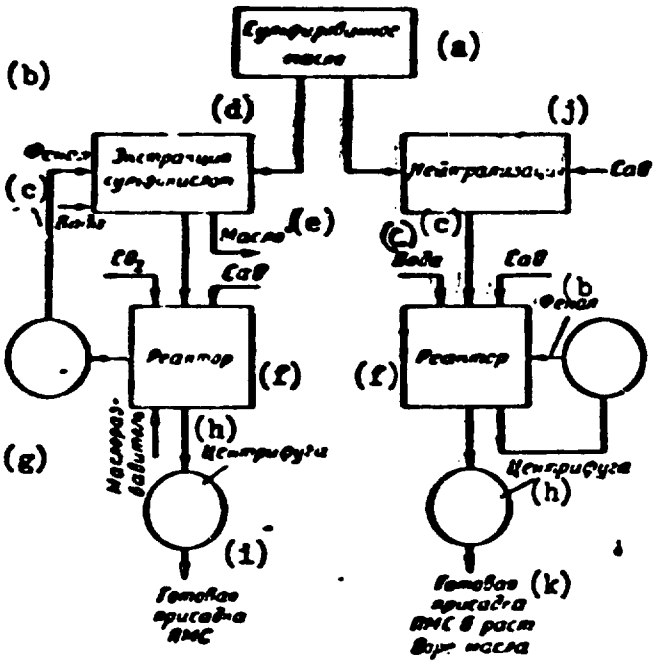
In the United States sulfonates of basic type predominate, but with still higher content of metal in molecule, reaching 10-multiple as against stoichiometrically necessary quantity according to first given formula. Structure of such sulfonates still is not exactly established [4].

Action of sulfonates with excess content of metal ("high-alkali") is based on ability to neutralize acid compounds and to disperse products of oxidation [1]. Number of method of obtaining sulfonates with increased content of alkaline metal are known. For instance, it is recommended to treat the usual sulfonate in the presence of excess amount of alkaline bivalent metal and water with CO_2 [5] or to treat the usual sulfonates or sulfo acids with excess amount of oxide of bivalent metal in the presence of "promoters", as which are used chiefly phenol compounds, nitro compounds, naphtols, sulfo acids and other substances [4].

Below are given two fundamental diagrams developed at VNII NP of obtaining of additive — multiash sulfonate (MPS) on the basis of petroleum raw material with the help of promoter of phenol.

First diagram (with separation of sulfo acids). Sulfonated oil, containing oil-soluble sulfo acids, is treated with aqueous phenol for separation of oil-soluble sulfo acids. With this sulfo acids are separated in lower layer — extract, containing (besides them) also phenol and water. Extract is diluted with oil (50% in extract). Then the whole mass is treated with calcium oxide under definite temperature conditions, water is driven off and CO_2 is omitted. With this larger part of phenol is separated; remaining part is driven off under vacuum. For isolation of mechanical

impurities the obtained additive is dissolved in organic solvent and centrifuged. After isolation of mechanical impurities the solvent is driven off. Consequently, by this method additive is obtained with use of promoter as selective solvent of oil-soluble sulfo acids.



Diagrams of obtaining additive PMS. KEY: (a) Sulfonated oil; (b) Phenol; (c) Water; (d) Extraction of sulfo acids; (e) Oil; (f) Reactor; (g) Oil-diluent; (h) Centrifuge; (i) Prepared additive PMS; (j) Neutralization; (k) Prepared additive PMS in solution of oil.

Second diagram (without separation of sulfo acids). Oil containing oil-soluble sulfo acids is treated directly with calcium oxide till absence of acid reaction. Then into oil phenol and water are introduced, and in the presence of excess CaO CO_2 is omitted. After termination of process product is centrifuged for isolation of mechanical impurities. With this 20% solution of additive in deeply purified oil is obtained.

Phenol used in the process of obtaining PMS is separated and is used repeatedly. Regulating relationship of phenol, calcium oxide and CO_2, additive PMS can be obtained with different content of metal as against stoichiometrical.

In the figure are given both diagrams of obtaining additive PMS.

Process of Sulfonation

Oil-soluble petroleum sulfo acids are formed in the process of reaction of sulfonating agent (strong sulfuric acid, oleum, gaseous SO_3 and others) with oil

fractions or with purified oils [6].

In our experiments as raw material for sulfonation served distillate oil of selective purification from sulfurous crudes AS-5 of production of Novokuibyshev factory, characterized by the following indices:

kinematic viscosity at 100°, cs.....6—8

pour point, °C..... 14

flash point in open crucible, °C.....210

In the experiments (content of free SO_3 18-20%) oleum was used, as the most accessible in our conditions, and in some experiments gaseous SO_3.

In the work special problem of study of expediency of use of one or another sulforating agent for obtaining oil-soluble sulfo acids was not posed. However, considering that oleum is the most accessible reagent, research was conducted in selection of optimum conditions of sulfonation. Similar study of sulfonation with oleum of distillate oil from sulfur-bearing crudes is set for the first time.

Dependence was clarified of ash content of solution of calcium sulfonate in oil (obtained from sulfonated oil as a result of neutralization of sulfo acids with calcium oxide on temperature of process of sulfonation and consumption of oleum. Experiments were conducted with oleum containing 20% free SO_3, with consumption of from 10 to 80% with respect to taken oil and temperatures from -10 to +70°.

end point 105°) in ratio 1 : 1. Oleum was fed in portions of 10% in each portion. After feed of each protion of oleum solution was allowed to settle 15 minutes and ar was separated. After last portion of oleum period of settling continued 18 hr, and full separation of tar occurred. For removal of SO_3 dissolved in acid solution, the latter was washed with water, taken in ratio to acid solution of 0.25 : 1. After period of settling of water in acid layer acid number was determined. Then solution of acid oil was neutralized by calcium oxide (3% on heavier acid solution) at a

temperature of 40° and reaction mass was mixed 2-3 hr during rise of temperature to 80°. Mechanical impurities were separated by centrifuging. Then alkylate was driven off, and in obtained product ash content was determined.

Table 1. Sulfonation of Oil AS-5 in Laboratory Conditions

Load: oil 200 g, alkylate 200 g

Consumption of oleum, % in taken oil	Temperature of sulfonation, °C	Amount of obtained tar, % in heavier oil**	Acid number of alkylate solution, mg KOH/g	Ash content of neutralized solution after distilling off solvent, %
10	-10	9.6	0.32	0.32
	30	10.9	0.89	0.59
	70	6.6	1.60	0.57
20	-10	15.0	0.52	0.48
	30	15.9	1.80	0.77
	70	10.7	3.67	0.99
40	-10	20.6	1.40	0.63
	30	24.3	6.90	1.74
	70	17.5	9.50	2.12
60	-10	24.6	4.50	1.15
	30	27.7	11.95	2.69
	70	19.6	14.85	2.94
80	30	31.7	18.2	2.80
12*	30	27.5	—	3.45

*Experiment was conducted with gaseous SO_3.

**Quantity of tar is given after subtracting supplied oleum.

In Table 1 are given results of experiments on sulfonation of distillate oil AS-5. With increase of temperature of sulfonation, ash content of prepared product is increased, especially from -10 to +30°. Further increase of temperature to +70° does not render so noticeable an influence on ash content, but causes impairment of color (Table 2).

Table 2. Color of Oil with Calcium Sulfonate Depending on Temperature of Sulfonation

Consumption of oleum, % in oil	Temperature of sulfonation, °C	Color of oil, brand NPA
60	+70	7.5—8.0
60	+30	5
60	-10	1.5—2

With increase of consumption of oleum (to 60%), ash content of product is increased. Increase of consumption of oleum to 80% does not cause further noticeable increase of ash content.

On the basis of these results for obtaining sulfonated oil on enlarged experimental installation consumption of oleum of 50% and temperature of sulfonation of 25-30° were accepted. Instead of washing by water for removal of dissolved SO_3 in sulfonated oil, blowing through of the latter with air was conducted.

Losses of oil in the form of acid tar during sulfonation on enlarged installation amounted to 20-25% of taken oil.

Extraction of Oil-Soluble Sulfo Acids From Acid Oil

Well-known method of separation of oil-soluble sulfo acids from acid solution is extraction of it by aqueous solutions of different alcohols [6]. In the work

stated extraction of sulfo acids was conducted by 65% solution of phenol; the latter simultaneously was promoter for obtaining of multiash sulfonates.

Acid gasoline solution, and also aqueous phenol, taken in quantity of 16% in solution of acid oil, were loaded in apparatus with mixing device. At a temperature of 65° the mass was mixed for 2 hr. After cooling to room temperature, contents was transferred to settling tank, where it settled, after which lower layer, containing phenol, water and sulfo acids was separated. From this layer subsequently was obtained additive PMS.

Below are listed results on yield of oil-soluble sulfo acids from acid oil.

Initial oil	AS-5 MKZ
Acid number of sulfonated oil in solution of gasoline (1:1), mg KOH/1g	10
Taken on yield of sulfo acids, wt %:	
solution of acid oil in gasoline	100*
phenol	10.7
water	5.6
Obtained parts by weight:	
solution of oil in gasoline	88.4
extract	25.8
Losses parts by weight	2.1
Analysis of extract:	
content of phenol, %	35
content of sulfur, %	1.7
acid number, mg KOH/1g	37.8
Analysis of solution of oil in gasoline:	
acid number, mg KOH/1g	0.24
content of phenol, %	1.2

*Content of gasoline in solution ~ 50%.

Sulfo acids, which are in acid oil, after extraction by phenol water are removed practically completely.

From solution of oil in gasoline, gasoline is driven off, and then separated oil is treated with 3% Zikeyevo earth.

Obtained oil had the following qualities.

Kinematic viscosity (in cs) at °C:

100	5.5
50	22.4
Index of viscosity	101.7
Acid number, mg KOH/1g	Absence
Sulfur, %	0.06
Color, brand NPA	1.5
Chemical composition, %:	
naphthenes and paraffins	89.8
light aromatic hydrocarbons	9.2
guns	1.0

Consequently, oil obtained during extraction contains up to 90% paraffin-naphthenic hydrocarbons, i.e., is deeply purified oil.

Obtaining FMS from Extract

Extract which is a mixture of phenol, water and sulfo acids, was loaded in a reactor supplied with mechanical mixer, reflux condenser and thermometer. There was loaded calcium oxide (13% in extract) and diluent — distillate oil AS-5 with viscosity at 100° of 6-8 cs in amount of 50% in extract. With constant mixing the temperature of reaction mass increased to 100-101° and at this temperature it was mixed 2 hr; then temperature was increased to 120-125° and from reaction mass water was removed. After removal of water for 1 hour with gradual increase of temperature to 155-165°, CO_2 was omitted.

Obtained mass was transferred to apparatus where phenol was driven off at residual pressure of 20-30 mm Hg.

After separation of mechanical impurities by centrifuging and distilling off of solvent, the content of calcium in such an additive was 3.5-4 times more than stoichiometrical.

Table 3. Characteristics of Additive PMS, Obtained According to First Diagram

Number of sample	Content of oil, %	Ash content sulfate, %	Ash content sulfate in conversion to 50% solution of additive in oil
2*	50	22.1	22.1
3*	57	19.4	22.1
6a*	60	19	23.!
16**	66	17.0	25.0
18***	46	23	21.2

*Samples were prepared in laboratory.
**Additive was prepared on enlarged installation.
***Additive was obtained with the use of gaseous SO_3.

In Table 3 is shown the characteristics of additive PMS, obtained according to first diagram, and also characteristics of additive obtained with the use of gaseous SO_3 instead of oleum.

Obtaining PMS According to Second Diagram

According to second diagram, as was already noted above, PMS is obtained in solution of deeply purified oil (20% solution).

Obtaining of Additive From Solution of Neutral Sulfonate

Solution of usual (neutral) sulfonate in deeply purified oil, obtained analogously to above-described laboratory method, was treated with additional amount of calcium oxide in the presence of phenol, water and CO_2 analogously to the first diagram. As a result ~ 20% solution of additive in oil was obtained. With this the amount of introduced calcium in sulfonate was 3.5-4 times more than stoichiometrical anount.

In Table 4 is shown the consumption of reagents for obtaining PMS according to second diagram, and also characteristics of obtained products.

Table 4. Characteristics of Additive PMS, Obtained According to Second Diagram

Number of batch	Taken on synthesis							Ash content sulfate, %			Kinematic viscosity* at 100° cs
	Solution of neutral sulfonate, g	Phenol		Water		Calcium oxide		Solution of PMS in oil	Initial neutral sulfonate	Ratio of ash content (obtained to initial)	
		g	%		%	g	%				
1	300	65	21.6	35	11.6	13	4.3	7.1	2.0	3.5	—
300	300	65	21.6	35	11.6	13	4.3	7.9	2.3	3.2	7.0
34	600	130	21.6	70	11.6	26	4.3	10.8	2.5	4.3	8.5

*Viscosity of initial solution of neutral sulfonate in oil 13-14 cs at 100°.

It is necessary to pay attention to lowering of viscosity of obtained solutions of PMS in oil as against viscosity of initial usual sulfonate. This can indicate an occurring change of chemical structure of obtained compound.

Positive side of first diagram is the use of promoters as selective solvent and the possibility of obtaining 100% additive or its solution in any oil used in motors.

Second diagram, according to which PMS is obtained in solution of deeply purified oil, is technologically simpler. By it is excluded the process of separation of sulfo acids from oil. However with this additive is dissolved in large amount (to 80%) of deeply purified oil. If its solution has sulfate ash content of 7.0%, then for obtaining of motor oil with ash content of 2% it is necessary to add up to 23% deeply purified oil, which can noticeably influence its final operational properties. Influence of deeply purified oil on operational properties of motor oil with additive is being studied at present. Obtained results will allow us to make more definite conclusions about expediency of use of this method in a number of cases.

Obtaining PMS From Neutral Sulfonate of Production of Yaroslavl' Factory Named after Mendeleyev

In laboratory conditions and on experimental installation of factory named after Mendeleyev there was synthesized additive of multiash sulfonate (PMS_{ya}) from 50% solution of oil of neutral sulfonate, obtained from sulfo acids formed during purification of white oils from nonsulfur-bearing raw material at factory named after Mendeleyev in Yaroslavl'*. Ash content of 50% solution of calcium sulfonate was equal to 4.9-6%. After obtaining from it additive PMS_{ya}, ash content (sulfate) reached 23-27%, i.e., ratio of ash contents (obtained to initial) amounted to 4-5.5.

Investigation of Operational Properties of PMS

In Table 5 are shown operational properties, checked on apparatus DK-2, of oil AS-9.5 with additives PMS and neutral calcium sulfonate and of base oil AS-9.5 MKZ without additive.

*All work on obtaining of neutral sulfonate was carried out by workers of factory named after Mendeleyev according to technology developed by them.

Table 5. Results of Appraisal of Oil AS-9.5 with Additives According to Laboratory Method of NAMI* (Instrument DK-2)

Sample	Content of additive in oil, %	Ash Content, %	Deposit after oxidation, %	Kinematic viscosity at 100°, cs	
				initial	after oxidation
Oil AS-9.5 NKZ without additives.....	—	—	9—10	9.5	—
Oil AS-9.5 with neutral sulfonate from oil AS-5.....	17	1.0	10.5	—	37.3
	10	0.6	9.6	—	30.7
Oil AS-9.5 with PMS from neutral sulfonate of oil AS-5.....	12	2.0	Absence	11.2	14.2
	6	1.0	Absence	10.5	15.7
Oil AS-9.5 with neutral sulfonate from white oils.....	42	2.4	7.8	15.1	39.3
	21	1.2	10.7	—	36.2
Oil AS-9.5 NKZ with PMS_{ya}.....	8	2.0	Traces	11.0	18.7
	4	1.0	3.0	10.9	19.4

*NAMI = State All-Union "Order of the Red Banner of Labor" Scientific Research Institute of Automobiles and Automobile Engines.

Stability of base oil AS-9.5 is sharply improved with addition to it of PMS, whereas neutral sulfonate does not improve this property.

Short-term tests on engines GAZ-51 and D-35 showed high effectiveness of additives PMS and PMS_{ya}, in spite of diversity of initial raw material.

Conclusion

Synthesis and fundamental technology have been developed of obtaining of highly effective component or additive, representing multiash sulfonate (PMS) with content of metal 3.5-5 multiple as against stoichiometric and with use of phenol as selective solvent and promoter of reaction.

As raw material were used distillate oils from sulfurous crudes with different level of viscosity and neutral products of sulfonation, separated in obtaining of white oils from nonsulfur-bearing crudes at factory named after Mendeleyev.

According to method of MANT (determination of deposit-formation and viscosity during oxidation) the advantage of obtained PMS additives over usual neutral sulfonate additives obtained earlier is shown.

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IMPROVEMENT OF TECHNOLOGY OF MANUFACTURE OF ADDITIVE TsIATIM-339*

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Essential technological deficiency of process of industrial production of alkylphenol additive tsiatim-339 is washing of catalyst — benzene sulfo acid, as a result of which significant amounts of phenol and benzene sulfo acid get into liquid waste. Laboratory of Permskiy Petroleum Oil Factory conducted work on investigation of possibility of liquidation of entry of phenol into industrial liquid waste, results of which are the subject of this report.

From formerly conducted works of VNII NP** it is known that separation of benzene sulfo acid from alkylate is possible in the form of its calcium or ammonium salt by treatment of alkylate with lime milk or ammonia. However for a number of reasons this method did not find industrial application.

For neutralization of benzene sulfo acid we tested as neutralizing component a solution of calcinated soda. Advantage of calcinated soda over alkali reagent is the fact that it excludes formation of sodium phenolates. Good solubility in water and bad in alkylphenol allows us to separate benzene sulfo acid in the form of aqueous solution of salt by means of short period of settling.

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*Additive designated by number and name of institute, the Central Scientific Research Institute of Aviation Fuels and Oils.

**All-Union Scientific Research Institute for Oil and Gas Refining and the Production of Synthetic Liquid Fuel.

Work was conducted according to the following diagram. After termination of process of alkylation, conducted according to the usual technology, contents of reactor were cooled to temperature of 95-97° and into zone of reaction a solution of calcinated soda was introduced. Temperature with this dropped to 85-90° and violent separation of carbon dioxide was observed. It was established that for complete neutralization of benzene sulfo acid 5% excess of calcinated soda is sufficient as against estimated amount. Soda was used in the form of 20-25% aqueous solution, ensuring formation of concentrated solution of sodium salt of benzene sulfo acid, which settles easily and is separated from alkylphenol at a temperature of 80-85°.

Alkylphenol after separation of lower layer contained up to 0.8% aqueous solution, which corresponds to content of dry salt up to 0.3%.

After evaporation of water, sodium salt of benzene sulfo acid was obtained, quantitative yield of which agrees well with calculating data (Table 1).

Alkylphenol obtained in such a way was dried in a vacuum according to formerly accepted technology. Laboratory and industrial samples of dried alkylphenol were obtained, whose quality is not inferior to alkylphenol prepared by the usual means (Table 2).

Main qualitative index, distinguishing alkylphenol of development types and the usual, is the presence of mechanical impurities, whose content reached 0.3%.

Mechanical impurities were sodium salt of benzene sulfo acid. Therefore it was important to clarify its influence on further technological processes. Several laboratory, and later also industrial samples were prepared of additive tsiatim-339 on the basis of alkylphenol, obtained without washing.

As can be seen from the data of Table 3, development types of additive do not differ from additive obtained by the usual means.

Table 1. Material Balance of Separation of Sodium Salt of Benzene Sulfo Acid

Product	Amount, g	% to phenol	Theoretical yield, g	% to theoretical yield
Taken:				
Phenol	150	100	—	—
Benzene sulfo acid	25	16.7	—	—
Polymer distillate	375	250	—	—
Altogether...	550	—	—	—
Obtained:				
Alkylphenol	430	—	480	89.6
Sodium salt of benzene sulfo acid	25.5	—	26.82	95.1
Losses	94.5	—	—	—
Altogether...	550	—	—	—

NOTE: Theoretical yield of alkylphenol was calculated on phenol.

As a result of conducted work the following diagram of obtaining alkylphenol without washing was suggested (Fig. 1). After achievement of required content of free phenol in the process of alkylation, alkylphenol is pumped into neutralizer - settling tank, equipped with mixing mechanism, in which first an aqueous solution of calcinated soda in amount required for neutralization is prepared.

Neutralization of benzene sulfo acid occurs with entry of alkylphenol into neutralizer. After pumping over of the entire amount of alkylphenol, the contents are mixed 0.5 hr and placed for period of settling for separation of aqueous solution of sodium salt of benzene sulfo acid from alkylphenol.

Table 2. Given Qualities of Obtained Alkylphenols

Number of sample	Free phenol, wt, %	Flash point, °C	Content of water, wt, %	Water-soluble acids	Specific gravity	Refractive index	Mechanical impurities, wt, %	Kinematic viscosity at 100°C, cs
Usual industrial samples								
83	0.80	132	0.06	Res.	0.925	1.5063	--	5.4
89	0.76	120	0.06	Res.	0.918	1.5055	--	5.3
94	0.62	110	0.03	Res.	0.918	1.5049	--	5.9
Experimental laboratory samples								
5	0.38	145	Res.	Res.	0.930	1.5130	--	7.2
6	0.65	136	0.02	Res.	0.925	1.5130	--	6.9
7	0.19	119	Res.	Res.	0.920	1.5110	--	6.5
Experimental industrial samples								
119	0.19	108	Res.	Res.	0.915	1.5054	0.28	6.5
125	0.06	118	0.06	Res.	0.920	1.5057	0.30	6.2

After 5-6 hrs aqueous solution is poured into crystallizer, and alkylphenol is pumped into siccative for draining and distilling off of nonreacting polymer distillate.

Sodium salt of benzene sulfo acid, evaporated in crystallizer, is unloaded and can be used in chemical industry.

Aqueous condensates from draining of alkylphenol and evaporation of water from sodium salt of benzene sulfo acid head to collector of condensate and are used for subsequent preparations of aqueous solutions of calcinated soda. Consequently, according to the suggested diagram, phenol waters formed in the process of production will circulate in the system, not getting into industrial liquid waste. The suggested diagram up to now has not been introduced into production.

Table 3. Characteristics of Obtained Samples of Additive Tsiatim-339

Number of sample	Content, %					Reaction	Solubility in oil	Kinematic viscosity at 100°, cs	Content of barium in additive, wt %	Degree of corrosion according to Pinkevich, g/m²
	Mechanical impurities	Ashes	Water	Chlorine	Sulfur					
Usual industrial samples										
83	0.13	9.0	0.03	Res.	4.2	Alk.	Complete	15.2	5.1	9.3
89	0.12	9.6	0.03	0.13	4.0	Alk.	Complete	15.8	5.3	8.6
94	0.14	9.2	0.02	0.20	4.1	Alk.	Complete	15.0	4.9	10.2
Experimental laboratory samples										
5	0.16	12.1	Res.	0.03	4.0	Alk.	Complete	21.6	6.99	9.8
6	0.20	11.7	0.12	0.12	4.1	Alk.	Complete	17.7	6.60	7.5
7	0.21	11.6	0.12	0.12	4.1	Alk.	Complete	17.6	6.60	8.1
Experimental industrial samples										
118	0.17	8.9	0.03	0.20	4.0	Alk.	Complete	15.1	—	9.4
125	0.13	8.6	Res.	0.20	4.1	Alk.	Complete	15.4	4.9	8.7

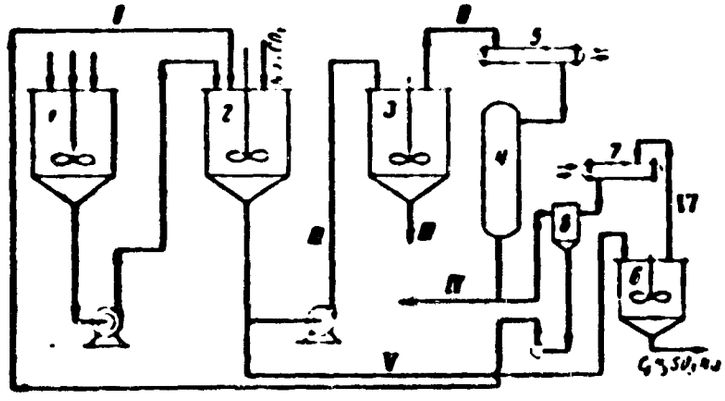


Fig. 1. Diagram of obtaining alkylphenol without washing.
1—alkylater; 2—neutralizer-settling tank; 3—siccative; 4—water separator; 5, 7—Condenser; 6—Crystallizer; 8—Collector of condensate.
Lines: I—phenol waters; II—water + distillate of polymer; III—alkylphenol; IV—waste of polymer; V—aqueous solution of $C_6H_5SO_3Na$; VI—Water + phenol.

Another work, of indubitable interest, is the use (widespread abroad) of method "abrupt temperature change" in process of alkylation of phenol by polymer distillate. Components (phenol, polymer distillate and benzene sulfo acid) loaded in alkylater for 3-4 hrs were heated to temperature of 110-115° and pumped through air refrigerator of tubular type, where mixture is cooled somewhat (Fig. 2). Reaction with this is noticeably accelerated (which one may see by increase of temperature in alkylater), and time of depletion of alkylphenol is significantly reduced. Content of free phenol with such a diagram of alkylation does not exceed 0.3%; this testifies to involvement in reaction of around 99.0% of phenol with reduction of general cycle of alkylation by 30% and economy of 10% of olefins.

Simultaneously with improvement of process of alkylation of phenol, factory workers performed great work on reduction of the cycle of sulfurization of alkylphenol. Dependence of anticorrosive properties of additive tsiatim-339 on the amount of loaded sulfur chloride was determined. As research showed, amount of it should be 22-24% on alkylphenol, as against 27-29% established by norms*.

Quality of sulphurized alkylphenol with this corresponds to all the presented requirements, and additive prepared on it possesses the best anticorrosive properties. Increase of number of turns of mixer in sulphurizer and atomization of sulfur chloride by means of use of atomizer leads to significant reduction of cycle with simultaneous stabilization of quality of sulphurized alkylphenol.

As a result of conducted works, the general duration of manufacture of additive tsiatim-339 is considerably abbreviated. However, noticeable growth of productivity still is not achieved in virtue of lag at last stage of production — barium-coating. It is possible to trust that after liquidation of this narrow place it will be possible to increase productivity of workshops by ~ 20%.

*Apparently, the author is considering the necessary stoichiometric amount. (Editor's note).

EXPERIENCE OF MASTERING OF INDUSTRIAL INSTALLATION FOR PRODUCTION OF ADDITIVE AZNII-7*

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During the last few years by administration of "Azerbaijan Petroleum Chemical Plant" measures have been conducted, allowing us significantly to improve the operational properties of motor and tractor and diesel oils. They include increase of production of oils of selective purification, and also addition to oils of effective multifunctional additives. On the basis of positive results of stand and operational tests, All-Union State Standards for motor and tractor oils with additives aznii-5 and aznii-8 were affirmed and in the near future All-Union State Standard for diesel oils with additive aznii-7 should be affirmed.

Data of tests confirming the effectiveness of action of additive aznii-7 on diesel oil from Baku raw material, allowed us to carry out its synthesis in industrial conditions. For this purpose IPKhP (Institute of Petrochemical Processes) of Academy of Sciences of AzSSR developed technology of synthesis of additive.

Industrial installation for synthesis of additive aznii-7, design of which was carried out by institute Giproazneft (State Institute of Design of Azerbaijan Petroleum Industry), was constructed by administration of "Azerbaijan Petroleum

*Additive designated by number and name of institute, the Azerbaijan Scientific Research Institute.

Chemical Plant" in 1960.

At present obtaining of additive aznii-7 in industrial conditions has been mastered.

Synthesis of additive aznii-7 occurs in six stages.

1. Sulfurization of kerosene, obtained during light thermal cracking of black oil by sulfur dichloride. Sulfurization is conducted at a temperature of 10° to 25°.

2. Alkylation of phenol by sulphurized kerosene in the presence of catalyst — aluminum chloride at a temperature of 90°.

3. Neutralization of products of alkylation by hydrate of barium oxide at a temperature of 90° and separation from deposit with the help of centrifuge.

4. Vacuum distillation of products not entering into reaction (saturated kerosene).

5. Saponification of sulfide alkylphenol compounds in solution of machine oil by hydrate of barium oxide at a temperature of 95-100°.

6. Drying and separation of prepared additive from deposit and mechanical impurities with the help of centrifuge.

Equipment of industrial installation is simple in manufacture. Basic process occurs in mixers of periodic action. For vacuum distillation of products not entering into reaction, vacuum evaporator is used, where light end products are separated by means of circulation through special atomizers, which allows us significantly to reduce time of distillation and rectification. Experience of such distillation gave positive result.

For separation of deposit and mechanical impurities for the first time NOGSh-325 centrifuges were used — continuously acting of settling type with screw unloading of deposit.

During industrial mastering of synthesis of additive on this installation there appeared a number of difficulties, which were removed in the course of mastering. Chief ones are the following.

1. For dispensing sulfur chlorides during sulfurization of cracking-kerosene fuel gauges were established, which during first supply went out of order. It was necessary to establish the usual measuring hoppers with oil-measuring glass, which, however, require considerable attention, since deposits of sulfur clog oil-measuring cocks.

Workers of KIP (Department of Engineering Design) of INKhP of Academy of Sciences of Azerbaijan Soviet Socialist Republic developed volume timer, ensuring continuous adjustment of feed of required amount of sulfur chlorides. This instrument requires finishing as far as selection of materials stable to the action of sulfur.

2. Preliminary cooling of cracking-kerosene in refrigerator to 0°C was provided for by design.

Reaction of sulfurization had to occur at a temperature of 25°, owing to heat of reaction of sulfurization and without removal of unnecessary heat.

Such a solution of [illegible]tion cannot be considered correct, since with accomplishment of sulfurization the temperature of products of reaction was increased to 55° and above, which caused side reactions.

In the course of mastering of production of additive it was suggested to conduct continuous circulation of products of reaction through refrigerator. This allowed us to conduct reaction strictly at a temperature of 20-25°. However on walls of refrigerator pipes a large amount of tar was deposited, and after every four cycles the refrigerator was completely clogged by tar. To avoid this it was necessary to establish an additional row of refrigerators and to organize periodic disconnecting and turning off of them for blowing through of steam.

3. It is specified to feed aluminum chloride manually into mixers for alkylation of phenol, which causes inevitable liberation of hydrogen chloride into atmosphere. At present the possibility of feed of aluminum chloride in the form of complex compounds with the help of pump is completed.

4. During mastering of process also the difficulty with utilization of deposits after sulfurization of cracking-kerosene and products of alkylation was met, since the obtained deposits are badly dissolved in oil products and have strongly acid reaction. Question of realization of these deposits till now has not been solved and at present they simply are burned. It is necessary that research organizations seriously study this question.

5. Oil screw pumps of type VVN-6, did not ensure normal operation of installation, since with the least entry into pump of even small amount of deposit the pump collapsed. It was necessary to quickly replace these pumps by centrifugal brands 4HK 5 x 1.

6. When installation finished normal operation we encountered the phenomenon of incrustation of deposits in receiving and ejecting pipelines. It was necessary quickly to alter pipelines, to lift them up and to house them in steam jacket. Into jackets steam is periodically allowed, after which these incrustations are melted. This measure gave fully positive results.

7. During carrying out of cycle of saponification it was established that during heating of sulfide alkylphenol to temperature of 135°, large amount of light and products is separated, which leads to disturbance of reaction of saponification and increase of viscosity of additive, and also to impairment of its solubility in oil. Optimum temperature rate of reaction of saponification was found, at which such phenomena no longer were observed.

8. Freeing of additive from mechanical impurities with the help of centrifuges also demanded finding of definite temperature rate, and also repeated jointing.

9. It is necessary especially to note difficulties caused by work of checking-measuring instruments, mainly by level gauges. Installation of AUS (automatic control system) in view of specific conditions of synthesis does not ensure control of conditions of installation and subsequently it is necessary to develop new types of regulating instruments for chemical processes.

Below is listed approximate material balance of synthesis of additive AZNII-7.

Taken in process, t/twenty-four hour period:

kerosene of thermal cracking	87.0
oil industrial 45	19.1
sulfur chlorides	13.05
phenol	14.2
hydrate of barium oxide	13.75
aluminum chloride	3.3

Obtained, t/twenty-four hour period:

additive AZNII-7	71.0
saturated kerosene	34.6
20% hydrochloric acid	41.65
Losses and waste	29.6

In Table 1 quality of obtained additive is given; in Table 2 — quality of diesel oils with additive AZNII-7.

For the purpose of further improvement of quality of additive AZNII-7, additional process is specified, consisting of sulfuric acid treatment of sulfide alkylphenol compounds (before saponification). Qualities of additive basically remain without change, but addition of additive obtained by modified technology increases its solubility in oil.

Table 1. Quality of Additive AZNII-7

Index	Norm	Methods of tests (All-Union State Standard)
Specific gravity d_4^{20}	1.0349	3900—47
Kinematic viscosity at 100°C, cs	8.76	33—53
Ash content, %	11.0	1461—52
Content of sulfur, %	3—4	1431—49
Flash point, °C	150	4333—48
Degree of corrosion according to Pinkevich of oil of industrial 50 in mixture with 3% additive, g/m^2	0—5	5162—49
Detergent properties of oil of industrial 50 in mixture with 3% additive according to method of PZV, in points	2—2.5	5726—53

Table 2. Quality of Diesel Oils with Additive AZNII-7

Index	Norms	
	Diesel oil of selective purification DP-11 with 5% additive aznii-7	Diesel oil of sulfuric acid purification DP-3 with 3% additive aznii-7
Density ρ_4^{20}	Not more than 0.910	—
Kinematic viscosity, cs:		
at 100°	11.5—12.5	Not less than 8.3
at 50°	—	Not more than 55
Ratio of kinematic viscosity at 50° to kinematic viscosity at 100°	Not more than 7.0	—
Coking capacity up to addition of additive, %	Not more than 0.25	Not more than 0.20
Acid number of oil, mg KOH:		
without additive	Not more than 0.075	Not more than 0.15
with additive	Not more than 0.050	Not more than 0.10
Ash content of oil, %:		
without additive	Not more than 0.007	Not more than 0.005
with additive	Not less than 0.5	Not less than 0.25
Content of water-soluble acids and alkalis in oil:		
without additive	Absence	
with additive	Weakly alkaline reaction	
Content of mechanical impurities in oil, %:		
without additive	Absence	
with additive	Not more than 0.10%	Not more than 0.05%
Content of water	Traces	
Flash point, determined in open crucible, °C	Not below 210°	Not below 196°
Pour point, °C, not above	-20°	-20°
Content of furfurole	Absence	—
Degree of corrosion according to Pinkevich, g/m², not more than	10	10
Detergent properties according to PZV, points	Not more than 2.5	—

NOTE: Addition of depressor up to 0.3% is permitted.

Designing of assembly of sulfuric acid treatment at present already has been completed and in the near future synthesis of additive aznii-7 will be carried out according to new technology.

Since 1961 automobile oils have to be produced with additive aznii-8, consisting of mixture of additive aznii-7 and detergent component of additive aznii-5, taken in

equal relationships. This will allow us significantly to improve their operational properties.

C H A P T E R IV

MECHANISM OF ACTION OF ADDITIVES

INVESTIGATION OF ACTION OF ADDITIVES, CONTAINING DIFFERENT FUNCTIONAL GROUPS, ON BUTYRIC FRACTIONS AND OIL

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Investigation of Effectiveness of Action of Additives of the Alkylphenol Type with Different Structure of Molecule

To study effectiveness of action of additives of the alkylphenol type of different structure on oils differing with respect to hydrocarbon composition, synthesis was carried out of additives of the type aznii-7** and aznii-6 on a base of unsaturated hydrocarbons (chiefly 1-alkenes), contained in narrow fractions of distillate of thermal cracking of paraffin. For the synthesis were used fractions evaporating within the limits of 100-110°, 190-200°, 240-260°, and 280-300°, in their physico-chemical properties corresponding to hydrocarbons with a content of 7, 11, 13, and 16 carbon atoms in a molecule. The influence was investigated of obtained additives of different structure on corrosivity and oxidizability of motor and reactor oils from a single Buzovny oil.

Results of investigation are given in Table 1.

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**Ed Note: aznii = AzNII = Azerbaydzhan Scientific Research Institute. The additives are named for the institute.

From these data it is clear that distillates of oil AK-10 and diesel oil as compared to corresponding purified oils are more corrosionally aggressive and are least stable to the influence of oxygen. With the addition of additives corrosive action of distillates on lead plates is significantly lowered and corrosion of plates by purified oils is almost removed. During oxidation of oils with shown additives according to method of AzNII, i.e., in more rigid conditions than in Pinkovich apparatus, stability of oils in significant degree is lowered. Investigation of action of additives of the aznii-7 and aznii-6 type, distinguished by location of sulfur in molecule, on oils of different hydrocarbon composition showed that additives containing sulfur in a side alkyl chain (additive aznii-7), are more effective than additives containing sulfur between aromatic nuclei (additive aznii-6).

These data were confirmed by results of research of corresponding additives using tagged atoms. It was shown that additive aznii-7 promotes formation of a more durable protective film on surface of metal and lowers wear to a larger degree than additive of the aznii-6 and tsiatim-339* type.

Effectiveness of action in oils of additives of one and the same type is lowered with increase of number of carbon atoms in side chain of molecule of additive.

Proceeding from this, for synthesis of investigated types of additives it is necessary to use fraction of unsaturated hydrocarbons, by molecular weight corresponding to hydrocarbons with 11-12 carbon atoms. It is necessary to consider the worst solubility in oils of additives synthesized on a base of lower-molecular fractions.

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*Ed. Note: tsiatim = TsIATIM = Central Scientific Research Institute of Aviation Fuels and Lubricants.

Table 1. Results of Laboratory Tests of Oils with Additives of the aznii-7 and aznii-6 Type

Additive	AK-10			Diesel oil		
	Distillate	Acid-contact purification	Selective purification	Distillate	Acid-contact purification	Selective purification
	Corrosivity according to Pinkevich, g/m^2					
Without additive.....	187	21.8	88.5	122	70.7	62.0
Aznii-7 (fraction 100-110°)..	23.4	0.2	0	16.0	0	0.2
Aznii-6 (fraction 100-110°)..	41.4	8.2	12.9	44.7	2.8	1.3
Aznii-7 (fraction 240-260°)..	28.3	2.8	1.5	18.7	2.9	0.2
Aznii-6 (fraction 240-260°)..	43.2	7.0	18.9	31.6	10.5	7.0
Aznii-7 (fraction 280-300°)..	31.1	4.7	2.8	25.3	5.6	0
	Stability according to AzNII, minutes					
Without additive.....	46	100	151	39	109	174
Aznii-7 (fraction 100-110°)..	40	63	84	32	68	101
Aznii-6 (fraction 100-110°)..	25	25	27	25	24	34
Aznii-7 (fraction 190-200°)..	30	54	61	27	55	74
Aznii-6 (fraction 190-200°)..	17	17	18	16	13	27
Aznii-7 (fraction 240-260°)..	28	38	62	28	54	80
Aznii-6 (fraction 240-260°)..	18	16	19	17	15	17
Aznii-7 (fraction 280-300°)..	25	30	46	23	26	44

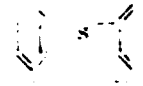
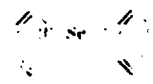
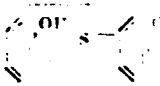
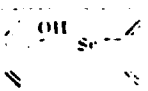
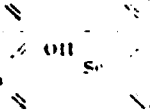
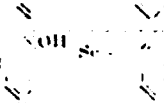
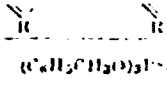
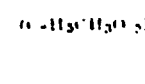
Synthesis and Investigation of Certain Sulfur- And Seleniferous Compounds As Additives To Oils

Considering that selenium is in one group of the periodic system of elements with sulfur and is more active as compared to the element sulfur, we made an attempt to synthesize certain seleniferous compounds and to compare effectiveness of their action with similar compounds containing sulfur.

Derivatives were obtained of benzene and phenol, having between aromatic nuclei sulfur or selenium, diphenyl sulfide, selenium diphenyl, dioxydiphenyl sulfide, selenium dioxydiphenyl, selenium dicetyldioxydiphenyl, selenium dialkyldioxydiphenyl, and also compound, in composition of which (besides sulfur or selenium) entered also phosphorous: tricresylseleniumphosphite, tricresylthiophosphite.

Physico-chemical properties of synthesized compounds are close to theoretically calculated ones.

Table 2. Results of Laboratory Investigation of Sulfur- and Selenium-Containing Compounds

Product	Formula	Corrosivity of lead plates (according to Pinkevich) g/m² on diesel oil	on machine oil SU	Stability according to AzNII, minutes lubricating oil (AK-10) induction period	time of absorption of 20 ml of oxygen	Diesel oil induction period	time of absorption of 20 ml of oxygen	Thermal stability (according to Folders) in mixture with oil MK-22, minutes
Initial oil		56	47	7	86	18	186	37
Difenylsulfide		61	57	11	104	19	196	31
Difenylselenium		9	10.4	17	110	27	219	40
Dioxydiphenyl-sulfide		−1	−3	10	96	18	181	37
Dioxydiphenyl-selenium		0	6	13	111	11	220	40
Dicetyldioxydi-phenylselenium		0	0	-		18	188	-
Dialkyldioxydi-phenylselenium		0	0	11	77	20	170	37
Tricresylseleno-phosphite		+26	—			23	220	+
Tricresylthio-phosphite		+1	—	—	—	—		

978

These compounds were investigated in laboratory conditions as anticorrosive and antioxidant additives. Almost all the shown compounds added to oils a 1% quantity, somewhat increased their stability (Table 2).

Compounds containing selenium act with a greater effectiveness than corresponding compounds containing sulfur. Diphenyl is more effective with respect to lowering corrosivity of oils and increase of stability than diphenyl sulfide.

Still more effective turned out to be derivatives of phenyl containing selenium. They absolutely removed corrosive aggressiveness of oils. Tricresylthiphosphite has better anticorrosive properties than tricresylseleniumphosphite.

Results of test of certain of the shown compounds on a four-ball apparatus showed that these compounds somewhat improve lubricating ability of airplane oil MK-22, while the most effective turned out to be alkyldioxydiphenylselenium.

Investigation of Different Alkylaromatic Hydrocarbons as Depressors

For clarification of influence of structure of additives on their ability to lower pour point of oils individual alkylaromatic hydrocarbons are synthesized with different length and quantity of side chains with different number of rings in molecule and their depressor properties are studied. Increase of length and number of side chains leads usually to improvement of depressor properties of alkylaromatic hydrocarbons (Table 3). During comparison of mono- and dialkyl-derived benzene, napthalene, anthracene, and tetralin it is easy to make sure of this.

The aromatic nucleus, containing two rings, ensures the obtaining of a highly effective depressor. Decrease or increase of number of rings lowers effectiveness of action of depressor. The most effective depressor is obtained from dicyclic aromatic hydrocarbons with long side chains. Synthesis of depressor of such type, obtained by condensation of napthalene with chlorinated paraffin, is carried out on an industrial scale (depressor AzNII).

Table 3. Results of Research of Depressor Properties of Synthesized Compounds

Product	Formula	Quantity of addition, %	Depression of pour point of oil with additive °C
Monoheptylbenzene.....		0.5	0
Diheptylbenzene.....		0.5	1
Triheptylbenzene.....		0.5	1
Monocetylbenzene.....		0.5	1
Dicetylbenzene.....		0.5	1
Tricetylbenzene.....		0.5	1
Mopoalkylbenzene, obtained from paraffin.....		0.5	1
Dialkylbenzene.....		0.5	15
Monoheptylnaphthaline....		0.5	0
Diheptylnaphthaline.....		0.5	1
Monocetylnaphthaline.....		0.5	1
Dicetylnaphthaline.....		0.5	3
Dialkylnaphthaline, obtained from paraffin...		0.1	16
Monocetylanthracene.....		0.5	2
Dicetylanthracene.....		0.5	3
Mopoheptyltetralin.....		0.5	1
Diheptyltetraline.....		0.5	1
Triheptyltetraline.....		0.5	6
Monocetyltetraline.....		0.5	1
Dicetyltetraline.....		0.5	8
Dialkylphenanthrene obtained from paraffin...		0.2	11
Depressor AzNII, factory.		0.1	13
Dialkylchloronaphthaline.		0.5	11
Dialkylnitronaphthaline..		0.1	11
Dialkylnitrochloronaphthaline		0.5	12
Dialkyl-α-naphtol.....		0.2	11

Investigation of depressors, synthesized by condensation of chlorinated narrow fractions of paraffin with napthalene, showed that their effectiveness also is increased with increase of molecular weight of fractions of paraffin.

With the introduction into napthalene nucleus of depressor of functional groups — chlorine and simultaneously chlorine and nitro group — the effectiveness of depressor is lowered 5 times. Depressor properties of dialkyl-derived napthalene are lowered also with the presence of a hydroxyl group in the napthalene nucleus. Presence of nitro group in napthalene nucleus renders no influence on depressor properties of dialkyl-produced napthalene.

Study of Response of Oils and Groups of Hydrocarbons to Depressors

Action of depressors was studied on narrow butyric fractions, obtained from Balakhany butyric and heavy oils, and also on different commercial oils and separate groups of hydrocarbons. As depressors were used AzNII depressor and additive aznii-tsiatim-1, which were added to butyric fractions of Balakhany oils before and after removal of aromatic hydrocarbons from them.

Investigated fractions of two oils, sharply distinguished in hydrocarbon composition, are significantly distinguished also with respect to response to depressors (Table 4). Upon addition of 0.3% depressor to fractions of Balakhany butyric oil, the pour point is lowered by 15–25°; upon addition of the same quantity of depressor to fractions of Balakhany heavy oil, the pour point is not changed.

Table 4. Investigation of Response of Butyric Fractions Separated from Baku Oils to Depressors

Boiling range of fraction °C	Lowering of pour point of fraction of Balakhany butyric oil upon addition of 0.3% depressor, °C				Lowering of pour point of fraction of Balakhany heavy oil upon addition of 0.3% depressor, °C			
	Initial		Dearomaticized		Initial		Dearomaticized	
	Additive aznii-tsiatim 1	Depressor AzNII	Additive aznii-tsiatim 1	Depressor AzNII	Additive aznii-tsiatim 1	Depressor AzNII	Additive aznii-tsiatim 1	Depressor AzNII
300-320	25	23	—	—	4	4	3	1
320-340	23	25	—	—	3	5	6	4
340-360	21	22	17	16	0	1	13	7
360-380	16	17	24	23	1	1	15	12
380-400	18	18	23	24	0	2	18	17
400-420	12	10	20	18	0	1	12	10
420-440	9	7	15	16	1	1	7	8
440-460	9	3	6	4	0	1	8	6
460-480	10	2	14	12	0	0	8	7

Dearomaticized fraction of Balakhany butyric and heavy oils have good response to depressors. From this it follows that aromatic hydrocarbons decrease reception of oils to action of depressors.

In Table 5 are data showing response to depressor of oils of different origin and oils of separate structural-group fractions obtained from these. Upon addition of depressor to distillate of oil AK-10 from Balakhany butyric oil, its pour point is lowered by 6°, from oil of the deposit Neftyanyye Kamni by 14°, and depression of distillate of Binagadin oil equals zero. In this case not only aromatic hydrocarbons play a role; in very strong degree with respect to response are distinguished also naphthene-paraffin hydrocarbons of distillate. For instance, if naphthene-paraffin hydrocarbons of a distillate of oil AK-10 of Balakhany butyric oil give a reduction of pour point by 17°, then naphthene-paraffin hydrocarbons of a corresponding distillate of oil of the Neftyanyye Kamni deposit and Buzovny oil give depression of 30-33°, and naphthene-paraffin hydrocarbons from distillate of Binagadin oil, 11° in all.

Receptivity of groups of hydrocarbons and tarry substances, separated from distillates and oils of certain Baku oils, to AzNII depressors.

Evidently, here the response is influenced not so much by naphthenic hydrocarbons, whatever the content and nature of paraffin hydrocarbons in the composition of these fractions.

Analogous data are obtained on commercial oils from oils of different origin. If in oils AK-6 and AK-10, AS-9.5 from Balakhany butyric upon addition of depressor the pour point is lowered approximately by 12-17°, then corresponding oils from Balakhany heavy oil absolutely do not receive the depressor. Consequently, tar and aromatic hydrocarbons almost completely paralyze ability of depressors to lower pour point of oils. Conversely, paraffinaceous distillates and naphthene-paraffin hydrocarbons have a good response to depressors.

From what has been said it follows that during application of depressor additives it is necessary to combine investigation of hydrocarbon composition of

oils with selection of optimum degree of their purification.

Table 5. Receptivity of Groups of Hydrocarbons and Tarry Substances, Separated from Distillates and Oils of Certain Baku Oils, to AzNII Depressors

Groups of Hydrocarbons	Balakhany		Binagadin oil		Oil of Nefty-anyye Kamni deposit		Buzovny oil	
	Pour point, °C	Depression, °C	Pour point, °C	Depression, °C	Pour point, °C	Depression, °C	Pour point, °C	Depression, °C
Distillate of oil AK-10.....	-20	6	-24	0	-8	14	-12	13
Naphthene-paraffin hydrocarbons.....	-12	17	-24	11	-4	30	-5	33
Deparaffinated by carbamide naphthene-paraffin hydrocarbons.....	—	—	—	—	—	—	-20	16
Aromatic hydrocarbons.....	-18	0	-16	0	-18	1	—	—
Including:								
light.....	—	—	—	—	—	—	-20	17
average.....	—	—	—	—	—	—	-19	0
heavy.....	—	—	—	—	—	—	+15	9
Tarry substances.....	+24	0	+40	0	+26	0	—	—
Oil AS-9.5.....	-20	12	-24	0	-6	18	-6	21
Naphthene-paraffin hydrocarbons.....	-10	20	-22	12	-2	33	—	—
Aromatic hydrocarbons.....	-20	2	-18	1	-17	1	—	—
Aromatic hydrocarbons of extract from selective purification of distillate of oil AK-10.....	-12	0	-10	0	-10	0	—	—
Distillate of diesel oil.....	-18	12	-22	1	-4	20	—	—
Naphthene-paraffin hydrocarbons.....	-6	26	-16	14	-2	28	—	—
Aromatic hydrocarbons.....	-18	0	-16	0	-14	0	—	—
Tarry substances.....	+28	0	+44	0	+31	0	—	—
Diesel oil.....	-8	24	-22		-2	28	—	—
Naphthene-paraffin hydrocarbons.....	-4	28	-15	15	+6	36	—	—
Aromatic hydrocarbons.....	-20	1	-19	0	-16	0	—	—
Aromatic hydrocarbons of extract from selective purification of distillate of diesel oil.....	-8	0	-7	0	-6	0	—	—

Response of Oils and Groups of Hydrocarbons Separated from Them to Antioxidant Additives

The response of a number of distillates and oils, and also groups of hydrocarbons separated from them to antioxidant additives was studied.

Unpurified butyric distillates or badly purified oils have a weak response to antioxidants. Thus, distillates AS-9.5, obtained from oils Binagadin, Balakhany, butyric oils and oil of the Neftyanyye Kamni deposit, do not absorb antioxidant additives —α-naphthol and paraoxydiphenylamine. As compared to corresponding distillates the stability of purified oils is sharply increased, while stability of lubricating oil AS-9.5 of Balakhany butyric oil is higher than stability of oils from remaining oils. Purified oils have good response to antioxidants.

Study of response of oils of different degree of purification to antioxidants showed that with increase of degree of purification the response of oils to additives is increased.

Naphthene-paraffin hydrocarbons, separated from distillates and oils of Baku oils — Balakhany butyric, Buzovny, Binagad and oil of the Neftyannye Kamni deposit, have a low stability; however, they possess good response to antioxidants (Tables 6 and 7). At the same time aromatic hydrocarbons and tar, being very stable, are not sensitive to the shown additives.

It is interesting to note that corresponding aromatic, and also naphthene-paraffin hydrocarbons, separated from oils of different petroleums differ in stability, and also in receptivity to antioxidants; this is connected with hydrocarbon and structural composition of oils from which are separated groups of hydrocarbons. General regularities in change of stability of butyric components separated from oils of different petroleums, are identical.

Table 6. Results of Investigation of Response to Antioxidants of Groups of Hydrocarbons Separated From Distillates and Oils of Different Origin

Groups of Hydrocarbons	Quantity of antioxidant, %		Stability according to AzNII, minutes					
			Balakhany butyric oil		Binagadin oil		Oil of Neftyanyye Kamni deposit	
	α-naphthol	para-oxydiphenyl-amine	induction period	time of absorption 20 cm³	induction period	time of absorption 20 cm³	induction period	time of absorption 20 cm³
Distillate of oil (AK-10)								
Naphthene-paraffin.....	—	—	7	114	7	112	6	90
	0.20	—	87	274	63	290	27	187
	—	0.20	89	583	70	440	35	171
Aromatic.....	—	—	45	270	85	236	38	274
	0.20	—	42	266	37	180	38	240
Tarry substances.....	—	—	35	178	27	155	26	170
	0.20	—	34	175	26	145	27	163
Oil AS-9.5								
Naphthene-paraffin.....	—	—	7	115	7	144	6	95
	—	0.20	90	585	71	445	44	178
Aromatic.....	—	—	25	152	28	160	26	147
	0.20	—	31	170	33	155	33	160
Tarry substances.....	—	—	30	150	21	145	20	155
	0.20	—	31	146	19	140	22	150

Investigation of influence of aromatic hydrocarbons and tarry substances on stability against oxidation of naphthene-paraffin hydrocarbons separated from distillates and oils of different origin, showed that stabilizing action of aromatic hydrocarbons and tarry substances depends on their character, and also on origin of naphthene-paraffin hydrocarbons themselves.

Upon addition of aromatic hydrocarbons and resins it is possible to reach sharp improvement of stability of naphthene-paraffin hydrocarbons.

Table 7. Results of Investigation of Receptivity of Groups of Hydrocarbons Separated from Distillate of Oil AK-10 of Buzovny Oil, to Antioxidant Additives

Additive	Quantity of additive, %	Stability AzNII*, minutes					
		Naphthene-paraffin hydrocarbons		Light aromatic hydrocarbons		Average aromatic hydrocarbons	
		induction period	time of absorption of 10 ml of oxygen	induction period	time of absorption of 10 ml of oxygen	induction period	time of absorption of 10 ml of oxygen
Phenyl-α-naphthylamine.....	—	22	114	40	174	34	137
	0.01	25	173	—	—	—	—
	0.03	57	400	28	148	—	—
	1	—	—	36	150	—	—
Para-Oxydiphenylamine.....	0.02	54	295	45	168	29	123
	0.05	109	588	16	77	—	—
	0.10	101	562	—	—	—	—
	0.15	86	578	—	—	—	—
α-naphthol.....	0.2	106	249	35	156	31	114
	0.3	—	—	42	132	—	—
	0.4	109	327	36	110	—	—
2.6-di-tert-butyl-4-methyl-phenol (Ionol).....	0.01	56	434	—	—	—	—
	0.02	59	533	25	121	—	—
	0.3	53	467	38	185	32	109
Santolube 394.....	0.03	11	291	40	157	—	—

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Response of Different Groups of Butyric Hydrocarbons to Multifunctional Addition AZNII-7

We studied stability and antioxidant properties of oils, distillates and different groups of hydrocarbons separated from distillate of Buzovny oil, and response of them to additive aznii-7, and also influence of aromatic hydrocarbons and tarry substances on response of methano naphthene hydrocarbons to additive aznii-7.

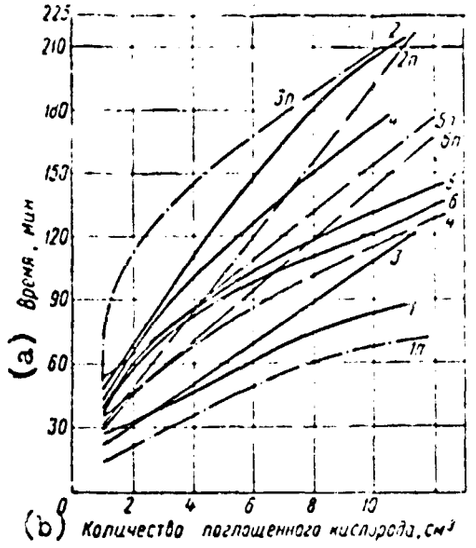


Fig. 1. Results of determination of stability according to method of AzNII. 1) distillate of oil AK-10 of Buzovny oil; 2) oil AK-10 of selective purification; 3) naphthene-paraffin hydrocarbons; 4) light aromatic hydrocarbons; 5) average aromatic hydrocarbons; 6) heavy aromatic hydrocarbons; 1n-6n — corresponding products with 3% additive aznii-7.
KEY: (a) Time, minutes; (b) Quantity of absorbed oxygen, cm^3.

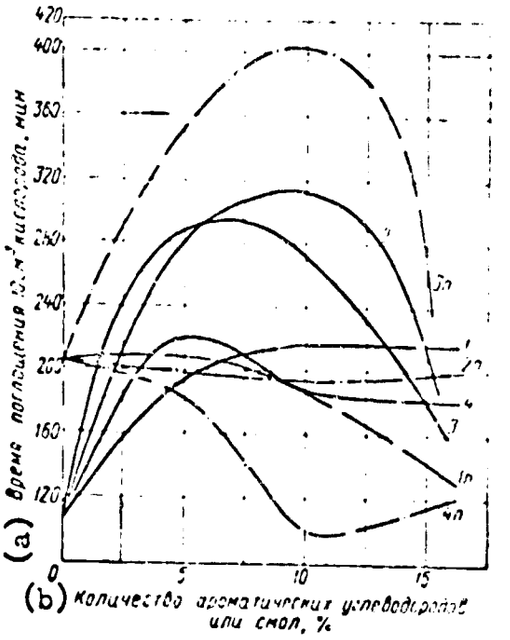


Fig. 2. Influence of aromatic hydrocarbons and tarry substances on change of stability of naphthene-paraffin hydrocarbons and response to additive aznii-7.
Naphthene-paraffin + hydrocarbons: 1) light aromatic; 2) average aromatic; 3) heavy aromatic; 4) tarry substances; 1n-4n—corresponding products with 3% additive aznii-7.
KEY: (a) Time of absorption of 10 cm^3 oxygen, min; (b) Quantity of aromatic hydrocarbons or resins, %.

It is established that additive aznii-7, as other multifunctional additives, lowers stability of distillates and oils (see Table 1).

Naphthene-paraffin hydrocarbons possess low stability and anticorrosive properties, but they very effectively absorb additive aznii-7 (Fig. 1-3). Their stability during addition of additive is increased almost twice.

Aromatic hydrocarbons have best stability and anticorrosive properties, but weak receptivity to additive aznii-7, with the exception of light aromatic hydrocarbons.

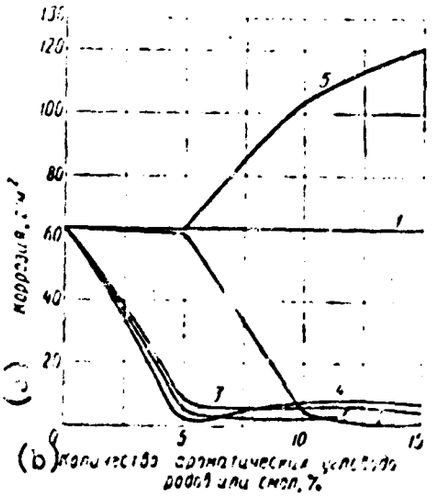


Fig. 3. Influence of aromatic hydrocarbons and tarry substances on change of corrosiveness of naphthene-paraffin hydrocarbons. Naphthene-paraffin + hydrocarbons: 1) light aromatic; 2) average aromatic; 3) heavy aromatic; 4) resin; 5) resin not soluble in phenol; 6) resins soluble in phenol. KEY: (a) Corrosion, g/m^2; (b) Quantity of aromatic hydrocarbons or resins, %.

Investigation of influence of aromatic hydrocarbons and tarry substances on working properties of naphthene-paraffin hydrocarbons and on their receptivity to additive aznii-7 showed that naphthene-paraffin hydrocarbons in combination with aromatic hydrocarbons or resins during a definite concentration of the latter possess higher qualities. However, the presence of these groups of hydrocarbons and resins in definite degree lowers response of naphthene-paraffin hydrocarbons to additive aznii-7.

Resins soluble in phenol contain approximately twice more sulfurous and nitrous compounds as compared to resins not soluble in phenol, in consequence of which they significantly lower corrosiveness of naphthene-paraffin hydrocarbons.

ABOUT MECHANISM OF ACTION OF CERTAIN TYPES OF ADDITIVES TO OILS (Detergent, Anticorrosive, and Antiscoring Additives)

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VNII NP*

On RUM-1 set up with radioactive rubbing parts is investigated influence of composition of different alkylphenolate and sulfonate additives on effectiveness of their neutralizing action [1-3]. It is shown that at the basis of mechanism of anticorrosive action of neutralizing additives lie electrochemical processes and that the most effective additives have to contain cations with the biggest negative normal electrode potential, and during neutralization of aggressive acids have to form readily soluble salts which do not render an abrasive action on friction surface. It is established also that the most effective neutralizing action belongs to the additive whose cations are able to be easily dissociated, in particular alkylphenolate additive [3, 4].

In recent years we and other authors discovered that during mixing of components of additives their functional action can worsen [5-8]. The causes of suppression of functional action were in detail investigated with the help of a laboratory installation [5]. The presence of a suppression effect was established also during comparison of results of determination of neutralizing action on laboratory installation RUM-1 with results of stand motor tests.

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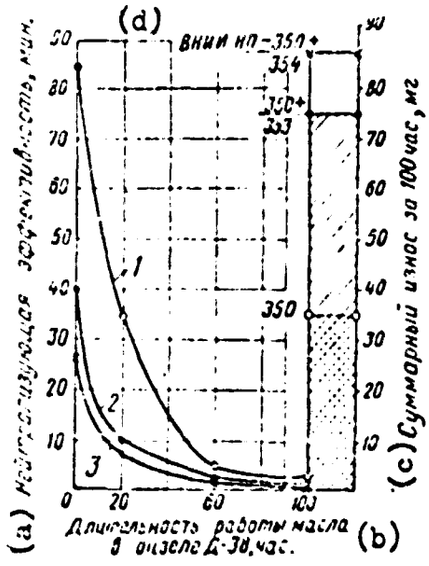


Fig. 1. Change of neutralizing effectiveness of oil DS-11 with additives depending upon period of its work in diesel engine D-38 (according to tests on laboratory RUM-1 installation). For comparison is shown loss of weight of set of piston rings for 100 hour tests of diesel engine on the same oils.
1) DS-11 + 2.86% vnii np-350; 2) DS-11 + 2.86% vnii np-350 + 1.11% vnii np-353; 3) DS-11 + 2.86% vnii np-350 + 1.14% vnii np-354.
KEY: (a) Neutralizing effectiveness, minutes; (b) Length of operation of oil in diesel engine D-38, hours; (c) Total wear after 100 hours, mg; (d) Vnii-np.

On motor D-38 by the 100-hour method (n = 1420 rpm, consumption of fuel 7.5 kg/hour, temperature of cooling water 95°, temperature of oil in crankcase 90-95°, diesel fuel with content of sulfur 1%) jointly with V. D. Reznikov was tested oil DS-11 NKZ 2.86% additive vnii np-350 and oil with the same additive in mixture with dialkyldithiophosphate components: in one case with 1.11% vnii np-353, and in the other case with 1.14 vnii np-354. After 20, 60, and 100 hours work of motor, samples of oils were removed whose neutralizing effectiveness then was determined on a laboratory installation.

In Fig. 1 is shown loss of weight of set of piston rings of motor D-38 after 100 hours and change of neutralizing effectiveness of oils with their use in the motor. As can be seen, the distinction in neutralizing effectiveness of initial oils containing an equal quantity of barium, caused by overwhelming action of dialkyldithiophosphate components, is kept during the whole work period of oil in motor, which also determined distinction in total wear [illegible] of piston rings for 100 hours during operation of motor on an oil with these additives.

At the same time results of these motor tests, given in Table 1, show that increase of wear of piston rings, combined with suppression of neutralizing action of barium alkylphenolate by dialkyldithiophosphate components is accompanied by noticeable decrease of quantity of scale, especially on pistons of motor.

Table 1. Results of Motor Bench Tests of Oils with Additives on Diesel Engine D-38

Index	Oil DS-11 with additives		
	2.86% vnii np-350	2.86% vnii np-350 + 1.11% vnii np-353	2.86% vnii np-350 + 1.14% vnii np-354
Quantity of scale on set of rings, g:			
Compression.....	0.109	0.132	0.092
Oil-removable.....	0.010	0.065	0.048
Quantity of scale in grooves of piston, g.....	0.930	0.373	0.317
Quantity of scale on piston (besides bottom), g.....	1.850	0.995	0.815
Wear of sets of piston rings, mg:			
Compression.....	30	65	72
Oil-removable.....	5	10	15

Apparently, in a number of cases it is necessary to apply a mixture of components of additives which would possess satisfactory detergent action with a certain impairment of neutralizing, and consequently also antiwear properties. However, it is more expedient to select such mixtures of components of additives in which effects of suppression of any functional properties are absent.

The Mechanism of Action of Anticorrosive and Antiscoring Additives

During the study of mechanism of action of anticorrosive additives to oils it was established that the most effective protection of bushings from nonferrous metals and alloys from corrosion under the action of products of oxidation of oil is attained in cases when the protective film created on surface of metal consists of

molecules of additive, forming a complex with the metal [3, 10, 11]. This led to the conclusion that the biggest anticorrosive effectiveness is guaranteed by polar sulfur- or phosphorous-containing compound, in the molecules of which the shown elements have the most durable bonds.

Results of study of mechanism of chemical destruction of anticorrosive protective films confirmed this conclusion: it was shown [11, 12] that destruction of film, leading to loss of anticorrosive effect, takes place by means of solvational breakaway of radicals of additive by acids. Consequently, durability of bonds of sulfur or phosphorous in molecules of additive determines duration of preservation of anticorrosive effect, other things being equal.

The investigations conducted allowed a clear determination (absent up to now) of fundamental distinction in requirements presented to chemical compounds during selection of anticorrosive and ant scoring additives to oils. This distinction results in the fact that anticorrosive additives, as was shown above, have to possess durable bonds of sulfur or phosphorus in molecules, whereas antiscoring additives have to easily chip sulfur, phosphorus or chlorine for formation on metal of corresponding sulfide, phosphides or chlorides at high contact temperatures. By such fundamental distinction between shown forms of additives is explained the biggest antiscoring effectiveness (established by many authors) of chemically-active compounds which are corrosively aggressive with respect to metals protected by them from scoring [13-16].

All the above-stated led to the conclusion that creation of the most effective antiscoring additives is possible not only as a result of the usually applied selection of chemical compounds, which would ensure a sufficient antiscoring effect with minimum corrosive influence [13, 17], but also selection of two-component additives which are a combination of the most effective antiscoring and anticorrosive components.

For investigation and selection of such two-component additives in laboratory conditions in the VNII NP is applied radiometric determination of corrosive aggressiveness of oil with additive in combination with evaluation of its antiscoring properties on the usual four-ball apparatus [18].

Corrosive aggressiveness was investigated with respect to radioactive copper of different sulfur- and chlorine-containing compounds and their combinations, finding use as antiscoring additives [17]. Of a number of investigated compounds, the biggest chemical activity was in the compound of 3% dibenzyldisulfide with 7% chlorinated paraffin. According to tests on four-ball apparatus this compound ensured a high antiscoring effect.

Table 2. Results of Determinations of Corrosive Aggressiveness and Antiscoring Effectiveness of Oil with Additives at a Temperature of Oil of 150°

Tested sample	Corrosion of copper, kg		Maximum load to seizing (four-ball machine), kg
	after 10 hours	after 15 hours	
Oil of selective purification of viscosity ν_{100} = 14 cs...	0.03	0.05	79
The same + 3% dibenzyldisulfide + 7% chlorinated paraffin.....	15.6	18.2	126
The same + 3% dibenzyldisulfide + 7% chlorinated paraffin + 6% anticorrosive additive.....	0.9	8.8	126

To select the anticorrosive component in oil with dibenzyldisulfide and chlorinated paraffin, different additives were introduced. Some of them ensured a lowering of corrosive aggressiveness with respect to copper and steel. In Table 2 are given results of radiometric determinations and data of tests carried out on a four-ball apparatus for oil of selective purification having viscosity ν_{100} = 14 cs with the most effective of the tested anticorrosive additives.

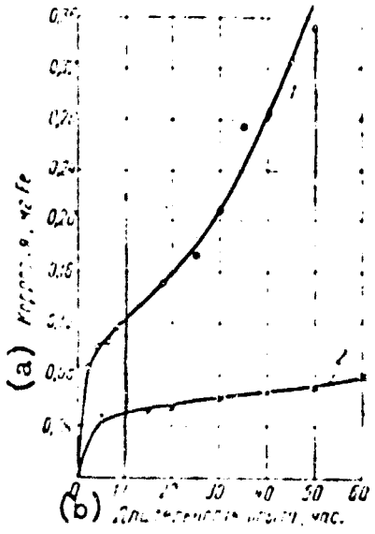


Fig. 2. Corrosion of steel under the action of oil with additives. Experiments are conducted at a temperature of oil of 200°. 1) oil of selective purification $\nu = 14$ cs + 3% dibenzyldisulfide + 7% chlorinated paraffin; 2) the same (that and 1) + 0.5% triphenylphosphite. KEY: (a) Corrosion, milligrams Fe; (b) Duration of experiment, hours.

Upon introduction of additive corrosive aggressiveness of oil was sharply lowered without impairment of antiscoring properties. However, this additive ensured effective anticorrosive action in conditions of tests only for 10 hours.

Along with the empirical selection of anticorrosive components was conducted also a radiometric investigation of anticorrosive properties of phosphorous-containing compounds, proceeding from the earlier established [3, 10, 11] ability of metal phosphide not to be dissolved under action of oxidation products of oil. As can be seen in Fig. 2 introduction in oil of 0.5% triphenylphosphite ensured effective reduction of corrosion of steel (at a temperature of oil of 200°) under the action of oil of selective purification with 3% dibenzyldisulfide and 7% chlorinated paraffin.

About Mechanism of Action of Detergent Additives

Using the radioindicator method of investigation of electrokinetic processes [19, 20] data were obtained about mechanism of detergent action of certain additives introduced in different concentrations into motor oils.

It was shown that mechanism of detergent action of these additives may be considered, proceeding from micellar theory of solutions of surface-active materials. In Fig. 3 for example are given obtained dependencies of speed of electrophoresis

on concentration of different additives in oil AS-5 from sulfurous oil. Introduction of additive PMS_{ya} (1-st group, ash content 17%) in any concentrations caused shift of tagged carbon black only on cathode, whereas additive tsiatim-339* caused a shift of carbon black only in the direction of the anode. Dialkyldithiophosphate additives vnii np-353 and vnii np-354 up to definite concentrations caused shift of carbon black onto the anode, and with large concentrations — onto the cathode.

The character of curves shown in Fig. 3 can be explained proceeding from the theory of McBean about the presence in solutions of surface active materials of micelles of different dimensions and types, depending upon concentration of shown substances, and also considering established analogy in volumetric properties of aqueous and hydrocarbon solutions of surface active materials [21]. Thus, in the case of additives vnii np-353 and vnii np-354 with a low concentration of them in oil, obviously, small strongly charged ionic micelles are formed, ensuring a high speed of electrophoresis of carbon black solubilized by them. With an increase of concentration of these additives in oil big weakly charged micelles start to predominate, as in a consequence of which speed of electrophoresis of carbon black is lowered. Upon achievement of definite concentrations of additives in oil with micelles antiions start to associate, changing the direction of electrophoresis.

Micellar character solutions of additive PMS_{ya} confirm data of Table 3, in which are given results of measurements of electrical conductivity at 100° of solutions of this additive and alkylphenolate additive vnii np-350 in oils of various viscosity AS-5 and AS-9.5 from sulfurous oils. The shown additives were introduced in oils in such quantities that concentration of cations in oil was identical.

*Ed. Note: The additive is named after the research institute TsIATIM = tsiatim = Central Scientific Research Institute of Aviation Fuels and Lubricants.

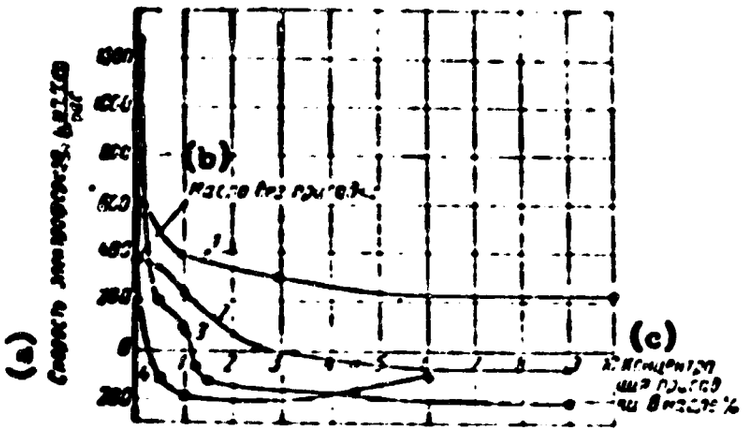


Fig. 3. Influence of concentration of different additives on speed of electrophoresis of the tagged carbon black in oil AS-5 from sulfurous oil.
1) tsiatim-339; 2) vnii np-354; 3) vnii np-353; 4) PMS_{ya}.
KEY: (a) Speed of electrophoresis, imp/sec/hour; (b) Oil without additive; (c) 10 concentration of additive in oil, %.

Table 3. Electrical Conductivity at 100° of Oils With Alkylphenolate and Sulfonate Additives

Additive	Content in oil, %	Base oil	Current through oil at 90v	
			ma	%
Vnii np-350.....	5	AS-9.5	1.57	100
		AS-5	1.75	111
PMS_{ya}.....	2	AS-9.5	0.50	100
		AS-5	1.10	220

From Table 3 it is clear that with decrease of viscosity of base oil by approximately two times, for the solution of sulfonate additive is observed a growth of electrical conductivity by more than two times, and for the solution of alkylphenolate additive by only 11%. This is the result of a significantly larger ratio of charge of particles (ions) to their mass during ionic electrical conductivity in a solution of alkylphenolate additive than during electrophoresis of

electrical conductivity with the help of colloidal micelles in a solution of sulfonate additive, when due to decrease of viscosity resistance to shift of these micelles decreases significantly sharper, transferring electrical charge.

Consequently, it is possible to assume that mechanism of action of certain detergent additives is combined with micellar structure of solutions of these additives in oils and ability of micelles to solubilize carbon black particles, whereas mechanism of action of other additives is combined with their ability to dissociate in oils and to ensure ionic adsorption on carbon black particles and surfaces of metals.

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ABOUT MECHANISM OF DETERGENT ACTION OF ADDITIVES

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In recent years there has been wide use of polyfunctional additives, which, besides other properties, possess detergent action. For certain additives this property is expressed so strongly that they are usually called detergent additives. The term "detergent additives" became widely used first of all because the action of such additives in certain relations is similar to the action of well-known washing substances, applied in aqueous solutions (soap — salts of organic acid, sulfonates, and others).

In one of our early works [1] it was indicated that the term "detergent" in application to considered type of additives should not be considered a good choice. A rational name of the type of additives should have a scientific foundation and first of all reflect the real mechanism of action.

In many cases the effectiveness of washing action of additives is judged by relative cleanness of the main parts of the (piston group) motor, which is working a definite time with application of lubricating oil containing an additive: the quantity formed during operation of motor is measured of carbonaceous deposit, varnishes, scales; the state of the piston rings (scorching of rings) etc., is determined.

Such evaluation of additive (or mixture of additives) is overall and can characterize not only its detergent action. Really, the additive can possess properties of an antioxidant; upon application of such additive will decrease quantity of products not soluble in the processed oil, which in turn will positively be reflected on the total cleanness of the motor. The very same can also be said relative to anticorrosive and even antiwear action of additives, which can be reflected in the total state of the motor and relative cleanness of piston group. However, the shown properties of additives have no relation to their detergent action and have to be investigated by specific methods, in this or that measure by methods based on our knowledge of the mechanism of action of additives. Thus, antioxidant action of additives should be investigated by those methods which are used for typical antioxidants.

Consequently, for the characteristics of detergent action of additive it is important to separate this action from other properties of the additive for which it is necessary to know mechanism of the washing action itself of the additives.

To the mechanism of detergent action of additives is devoted a large number of works; however, a significant part of the works carries the character of assumptions, not always sufficiently founded by experimental data.

All works considering mechanism of action of detergent additives can be divided into two groups. To the first group belong works in which the main attention is to the dispersive action of detergent additives; in the second group are works in which this mechanism is considered in other aspects.

Let us consider certain positions advanced in works of the second groups.

Denison and Clayton [2] showed that deposits forming in the piston group during operation of motor contain significant quantities of oxy-acids not soluble in oil, and expressed the assumption that detergent additives of the salts of organic acids type (soap), for instance naphthenates of aluminum, can react with oxy-acids, forming compounds soluble in oil. In the opinion of other authors

[3, 4], such detergent additives as salts of organic acids and alkylphenolates, can be catalysts of oxidations which promote transformation of undesirable products of oxidation of oil hydrocarbons — oxy-acids and asphaltenes — into carbenes and, possibly, carboids; the latter are easily washed off from metallic surface and form a suspension with oil.

The shown presentations reflected the initial period of research in the region of detergent additives, combined with application of detergent additives of the salts of organic acids type. Besides salts of organic acids, other types of additives possessing detergent action now are wide-spread, for instance sulfonates and dialkyldithiophosphates which cannot chemically react with oxy-acids, but which, nonetheless, possess the detergent action common for all this class of additives. But it is proven also that alkylphenols are catalysts of oxidation of oxy acids.

Recently A. V. Druzhinina, T. S. Tarman'yan and I. V. Morozova also explained [6] the mechanism of detergent action of additive tsiatim-339, barium alkylphenolate disulfide, by chemical reaction of this additive with organic acids obtained during oxidation of hydrocarbons of oil. In the opinion of the authors are formed oil-soluble salts of organic acids and free alkylphenol disulfide, which in turn, changes asphalt-tar substances into a butyric solution, preventing, thereby, their deposit on motor parts. The authors did not confirm their assumption by experimental means which it would have been possible to do, introducing free alkylphenol directly in the processed oil and studying its influence on properties of oil. Such a check was made by N. I. Itinskaya and M. D. Degtyarev [7], which showed that detergent action of additive tsiatim-339 cannot be combined with formation of free alkylphenol, if, of course, he will be formed*.

*The authors of this work [7] base their own conclusions on references to the data of a table, which, apparently, by the fault of the authors or the editorial office is lacking in the article.

A larger part of researchers connects the detergent action of the additives first of all with their dispersive ability. This position is shared also by the authors of this report. Certainly, individual additives, besides their own detergent action, can possess specific features, for instance, neutralizing action. Certain additives contain components which neutralize acids forming as a result of combustion of sulfurous compounds of sulfurous fuels. However, this action of additives must be considered as a neutralizing action, not confusing it with detergent action.

The dispersive action of additives in this or that measure is discussed in a number of works of Soviet [1, 8-13] and foreign authors [14-22]. In certain works are also considered methods of determination of dispersive ability additives. A short summary of proposed methods is given in the works of P. I. Sanin and N. S. Nametkin [1] and in recent work of Ye. A. Myshkin [13].

Of the enumerated works one should stop relatively closer to the time of works of the English researchers Baddeley, Garner, and other [21, 22] and French researchers Courtel, Larbre, and Bernelin [17, 18].

The first researchers in their interesting and fundamental work studied condition of stabilization of suspensions with the help of detergent additives and made an attempt to prove the adsorptive character of the mechanism of action of these additives by experimental means. The obtained results, however, could not serve as a sufficient base for quantitative interpretation of the process of adsorption, since experiments were conducted with an additive (naphthenate of aluminum) which is not an individual compound, and quantitatively the additive was determined in hydrocarbon solution according to change of surface tension of its solutions on boundary with water.

French researchers showed that stability of suspensions consisting of lubricating oil and carbonaceous particles, forming mainly as a result of incomplete combustion of hydrocarbons of fuel, in significant degree depends on temperature.

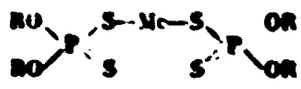
The suspension, stable at relatively moderate temperatures, at increased temperatures can become unstable; in this case is observed adhesion of carbonaceous particles, formation of big flakes (flocculation), which easily fall from oil. This process can be observed in the motor in the most heated of its parts. The authors also proposed a method of determination of dispersive properties of additives, founded on determination of temperature limit, higher than which in standard conditions flocculation of carbonaceous particles takes place.

This work is dedicated to investigation of mechanism of dispersive action of additives.

A larger part of the investigation was conducted with polyfunctional additives of the metal dialkyldithiophosphates type and, especially, nickel dialkyldithiophosphate. As was shown in [23], di-n-octadecyldithiophosphate $[(C_{18}H_{37}O)_2PSS]_2Ni$ possesses strong detergent action; in the presence of this additive (1.5%) detergent properties of oil MS-20 (Emba) are improved, according to PZV estimation from 4.5 to 0.5 point. The use of additives which are individual compounds, excluded the influence of unknown components, usually assisting in technical additives. Additives of the nickel dialkyldithiophosphate type were selected also because their hydrocarbon solutions have a specific (violet) color that was used for quantitative colorimetric determination of concentration of additives in experiments on adsorption.

Surface Activity of Nickel Dialkyldithiophosphates

The chemical structure of dialkyldithiophosphates of bivalent metals (nickel, zinc, calcium, barium)



gives a basis for attributing them to surface active materials possessing a dipolar, two-branched structure. A molecule of dialkyldithiophosphate of metal contains a polar group and four hydrocarbon radicals, which can have a different structure.

Surface activity of dialkyldithiophosphates was studied first of all by removal of isotherms of surface tension of solutions of dialkyldithiophosphates in a hydrocarbon medium on boundary with water.

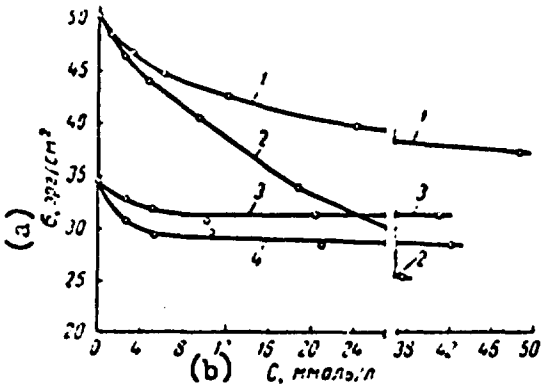


Fig. 1. Isotherms of surface tension $\sigma = f(c)$ of dialkyldithiophosphates of nickel in heptane and benzene on boundary with water.
1) solution $[(C_4H_9O)_2PSS]_2Ni$ in heptane; 2) solution $[(C_{10}H_{21}O)_2PSS]_2Ni$ in heptane; 3) solution $[(C_{10}H_{21}O)_2PSS]_2Ni$ in benzene; 4) solution $[(C_{18}H_{37}O)_2PSS]_2Ni$ in benzene.
KEY: (a) σ erg/cm^2; (b) C, mmole/l.

As samples of metal dialkyldithiophosphates were taken di-n-butyl-, di-n-decyl- and di-n-octadecyldithiophosphates of nickel. Solutions of nickel dialkyldithiophosphate in heptane, and also in benzene were used, since di-n-nickle octadecyldithiophosphate will readily dissolve in benzene and will badly dissolve in heptane. Surface tension $\sigma_{1,2}$ was determined by finding the biggest pressure drops using P. A. Rebinder's [24] instrument.

The obtained isotherms of surface tension $\sigma = f(c)$ are shown in Fig. 1, corresponding to them are isotherms of adsorption $\Gamma = f(c)$ in Fig. 2.

In Figs. 1 and 2 it is clear that surface activity (adsorbability) in number of nickel dialkyldithiophosphates increases with increase of length of hydrocarbon radicals (C_4, C_{10} and C_{18}). The biggest surface activity is possessed by di-n-octadecyldithiophosphate of nickel. Determined by graphs, the limiting maximum value of adsorption (Γ_{max}), corresponding to full saturation of adsorptive layer on a heptane-water boundary, was equal for di-n-butyldithiophosphate to $1.35 \cdot 10^{-10}$ and for di-n-decyldithiophosphate, to $3.33 \cdot 10^{-10}$ mole/cm^2. During adsorption from benzene the adsorbabilit, of nickel dialkyldithiphosphates noticeably drops: the value of Γ_{max} for di-n-decyldithiophosphate of nickel constituted $0.8 \cdot 10^{-10}$ and for di-n-octadecyldithiophosphate nickel $0.95 \cdot 10^{-10}$ mole/cm^2. The latter is

in connection with the easy polarizability of benzene [25].

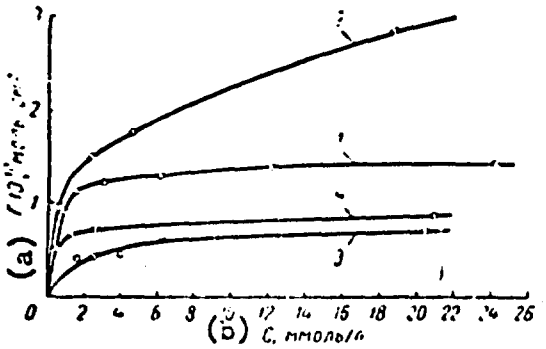


Fig. 2. Isotherms of adsorption $\Gamma = f(c)$ of nickel dialkyldithiophosphate on a heptane—water and benzene—water boundary.
1) $[(C_4H_9O)_2PSS]_2Ni$, heptane—water; 2) $[(C_{10}H_{21}O)_2PSS]_2Ni$, heptane—water; 3) $[(C_{10}H_{21}O)_2PSS]_2Ni$, benzene—water; 4) $[(C_{18}H_{37}O)_2Ni$, benzene—water.
KEY: (a) $\Gamma 10^{10}$, mole/cm^2; (c) C, mmole/l.

Calculated values of minimum area ($S_{мин}$), occupied by a molecule in a saturated layer on a heptane-water boundary for nickel butyl- and di-n-decyldithiophosphates were accordingly 123.0 and 49.9A^2. It was possible to assume that for identical polar groups of both dialkyldithiophosphates for identical arrangement of hydrocarbon groups, for example, vertical in relation to boundary of section, the magnitudes $S_{мин}$ will be close. The obtained distinction in these magnitudes indicates that hydrocarbon groups of nickel dialkyldithiophosphates in adsorptive layer have another location, while to more high-molecular dialkyldithiophosphate corresponds also denser packing of hydrocarbon groups in adsorptive layer. Consequently, nickel dialkyldithiophosphates are surface active materials and can be adsorbed from hydrocarbon medium onto a hydrocarbon medium — water boundary. As will be shown below, they can be adsorbed also onto the surface of carbon particles (carbon black).

Adsorption of Nickel Dialkyldithiophosphates on Carbon Black from Solutions in Toluene

The method of determination of adsorption of nickel dialkyldithiophosphates on carbon black was concluded in the following way. From a definite quantity of dialkyldithiophosphate solution in toluene and carbon black was prepared a suspension (carbon black — toluene). After establishment of adsorptive equilibrium (mixing

of suspension in ampul for 6 hours) and subsequent deposit of carbon black was determined the quantity of dialkyldithiophosphate, remaining in solution; then according to the difference (with respect to the taken quantity of dialkyldithiophosphate) was established the quantity of it adsorbed onto the carbon black. As it turned out, the color of the obtained diluted solutions of nickel dialkyldithiophosphates was insufficient for quantitative colorimetric determination; therefore, the dialkyldithiophosphates were decomposed, and the obtained salts of nickel were changed into intensely colored complex compounds of nickel with dimethylglyoxime, the nickel content in which was determined by colorimetric means [26].

In Fig. 3 are given results of experiments of adsorption of nickel dialkyldithiophosphate onto carbon black at different concentrations of carbon black in toluene. The equilibrium concentration of dialkyldithiophosphate in separate experiments was changed within the limits of 37-700 milligram or from 0.03-0.5 mmole/l solvent — toluene. The obtained dependencies of quantity of adsorbed dialkyldithiophosphate on its equilibrium concentration are typical isothermic adsorptions.

These experiments showed that "detergent" additive - nickel dialkyldithiophosphate — indeed is adsorbed from hydrocarbon solution onto particles of carbon black.

We noticed that during relatively large concentrations of carbon black in toluene is observed agglomeration of particles of carbon black which should lead to a decrease in specific surface of carbon black and correspondingly to a decrease of quantity of adsorbed dialkyldithiophosphate (see Fig. 3). Quantity of additive adsorbed per gram of soot significantly is increased with decrease of concentration of soot. For very diluted suspensions (containing 0.0026 and 0.0061% soot) the isotherms of adsorption practically coincide. It is possible to consider that for shown concentrations and below aggregation is practically not observed. Further study of adsorption was conducted on suspensions with small concentration of soot.

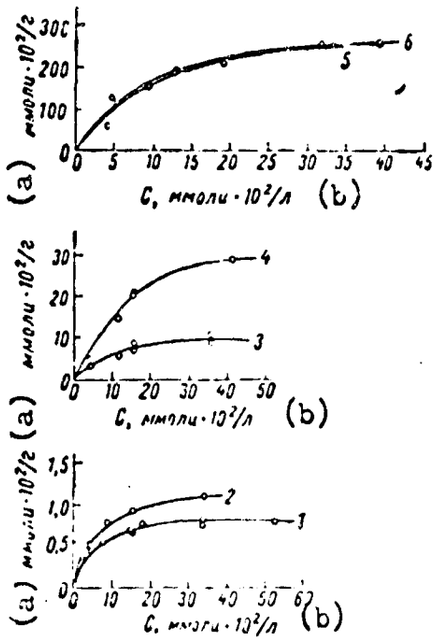


Fig. 3. Isotherms of adsorption of nickel di-n-octadecyldithiophosphate onto carbon black. Concentration of carbon black: 1) 0.51%; 2) 0.25; 3) 0.025; 4) 0.013%; 5) 0.0025; 6) 0.0061%. KEY: (a) mmole·10^2/g; (b) C, mmole·10^2/l.

Isotherms were removed of adsorption of nickel di-n-butyl-di-n-decyl- and di-n-octadecyldithiophosphates onto soot and thus is established the influence of length of hydrocarbon radicals of dialkyldithiophosphates on their adsorbability. The quantity of dialkyldithiophosphate adsorbed on 1 g soot decreases with increase of hydrocarbon radicals, and consequently also with increase of molecular weight of dialkyldithiophosphate. The calculated molecular weight of di-n-butyl-, di-n-decyl- and di-n-octadecyldithiophosphates equal 541.4, 878.0, and 1326.8.

Values of maximum -- limit -- adsorption, corresponding to full saturation of adsorptive layer onto toluene -- soot boundary (A_∞), determined by isotherms of adsorption [27], are given in Table 1.

Table 1. Value of Limit Adsorption of Nickel Dialkyldithiophosphates on Soot (mmole/g soot)

Soot -- Toluene Suspension

Compound	Channel black	Thermal black
Nickel di-n-butyldithiophosphate.....	5.70	16.00
Nickel di-n-decyldithiophosphate.....	4.08	6.89
Nickel di-n-octadecyldithiophosphate.....	3.17	5.88

Thus, during adsorption of nickel dialkyldithiophosphates onto soot (from solution in toluene) regularity was obtained with respect to influence of length of hydrocarbon radicals, the opposite observed for adsorption onto hydrocarbon -- water boundary. Apparently, hydrocarbon radicals of molecules of nickel dialkyldithiophosphates adsorbed onto soot, have another location in space than in the case of adsorption onto a hydrocarbon -- water boundary; molecules with longer radicals have a less compact structure and occupy a larger area on surface of soot. If one were to convert into weight quantities, then 1 g channel black adsorbed 3.1 g di-n-butyldithiophosphate, 3.6 g di-n-decyldithiophosphate, and 4.2 g di-n-octadecyldithiophosphate.

Molecules of additives of the dialkyldithiophosphates type are adsorbed from hydrocarbon solutions onto particles of soot. As a result of such adsorption, as will be shown below, adhesion is prevented (aggregation, flocculation) of the particles of soot, and also there occurs dispersion (peptization) of already formed enlarged particles of soot with formation of small particles. As a result of adsorption, particles of soot are covered by a layer of molecules of nickel dialkyldithiophosphate, turned by the hydrocarbon groups into hydrocarbon medium. Accordingly oleophilousness of particles sharply increases, and the suspension as a whole becomes stabilized.

It is necessary to note that the surface of particles of different types of soot is nonuniform and in this or that measure is oxidized. Especially this pertains to channel black, which, judging by data of elementary analysis, contains up to 3% oxygen [28]. The character of the surface of soot particles, apparently, also ensures adsorption of molecules of dialkyldithiophosphates by the polar part, whereas nonpolar part of molecules (hydrocarbon radicals) is changed into hydrocarbon medium.

Electron-Microscopic Study of Action of Nickel Dialkyldithiophosphates On a Suspension of Soot

Photographs made of preparations of soot obtained from samples of soot suspension in toluene, without additive and with additive nickel dialkyldithiophosphate, using an electron microscope (EM-100), which gave an increase of 15,700 times*.

Sample of suspension after preliminary treatment by a special method was applied and was secured on a film of nitrocellulose, and then the survey was made.

The addition prevents adhesion of particles of soot in bigger aggregates or will disconnect (disperses) already formed big aggregates (Fig. 4). Apparently, both phenomena are observed.

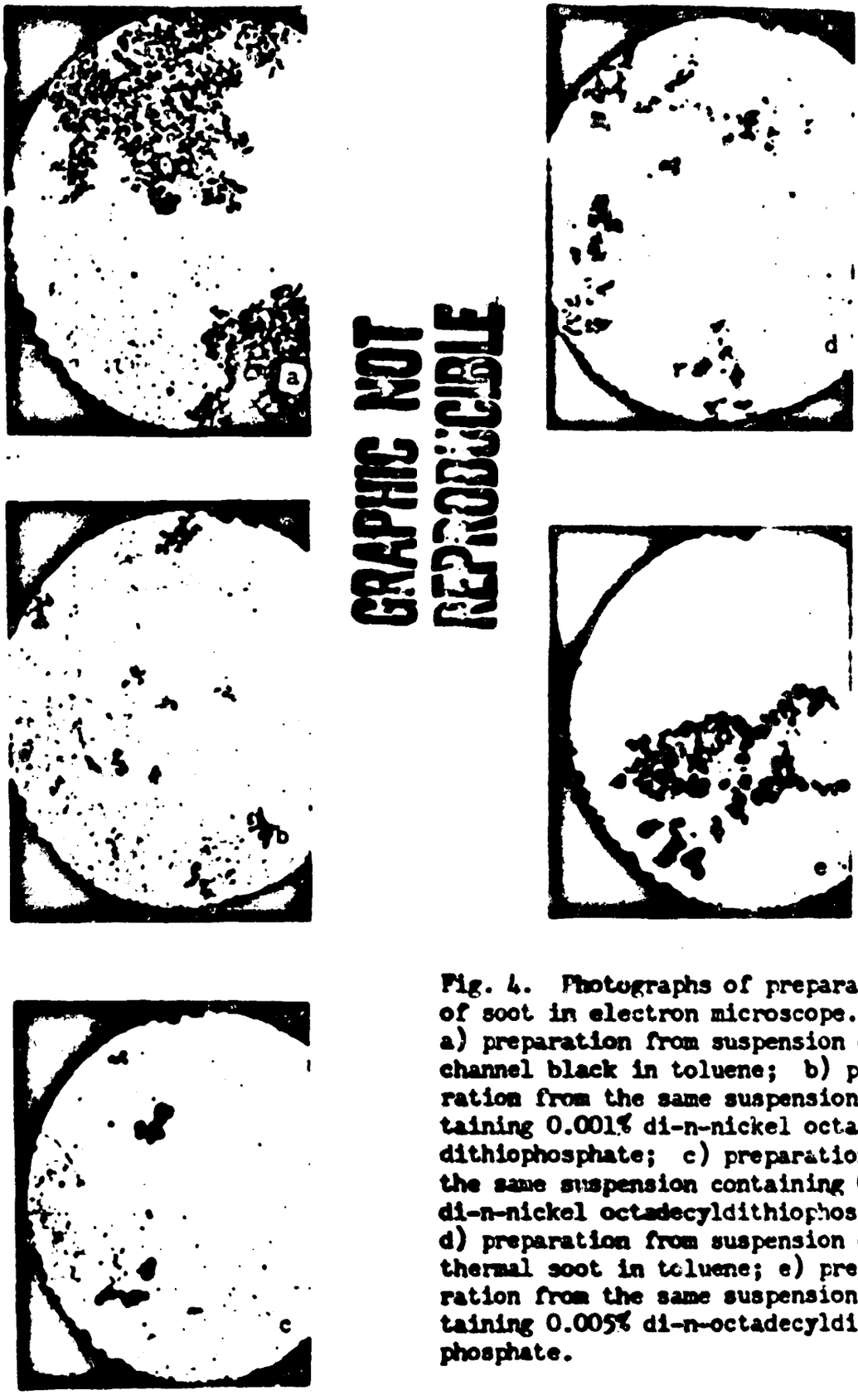
By electron-microscope photographs one can determine average magnitude of particle of soot and by quantitative results of adsorption — average of molecules adsorbed on one (averaged) particle of soot.

In Fig. 5 is given the distribution of particles by their dimensions of the thermal (dispersed) soot we used. Dimension of diameters of particles was determined by a method described in literature [29] after an additional photographic increase (3.5 times) of photographs of soot obtained in the electron microscope. The total increase was 55,000 times.

With respect to average diameter of particles of soot was determined magnitude of surface of particle. Conditionally it was assumed that all particles have spherical form. From the average magnitude of the surface of one particle of soot and specific surface of the soot — total surface of all particles in 1 g soot (for thermal soot, specific surface was 32.9 m^2/g, for channel soot it was assumed equal to 100.6 m^2/g [29]) was determined the number of particles in 1 g soot.

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*Authors express gratitude to P. A. Tesner for allocation of samples of soot and possibility of obtaining electron-microscope photographs.



GRAPHIC NOT REPRODUCIBLE

Fig. 4. Photographs of preparations of soot in electron microscope. a) preparation from suspension of channel black in toluene; b) preparation from the same suspension containing 0.001% di-n-nickel octadecyldithiophosphate; c) preparation from the same suspension containing 0.01% di-n-nickel octadecyldithiophosphate; d) preparation from suspension of thermal soot in toluene; e) preparation from the same suspension containing 0.005% di-n-octadecyldithiophosphate.

For thermal and channel black the obtained values were: average diameter of particle 720 and 306A; average magnitude of surface of particle $16.3 \cdot 10^5$ and $29.4 \cdot 10^4 A^2$; number of particles in 1 g soot $2.0 \cdot 10^{13}$ and $3380 \cdot 10^{13}$.

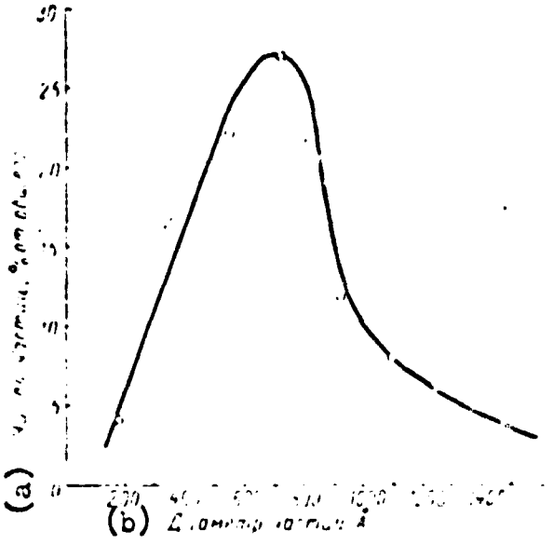


Fig. 5. Distribution of particles of thermal soot according to their dimensions.
KEY: (a) Number of particles, % of total; (b) Diameter of particles, A.

Knowing the number of particles in 1 g soot and the limit adsorbed quantity of dialkyldithiophosphate on 1 g soot (see Table 1), it was easy to determine the number of molecules of dialkyldithiophosphate adsorbed on one particle of soot. In the case of channel black on one particle of soot was adsorbed $10.2 \cdot 10^4$ molecules di-n-butyl-dithiophosphate of nickel, $7.3 \cdot 10^4$ molecules di-n-decyldithiophosphate of nickel and $5.7 \cdot 10^4$ molecules di-n-octadecyldithiophosphate of nickel. For thermal soot values of $47.7 \cdot 10^7$; $20.5 \cdot 10^7$; $17.5 \cdot 10^7$ were obtained.

The obtained values, of course, are approximate, since during preparation of soot suspension in toluene it was not possible to obtain a suspension containing fully isolated particles of soot, which affects the magnitude of the total surface on which adsorption can occur.

Stabilization of Soot — Toluene Suspension Using Nickel Dioctadecyldithiophosphate

The above mentioned experiments fully prove that molecules of additive of the dialkyldithiophosphates type are adsorbed from hydrocarbon solutions onto particles of soot, which causes stabilization of such a suspension.

Stabilization of soot — toluene suspension was studied by two methods. By the first method was determined time of total deposit of soot (channel) from suspension in special cylinders or during centrifuging in a centrifuge supplied with a temperature adjustment device. By the second method was determined relative change of concentration of soot in suspension in time by means of measurement of optical density of suspension. Results obtained by the first method are presented in Table 2. For centrifuging 10 cm^3 suspension were taken; revolutions of centrifuge per minute were 1500; temperature of centrifuging was 20°.

Table 2. Stabilization of Soot--Toluene Suspension with the Help of Additive Nickel Di-n-octadecyldithiophosphate Concentration of Soot 0.013%

No. experiment	Concentration of additive, %	Time of total deposit of soot, minutes
1	Without additive	15
2	0.01	50
3	0.1	142
4	1.0	170
5	1.5	100
6	1.8	100

From data of Table 2 it is clear that time for total deposit of soot during centrifuging may be increased by addition of 1% of additive from 15 to 142 minutes, i.e., almost 10 times. Stabilizing effect of additive depends on its concentration. It is interesting besides to note that increase of concentration of additive above a certain optimum value (1%) leads to lowering of stability of suspension. As was shown [23], total action of additives of this type, determined by tests on PZV setup, also depends on concentration of additive, and the optimum corresponds concentration of approximately the same order.

Results obtained by the second, more objective method of determination of stability of suspension are of great interest.

According to law of Bouguer-Lambert-Beer the absorption of luminous flux passing through a layer of solution depends on thickness of this layer and concentration of solution. In the case of suspensions the following relationship was established [30]:

$$2{,}3D = \frac{\pi C l r^2}{\varphi},$$

where D — optical density, equal to $\lg \frac{I_0}{I}$ (I_0 — intensity of incident luminous flux; I — intensity of luminous flux, passed through layer of suspension); C — particle density in suspension; l — thickness of layer; r — average radius of particles; φ — density of dispersion medium.

Thus is observed a direct relationship between optical density and concentration of particles of suspensions. We measured the relative change of optical density of suspension in time, by which it was possible to judge relative change of concentration of suspension and, consequently, time needed for its deposit.

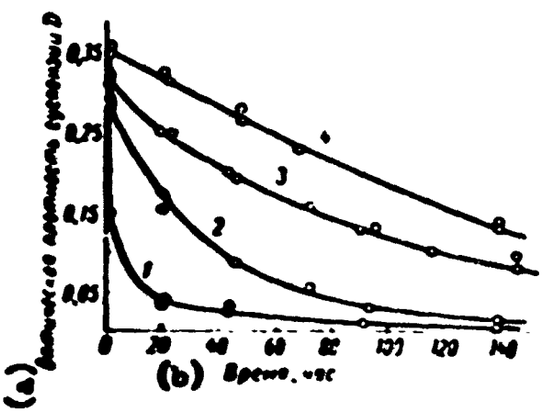


Fig. 6. Dependence of optical density of suspension (concentration of suspension) of soot in toluene on time needed for deposit.
1) soot — toluene suspension; 2) suspension containing nickel di-n-butyldithiophosphate $[(C_4H_9O)_2PSS]_2Ni$; 3) suspension containing nickel di-n-decyldithiophosphate $[(C_{10}H_{21}O)_2PSS]_2Ni$; 4) suspension containing nickel di-n-octadecyldithiophosphate $[(C_{18}H_{37}O)_2PSS]_2Ni$.
KEY: (a) Optical density of suspension D; (b) Time, hours.

After preparation the suspension (concentration of soot 0.0025%) was held in special cylinders in state of rest for a definite time, after which using a photoelectrocolorimeter FEK-M the optical density of upper layer of suspension (10 ml) was determined.

In the case of a suspension not containing additive (Fig. 6, curve 1), its optical density as soon as the first 20 hours drops to a value which is close to the optical density for pure toluene (order of 0.05); in other words, during this time particles of soot are practically completely precipitated in the taken volume of suspension.

In the presence of dialkyldithiophosphates the suspension is stabilized, the precipitation of particles of soot is delayed and correspondingly the change of optical density in time decreases. The obtained data also indicate that stabilizing effect of dialkyldithiophosphates increases with increase of length of hydrocarbon radicals contained in their molecule.

Disulfide of $(C_{18}H_{37}O)_2PSS\text{-}SSP(C_{18}H_{37}O)_2$, having a structure analogous to that of dialkyldithiophosphates, but not contained in molecule of metal and accordingly not possessing detergent action [23], almost does not stabilize suspension; the curve of change of optical density in this case is close to the corresponding curve for a pure suspension (curves 1 and 2, Fig. 7).

Zinc di-n-octadecyldithiophosphate is a less active stabilizer than corresponding dithiophosphate of nickel (curves 3 and 4, Fig. 7) which also is in accordance with their evaluation as detergent additives.

As was shown above, low-molecular nickel dialkyldithiophosphates, for instance nickel di-n-butyldithiophosphates, stabilize soot — toluene suspension in a smaller degree than do high-molecular dialkyldithiophosphates, although this dialkyldithiophosphate is adsorbed onto particles of soot in this case in a relatively larger quantity than nickel di-n-dioctadecyldithiophosphate. The number of molecules of nickel di-n-butyldithiophosphate adsorbed onto one particle of channel black, was approximately 2 times, and on one particle of thermal soot 3 times more than the number of molecules of di-n-octadecyldithiophosphate. However, hydrocarbon radicals of di-n-octadecyldithiophosphate are almost 5 times longer than hydrocarbon radicals of di-n-butyldithiophosphate, which has a decisive value. Apparently, only sufficiently long hydrocarbon radicals create the necessary oleophilousness of a particle covered by an adsorptive layer.

On the basis of obtained results of investigation the mechanism of detergent action of additives may be represented in the following form.

While a motor operates in lubricating oil, as a result of oxidation and compacting of oil hydrocarbons, and also incomplete combustion of hydrocarbons of fuel products not soluble in oil products are formed, separate from the formed suspension and are stored in the form of carbon deposits, laquors, and scales on separate, usually the most heated motor parts.

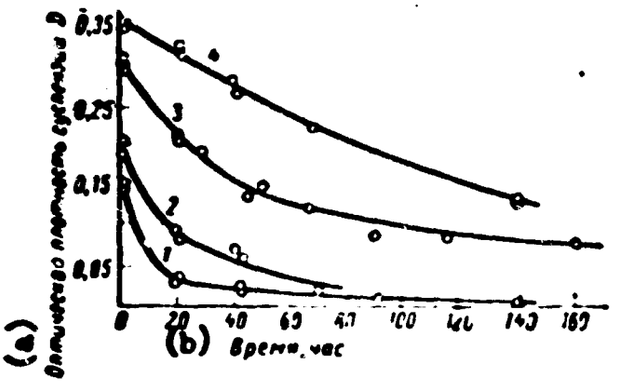


Fig. 7. Dependence of optical density of suspension (concentration of suspension) of soot in toluene on time needed for deposit.
1) soot — toluene suspension; 2) suspension containing disulfide, $(C_{18}H_{37}O)_2PSS$ — $SSP(CC_{18}H_{37})_2$; 3) suspension containing zinc di-n-octadecyldithiophosphate, $[(C_{18}H_{37}O)_2PSS]_2Zn$; 4) suspension containing nickel di-n-octadecyldithiophosphate $[(C_{18}H_{37}O)_2PSS]_2Ni$.
KEY: (a) Optical density of suspension D; (b) Time, hours.

Additives of the considered type, to which should belong certain salts of organic acids, alkylphenolates, sulfonates, and dialkyldithiophosphates, are surface active materials which are adsorbed from a hydrocarbon medium (oil) onto the surface of insoluble particles, preventing, thereby, their adhesion (agglomerating) into bigger particles and precipitation from butyric suspension. The formed big agglomerates, in which small particles are combined by relatively insecure molecular cohesive forces, can in the presence of additives be destroyed and dispersed. The metallic surface of a motor, being in contact with oil, is covered by an adsorptive layer of molecules of additives which also prevents the deposit onto this surface of insoluble products. It is possible to consider at the same time that part of the loose deposit already formed on the surface will be suspended as a result of adsorption of additive and opening of cohesion surfaces of particles by adsorptive layers (two-dimensional pressure adsorption layers according to P. A. Rebinder).

Total action of additives is concluded, consequently, in increase of dispersiveness of butyric suspension which forms during operation of motor, and stabilization of this suspension. In other words, the process of adsorption dispersion of products not soluble in oil is observed. Since during adhesion of particles (flocculation) in oil relatively loose aggregates are formed, their dispersion can be considered peptization [31].

In cases when butyric suspension gets in the most heated parts of the motor, and the additive is insufficiently surface active, desorption of the additive occurs; the dispersed phase turns out to be insufficiently protected, insoluble particles are connected in relatively big aggregates (flocculation), and are precipitated onto the metallic surface [17, 18].

Consequently, the "detergent" action of additives can be considered as dispersive (or peptizing) action and correspondingly detergent additives should be called dispersers (or peptizers).

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MECHANISM OF ACTION OF DETERGENT AND ANTIOXIDANT ADDITIVES IN LAQUOR DEPOSITION (Working Hypothesis)

K. K. Papok

During contact of hydrocarbons with metal heated to a high temperature, carbon substances are formed precipitating onto surface of metal in the form of a thin strong layer, which is called laquor deposit, or laquor.

Laquor deposits are products of the oxidation of hydrocarbons. The speed of their formation depends on a whole series of factors, including temperature of heating, catalytical action of metal, character of contact of hydrocarbons with surface (in liquid form or in vapor form), and also on chemical composition of the hydrocarbons.

The chemical composition of laquor deposits is inconstant and depends upon the above factors, and also length of process. In the composition of laquor can be the most diverse relationships among the following products: initial product, resin, oxy-acid, asphaltenes, carbenes, and carboids.

In an internal-combustion engine laquor deposits are formed mainly on the lateral and internal walls of pistons and on the heads of connecting rods. The appearance of the laquor deposits very harmfully affects reliability of work of engine, economy, and service life. Laquor deposits in most cases are the cause of

scorching of piston rings. Laquor in the engine can be formed due to three causes: 1) oxidation of film of oil on surface of heated part; 2) deposit from oil onto surface of part of products of oxidation and incomplete combustion formed in other places of the engine, and 3) condensation of products of oxidation of fuels and oils from gases penetrating from combustion chamber into crankcase.

In this work only the first case is condisered.

Features of Oxidation of Oil in Flow and at Rest

In an internal-combustion engine oxidation of oil in film on heated parts take place in two principally different conditions — in dynamic and static conditions, i.e., in flow and at rest.

In flow, oil is oxidized during operation of engine, when as is known, a continuous circulation of lubricating oil is carried out and parts of the engine are always being washed by new portions of oil. Oxidation of oil at rest occurs only when the engine is stopped, when circulation of oil ceases, and the parts for a definite time after stop of motor still preserve a sufficiently high temperature. And although at rest the oil on heated parts is by time significantly less than in flow, oxidation of oil in static conditions essentially affects laquor deposition in motors.

It is well-known that on parts lubricated by oil a boundary layer from oriented molecules of oil will be formed. Also it is well-known that the more polar-active molecules are more easily adsorbed onto surface of metal, displacing the less active molecules. When along a heated metallic surface moves a layer of oil, then adsorbed layers of oil are not touched. Molecules of oils appearing in boundary layer are held strongly on surface of metal, as if in a welded state. And only when in moving layers of oil there turn out to be more polar-active molecules than molecules which are in the boundary layer, there occurs displacing of molecule from boundary layer into flow.

Thus can in known measure can the boundary layer be renewed until under the action of temperature, atmospheric oxygen and catalysis of metal, molecules in the boundary layer will not undergo essential changes.

Products of oxidation of hydrocarbons: resins, oxy-acids, and asphaltenes are more polar-active than hydrocarbons, and therefore, it is natural that with oxidation of boundary layer of oil the products of oxidation which are formed will be more strongly held on the surface than the adsorbed layer from unchanging molecules of oil. In time the boundary layer of oil turns into laquor.

Thus, during oxidation of oil in flow only the boundary layer of oil is subjected to deep oxidation. In conditions of rest occurs in principle an excellent picture of oxidation of oil in a film.

First, laquor deposition precedes evaporation of a significant quantity of oil; for instance, depending upon fractional composition of the oil, in 30 minutes can be evaporated up to 80-90% oil from that remaining in the form of film on surface of part. Consequently, into formation of laquor go the heaviest fractions of oil and all alien insoluble substances located in the oil.

Secondly, if in conditions of flow restoration of molecules of oil in boundary layer is possible, then in conditions of rest similar replacement is practically excluded.

During oxidation of film of oil in conditions of rest a decisive role belongs to fractional composition and, as will be shown somewhat later, antioxidant properties.

In conditions of rest laquor deposition depends greatly on thickness of butyric layer. The thinner the butyric layer, the faster and at lower temperature can it be turned into laquor. On oils of light fractional composition owing to their great volatility while the engine is stopped on the parts are formed more films of oil than on oils of heavy fractional composition.

On the basis of what has been presented can be made the conclusion that oils of light fractional composition in conditions of frequent stops of motor have to be more unsafe with respect to fast laquor deposition than oil of heavy fractional composition. This position subsequently was confirmed by experiment.

Mechanism of Action of Additives During Laquor Deposition

The most effective means of combatting laquor deposition in motors is application of detergent and antioxidant additives in oils.

Under the general name of antioxidant additives are known additive of two types:

a) additives delaying start of oxidation of oil which is in a thick layer (in the system), or otherwise increasing induction period of oxidation. Such additives usually act at moderate temperatures (not higher than 150-200°). They are used in turbine, transformer, instrument, and other similar oils;

b) additives preventing oxidation and decomposition of oils which are in a film (thickness approximately up to 200) on metallic surface at high temperature (approximately from 150 to 300°). Similar additives are used mainly in motor oils. We agree to call them thermal additives. Subsequently, talking about antioxidant additives, we consider only thermal additives.

Not claiming complete knowledge of so complicated a phenomenon, as laquor deposition in a motor, for explanation of distinction in action of detergent and antioxidant additives in laquor deposition on a metallic surface (questions of behavior additives in volume in this work are not considered) a working hypothesis is offered, founded on the following positions.

1. During operation of motor on oil containing a sufficient quantity of additive, on the whole surface of parts of motor lubricated by the oil will be formed a solid boundary layer from adsorbed molecules of additive, which completely insulates molecule of hydrocarbons from contact with metal.

2. Effectiveness of action of additive depends on two factors: period of life of molecules of additive on heated surface, i.e., on their thermo-oxidizing stability and character of products for men during oxidation of molecules of additive.

We consider that the observed detergent effect occurring here, and the fact that after operation of motor on oil containing detergent additive, parts of the motor with a high temperature turn out to be clean and without any laquor deposit, are explained by the following.

Molecules of detergent additive, being adsorbed on parts of motor, form a strong protective layer which excludes any contact of hydrocarbons with metal.

The boundary layer from adsorbed molecules of detergent additive through a definite time under the action of high temperature, which catalyzes the influence of metal and atmospheric oxygen, undergoes changes leading to formation of dispersed phase which cannot be held to the metallic surface. In conditions of flow of oil (detergent effect appears only in dynamic conditions) the formed products of decomposition of molecules of additive are carried off, and the breach formed in the boundary layer is immediately replaced at the expense of new molecules of additive so that molecule of hydrocarbons as before turn out to be isolated from the metal by a living fence of molecules of the detergent additive (Fig. 1, III).

In this case, for protection of parts from formation of laquor deposits, the period of life of molecules of detergent additive on heated metallic surface does not have a decisive value and only will affect expenditure of additive. The faster in the given conditions a molecule of additive is destroyed, the higher should be its concentration in oil in order to obtain a detergent effect for an identical interval of time.

This, apparently, explains why even detergent additives with a very low thermo-oxidizing stability, such as calcium sulfonates, turn out to be effective, but only during a high concentration in oil.

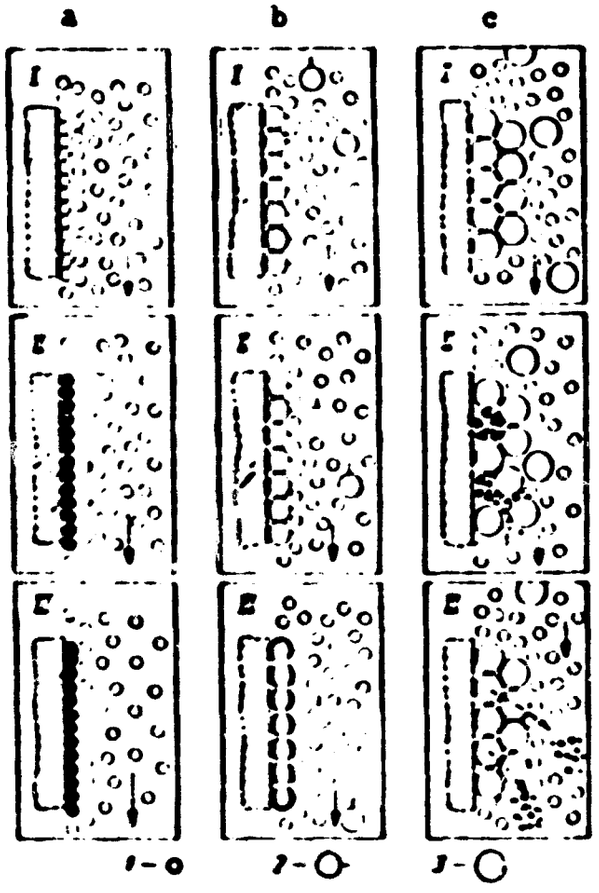


Fig. 1. Mechanism of action of antioxidant and detergent additives during laquor deposition.
1) molecule of oil; 2) molecule of antioxidant additive; 3) molecule of detergent additive. Figures I, II, III conditionally designate periods of time.

Speed of destruction of molecules of additives is also connected with speed of contamination of oil. A detergent additive with low antioxidant properties will contaminate oil faster than one with high properties (Fig. 2).

Molecules of antioxidant (thermal) additive, just as molecules of detergent additive, form on the parts a strong boundary protective layer, insulating the hydrocarbons from contact with metal. But, in distinction from molecules of detergent additive, under the action of high temperature which catalyzes the influence of metal and atmospheric oxygen, they form oxidation products possessing the ability to be firmly held on the metallic surface in the form of a characteristic laquor layer. Consequently, molecules of the antioxidant additive after their own destruction like "dead" bodies block the hydrocarbons' access to metallic surface (see Fig. 1, II). But the very fact of formation of a laquor layer is undesirable, since laquor deposits cause motor malfunction.

Therefore, for appraisal of quality of antioxidant additive, the period of life of its molecules on a heated metallic surface up to transformation into laquor has a decisive value. The effectiveness of an antioxidant additive is

proportional to the period of life of its molecules. The longer the boundary layer of molecules of antioxidant additive is kept, the more reliable will oil work in the motor.

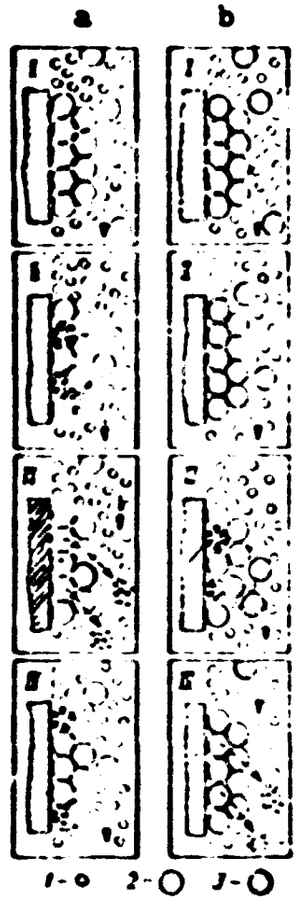


Fig. 2. Action of detergent additives possessing different antioxidant properties. 1) molecule of oil; 2) molecule of detergent additive with low antioxidant properties; 3) molecule of detergent additive with high antioxidant properties. Figures I, II, III and IV conditionally designate periods of time.

Molecules of antioxidant additives, adsorbed onto a metallic surface, have a larger period of life than those in the oil, and a larger period of life than a molecule of hydrocarbons to which the additive is added, otherwise it would not be necessary to talk about antioxidant properties of the additive.

Referring to the above material, it is possible to answer certain questions concerning additives.

Antioxidant additives are added to oil in small quantities, but detergent additives are added in large quantities because during operations of motor antioxidant additives are not expended on reduction of boundary layer on the parts, inasmuch as oxidized, decomposed molecules of additives remain on the parts in the form of laquor layer. Detergent additives during operation of motor are continuously expended on restoration of protective boundary layer, inasmuch as oxidized, decomposed molecules of additive are carried away from motor parts by flow of oil.

The high detergent properties of oil ensure cleanness of parts only during operation of motor, and when the motor is stopped the detergent action ceases, and oil with low antioxidant properties in conditions of rest in the most heated part of the piston (rings) will form rapidly a film of laquor layer. Furthermore, a detergent additive with low antioxidant properties will have a very short period of life on heated parts and, consequently, will rapidly abrade. As a result oil will be severely contaminated by products of decomposition and oxidation of additive, which, with insufficient filtration, can promote rapid oxidation of oil, especially when the motor is stopped.

A highly effective additive with respect to preventing laquor deposition and scorching of piston rings should possess the following properties:

a) high polar activity, significantly exceeding activity of molecules of oil to which it is added;

b) high thermo-oxidizing stability, i.e., the biggest period of life under given temperature conditions;

c) during oxidation and decomposition products form which do not hold to part surfaces.

In oil it is more preferable to add one additive, a molecule of which combines high antioxidant and detergent properties, than two different additives — antioxidant and detergent, — since in the case of combination of additives the detergent component will have a smaller period of life than a complex additive, and, therefore, it will abrade faster. Furthermore, part of the detergent component will be expended on oxidation products of antioxidant, forming in the system under the action of high temperature.

PHOSPHOROUS-ORGANIC COMPOUNDS REDUCING WEAR DURING FRICTION. MECHANISM OF THEIR ACTION

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We consider certain results of the investigation of the mechanism of action of additives lowering friction (coefficient of friction) and decreasing wear of metallic friction surfaces in conditions of high loads.

Additives of this type, which are sometimes called additives for super-high pressures, in most cases are organic compounds of chlorine, sulfur, and phosphorus. It was shown [1, 2] that especially active additives are phosphorous organic compounds containing chlorine or sulfur.

It is necessary to consider as fixed two facts about the mechanism of action of additives of the phosphorous organic compound type. First, additives of this type in conditions of friction at increased temperatures chemically react with metals of friction surfaces and, secondly, as a result of this reaction are formed compounds of phosphorus with metals, apparently, of the phosphide type [3-5].

For a deeper understanding of the mechanism of action of additives reducing wear, it is essential also to know how complicated organic compounds, for instance, trialkylphosphites, can in conditions of friction at increased temperatures form relatively simple compounds with metals — metal phosphides. This question could

be resolved only be detailed investigation of those transformations which synthetic additives undergo in conditions of increased temperatures.

Thermal Decomposition of Trialkylphosphites

We attempted to study thermal decomposition of trialkylphosphites, which, as the preceding investigation showed, are typical additives which reduce wear during friction. In literature this question is absolutely not dealt with. There is only one work by Zimmerman [6], dating to 1875, in which the author conducted decomposition of ethyl ester of phosphorous acid to determine the structure of this ester. After heating of phosphite in a sealed tube, in the products of decomposition by qualitative reaction using silver nitrate hydrogen phosphide was revealed. On the basis of this qualitative experiment Zimmerman made the assumption that the decomposition of triethylphosphite occurs with simultaneous formation of phosphorous acid and hydrogen phosphide.

We studied thermal decomposition of trioctadecylphosphite $(C_{18}H_{37}O)_3P$, tributylphosphite $(C_4H_9O)_3P$, and tributyltrithiophosphite $(C_4H_9S)_3P$.

Phosphites were obtained by the usual methods. Tributylphosphite and trioctadecylphosphite were obtained by reaction of corresponding alcohols with phosphorus trichloride in the presence of pyridine; tributyltrithiophosphite by reaction of butyl mercaptane with phosphorus trichloride in the presence of pyridine.

In Table 1 are given characteristics of the obtained phosphites.

Table 1. Characteristics of Phosphites

Formula	Melting point, °C	Boiling point, °C (pressure, mm Hg)	d_4^{20}	n_D^{20}
$(C_{18}H_{37}O)_3P$	55.0—56.0	—	—	—
$(C_4H_9O)_3P$	—	90—91(1)	0.9225	1.4320
$(C_4H_9S)_3P$	—	150—152(1)	1.0121	1.5439

The first experiments showed that during decomposition of trialkylphosphites phosphorous acid and hydrogen phosphide — phosphine —, and also unsaturated hydrocarbon corresponding to the alkyl groups of phosphite are indeed formed.

Thus, was confirmed the assumption of Zimmerman about the decomposition of triethylphosphite. Thermal disintegration of trioctylphosphite and tributylphosphite may be represented in the form of the following equations:

$$4(C_{18}H_{37}O)_3\,P \rightarrow 3H_3PO_4 + PH_3 + 12C_{18}H_{36}$$

$$4(C_4H_9O)_3P \rightarrow 3H_3PO_4 + PH_3 + 12C_4H_8$$

During decomposition a unique reaction takes place — simultaneous oxidation and reduction of trivalent phosphite phosphorus with formation of phosphorous acid and phosphine. The possibility is not excluded that in the beginning occurs detachment of unsaturated hydrocarbon (octadecyl and butylene) and then the known reaction of decomposition of phosphorous acid with formation of phosphorous acid and phosphine:

$$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3.$$

Somewhat more complicated is the reaction of decomposition of tributyltrithiophosphite, which suppositionally can take place according to:

$$4(C_4H_9S)_3P \rightarrow 3H_3PS_4 + PH_3 + 12C_4H_8$$

$$2H_3PS_4 \rightarrow 3H_2S + P_2S_5$$

In this case, in the products of reaction, besides phosphine and butylene, hydrogen sulfide was revealed.

Quantitative experiments of thermal decomposition of phosphites were conducted in the instrument schematically depicted in Fig. 1.

The reactor of the instrument was a retort of around 30cm^3, capacity prepared from quartz glass, supplied with a pocket for a thermometer and a tube for the nitrogen feed. Prior to entering the reactor the nitrogen was freed from traces of oxygen (alkaline solution of pyrogallol) and was dried (sulfuric acid). The upper drawtube of the retort was connected with a reflux condenser, which in turn

was connected with a spiral condenser serving to catch the liquid products of decomposition, and two absorbers with a solution of potassium permangante for determination of phosphine. The last absorber was joined with a drexyl phial, containing a solution of silver nitrate which was necessary to control fullness of absorption of phosphine in absorbers. All parts of the instrument were connected using thin sections.

The reactor was heated using Wood's alloy. The condenser of the reactor was cooled by ice water.

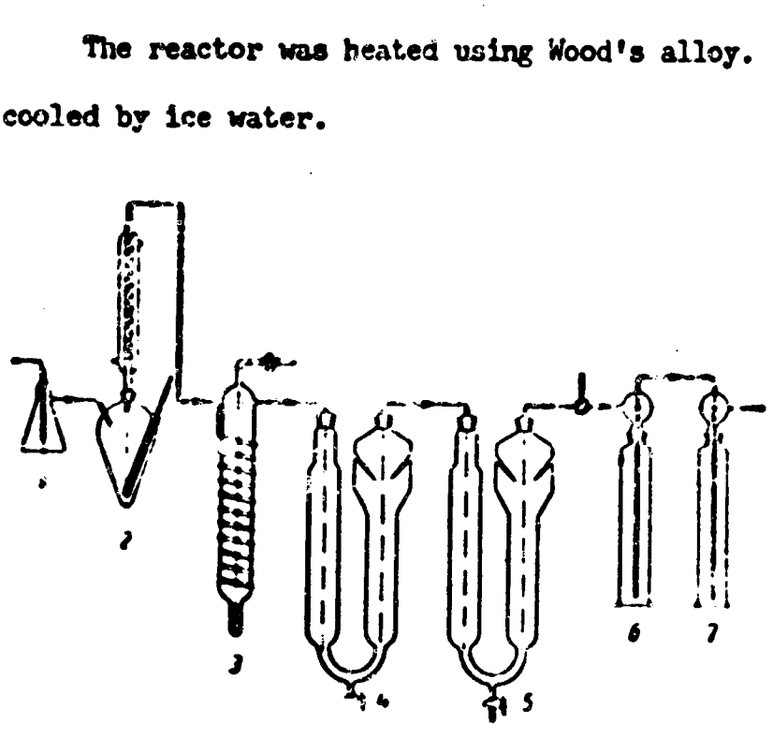


Fig. 1. Diagram of instrument for thermal decomposition.
1) safety phial; 2) reactor; 3) capacitor; 4 and 5) absorbers with solution of potassium permanganate; 6) safety Drexyl phial; 7) Drexyl phial with solution of silver nitrate.

The reaction of phosphite decomposition was conducted in the following manner.

Into the reactor was loaded a definite quantity of phosphite, in the majority of experiments 0.02 mole, or 17 g in the case of trioctadecylphosphite and 5 g in the case of tributylphosphite. Then in a current of dry nitrogen the phosphite was heated. Decomposition started at a temperature of 250-260°. In the case of tributylphosphite was observed a prolonged induction period — only after heating of phosphite at the experiment temperature for 2 hours did its decomposition start. The end of the decomposition was established by the absence of phosphine in the sample of gas (nitrogen) removed from the spiral condenser; for a qualitative reaction to phosphine a 1% aqueous solution of silver nitrate [7] was used.

Decomposition of Trioctadecylphosphite

During decomposition of trioctadecylphosphite will be formed phosphorous acid, phosphine, and octadecylene. Phosphorous acid and octadecyl remained in the reactor, but the gasiform phosphine was caught by the absorbers. In separate experiments there were also small quantities of undecomposed phosphite.

The quantitative determination of phosphine was conducted by means of its oxidation in phosphorous acid by potassium permanganate in an acid medium [8]. Oxidation of phosphine by nitric acid (specific gravity 1.4) [9] in our case gave the worst (understated) results.

For oxidation of phosphine exactly 215.5 cm^3 0.5N solution of potassium permanganate and 64.5 cm^3 40% sulfuric acid were taken. Each of the two absorbers was filled with 140 cm^3 of the obtained solution. Upon completion of the experiment of decomposition the contents of the absorbers was quantitatively transferred to a one-liter glass (residues of solution in the absorber were washed off by a definite quantity of a 0.5N solution of oxalic acid) and unreacting potassium permanganate was back-titrated by 0.5N solution of oxalic acid.

The remainder in the reactor, containing phosphorous acid and octadecyl, was processed by water and diethyl ester.

Phosphorous acid in aqueous solution was quantitatively determined by precipitation by molybdenum-acid ammonium with subsequent obtaining of ammonium-magnesium salt of phosphorous acid, and also during the direct obtaining of ammonium-magnesium salt.

Octadecylene was separated from the ether solution. Ether solution was dried by anhydrous sodium sulfate and then, after filtration and distillation of solvent the remainder was distilled in a vacuum.

The separated substance had following characteristic:

boiling point 139° at 2 mm Hg;

$d_4^{20} = 0.7903$, $n_D^{20} = 1.4471$;

MR_D found 84.51.

$C_{18}H_{36}$ calculated 84.86.

Analysis

Found (in %): C 85.63, 85.69; H 14.43, 14.33.

$C_{18}H_{36}$. Calculated (in %): C 85.63; H 14.37.

Characteristics of the obtained substance correspond to α-octadecyl, for which in literature is shown a boiling point of 179-180° at 18 mm Hg, $d_4^{20} = 7910$, $n_D^{20} = 1.4443$ [10].

According to equation of decomposition reaction of trioctadecylphosphite, mentioned above, from 17 g trioctadecylphosphite should be formed 0.1721 g phosphine, 1.4885 g phosphorous acid and 15.3390 g octadecylene. In our experiments we managed to determine 90-100% phosphine, around 85% phosphorous acid, and around 70% octadecylene, in conversion to the quantity of these substances required according to the equation.

These data fully confirm correctness of reaction equation offered for decomposition of trioctadecylphosphite.

Decomposition of Tributylphosphite

In experiments of decomposition of tributylphosphite the formed phosphorous acid was determined just as during decomposition of trioctadecylphosphite. The butylene was able to be separated, using in the above described instrument two condensers, cooled to -30°. In these conditions butylene, having a boiling point of -5°, was liquified in the condenser, but phosphine (boiling point -85°) together with nitrogen passed into the absorbers with a solution of potassium permanganate where it was determined.

For identification of butylene dibrombutane was obtained from it by action of bromine. Butylene slowly was evaporated from the condensers into two entrainment separators with glass cap, each containing 10 cm^3 bromine, at a temperature of -5 to -10°. Residues of butylene were displaced by nitrogen. Upon completion of reaction the surplus of bromine was removed by treatment by a 3% aqueous solution of caustic soda. The ether solution of bromide was washed by water to a neutral reaction and was dried by calcium chloride. After distillation of solvent the remainder was distilled in vacuum.

The obtained bromide had the following characteristics:

boiling point 158.0-159.0°; $d_4^{20} = 1.7886$.

Analysis

35.98 milligram subs.: 6.68 ml. 0.025N $Hg(NO_3)_2$

31.79 milligram subs.: 13.50 ml. 0.025N $Hg(NO_3)_2$

Found (in %): Br 74.19, 74.04.

$C_4H_8Br_2$. Calculated (in %): Br 74.01.

Characteristics of bromide correspond to 2.3-dibrombutane, which, judging by source material [11], has a boiling point of 157.3°, $d_4^{20} = 1.7916$. During decomposition of phosphite will be formed butylene with a double bond in position 2-3 [12].

Quantitative determination of butylene in experiments was conducted by means of measurement of its volume liquified in entrainment separator of condenser which gave approximate values, and by analysis of unliquified gas containing nitrogen in addition to butylene.

According to the reaction equation of the decomposition of tributylphosphite, from 5 g phosphite should be formed 0.17 g phosphine, 3.36 g butylene, and 1.47 g phosphorous acid. In experiments of full decomposition of phosphite, just as in experiments of decomposition of trioctadecylphosphite, 90% phosphine and 85% phosphorous acid was determined from the shown quantities; the quantity of determined butylene was around 60%.

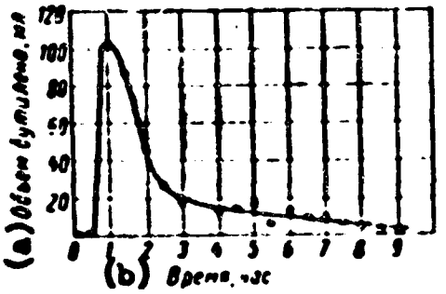


Fig. 2. Thermal decomposition of tributylphosphite. Temperature of experiment was 270°.
KEY: (a) Volume of butylene, ml; (b) Time, hours.

In experiments of the decomposition of tributylphosphite, in the intermediate condenser was stored a small quantity (of the order of 0.3-0.5 cm^3) easily volatile liquid, which was not investigated by us.

In one of the experiments was studied kinetics of decomposition of tributylphosphite. Occurrence of the reaction of decomposition was determined by the quantity of butylene formed. The gas, consisting of nitrogen and butylene*, was taken directly during the experiment for analysis (butylene was determined by absorption by an 83% solution of sulfuric acid in VTI** apparatus and gathered in Mariotte phials. Decomposition was conducted at 270°. After 10 hours the quantity of butylene formed constituted 85% of the quantity of butylene required according to the reaction equation.

In Fig. 2 is given the curve of dependence of decomposition of tributylphosphite (with respect to butylene) on time. Intense decomposition of tirbutylphosphite sets in after achievement of temperature of decomposition (270°) and is practically finished in the first 2 hours of the experiment.

The basic reaction of the decomposition of tributylphosphite is analogous to the reaction of the decomposition trioctadecylphosphite and, apparently, is common to the thermal decomposition of trialkylphosphites.

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*Phosphine in this experiment was reduced powdery iron, taken with large surplus (see experiments on decomposition of phosphites in the presence of metals).

**Ed. Note: VTI = F. Dzerzhinsky All-Union Heat Engineering Institute.

Decomposition of Tributyltrithiophosphite

The thermal decomposition tributyltrithiophosphite goes in the same manner as the decomposition of trialkylphosphites, with the formation of butylene and phosphine. However, the reaction here is complicated by the presence of sulfur phosphite in the molecule; qualitatively in the products of decomposition were revealed phosphine, hydrogen sulfide, and butylene.

Thus, the study of thermal decomposition of phosphites leads to the conclusion that at temperatures of the order of 250-280° phosphites undergo transformation, as a result of which are formed relatively simple and at the same time very reactive phosphine compounds, and in the case of tributyltrithiophosphite, hydrogen sulfide.

It was possible to assume that owing to the phosphine and hydrogen sulfide forming at increased temperatures, phosphide, sulfide, or phosphide-sulfide films are formed on metallic surface of friction. Formation of iron sulfide during action of hydrogen sulfide obtained during decomposition of trialkyltrithiophosphites does not require proof. Formation of phosphides of metals was established directly by experiments of thermal decomposition of tributylphosphite in the presence of metals.

Decomposition of Trioctadecylphosphite in the Presence of Metals and their Oxides

Decomposition of trioctadecylphosphite in this case was conducted in that same instrument and with those absorbers as decomposition of trioctadecylphosphite in the absence of metals.

In every experiment, into the reactor was loaded 4 g octadecylphosphite and 4 g metal or oxidized metal. Powdery reduced iron and copper were tested, and also powdery copper oxide (CuO) and mixed oxide of iron (Fe_3O_4).

Results of experiments are given in Table 2.

Table 2. Thermal Decomposition of Trioctadecylphosphite in the Presence of Metals and Their Oxides

No. experiment	Metal or oxide of metal	Conditions of decomposition		Quantity of free PH_3, %
		Duration, hours	Temperature, °C	
1	Fe	3.5	250—260	6.0
2	Fe_3O_4	4	250—260	7.5
3	Fe_3O_4*	4	250—250	37.5
4	Cu	2	210—225	10.0
5	CuO	3	250—260	0.0

*In granules.

In the last column is given percentage of free phosphine with respect to quantity of phosphine required according to the equation of decomposition of trioctadecylphosphite (taken to be 100%). Free phosphine, unreacting with metal, was determined by the usual means — oxidation by a solution of potassium permanganate, as shown above. From data given in Table 2 it follows that the main part of the phosphine formed during the decomposition of trioctadecylphosphite reacts with iron, copper, and their oxides, giving the corresponding phosphides of the metals iron and copper. In all experiments the quantity of definite free phosphine was insignificant. Granulated iron oxide (experiment 3), possessing a less well-developed surface than powdery iron (experiment 2), as one should have expected, could not take up all the separated phosphine which gave an increased yield of free phosphine.

After decomposition of trioctadecyl, the remainder in the reactor, a hard mass, was processed by ether, benzene, and alcohol to remove organic compounds — undecomposed trioctadecylphosphite, octadecylene, and, possibly, other products of decomposition.

The remaining powdery mass was processed by hot water to remove the phosphorous acid (phosphides of iron and copper are not decomposed by water at heating up to 100°) and was washed by alcohol.

In the purified powdery mass, the phosphides were qualitatively determined by decomposition by a 40% solution sulfuric acid with formation of phosphine (reaction with silver nitrate and oxidation by a solution of potassium permanganate).

In the second experiment (see Table 2) phosphorus phosphide in a mixture of iron and phosphide was quantitatively determined by the weight method.

Decomposition of trioctadecylphosphite took place in the same temperature interval (250-260°), as did the decomposition of trioctadecylphosphite in the absence of metals and their oxides. The only exception was the experiment with reduced powdery copper. In this case decomposition of trioctadecylphosphite occurred at a lower temperature (210-225°) and with a greater speed. Obviously, the reduced copper renders a catalytical action on the decomposition of trioctadecylphosphite.

Decomposition of tributylphosphite in the presence of iron and copper, and also their oxides, as in the case of trioctadecylphosphite also proceeds with the formation of phosphides. The temperature of decomposition of tributylphosphite in the presence of copper (and oxide of copper) was still lower than during the decomposition of trioctadecylphosphite, and in certain experiments constituted 140-190°. Here, besides the basic reaction which takes place with the formation of phosphorous acid, phosphine and butylene, side reactions were observed. The decomposition of tributylphosphite in the presence of metals took place without an induction period.

The obtained results indicate that the phosphine forming during the thermal decomposition of trialkylphosphites in the presence of iron, copper, and their oxides, will form phosphides of iron and copper. It is possible that during the influence of such a strong reducing agent as phosphine, oxides in the beginning

are reduced to metals which then from phosphides. It is possible to allow also that phosphine at increased temperatures is decomposed into phosphorus and hydrogen, and then phosphorus with metal gives phosphide.

Conclusions

1. Synthetic additives of the trialkylphosphites and trialkyltrinitrophosphites types, at a definite temperature of the order of 250-260° are decomposed with formation of simpler compounds. For tributylphosphite the thermal decomposition may be expressed by the equation

$$4(C_4H_9O)_3P \rightarrow 3H_3PO_4 + PH_3 + 12C_4H_8$$

For trialkylphosphites this may be expressed by the general equation

$$4(C_nH_{2n+1}O)_3P \rightarrow 3H_3PO_4 + PH_3 + 12C_nH_{2n}$$

Trialkyltrithiophosphites at increased temperatures undergo an analogous transformation, but in this case along with the phosphine and unsaturated hydrocarbon hydrogen sulfide will be formed.

2. In the presence of metals and their oxides (Fe, Fe_3O_4, Cu, CuO) thermal decomposition goes according to the above equation, but here the main part of the phosphine which forms reacts with metals (and their oxides), forming phosphides of metals.

Metals (copper) catalytically affect decomposition of phosphites: decomposition starts at a lower temperature and goes with greater speed.

3. Mechanism of action of additives of the trialkylphosphites type.

Trialkylphosphites are adsorbed onto metallic friction surfaces from butyric solution. In conditions of boundary friction, under high loads the places of contact develop temperatures exceeding thermal stability of the trialkylphosphites. The trialkylphosphites are decomposed with formation of phosphine, which reacts with metal (or oxide of metal) of the friction surface, forming a phosphide of this metal.

4. Trialkyltrithiophosphites in conditions of increased temperatures are decomposed with formation of phosphine and hydrogen sulfide, which correspondingly give a phosphide and sulfide of metal. Since iron sulfide is melted at a higher temperature (1193°) than eutectic mixtures of phosphides of metal, the phosphide-sulfide film which is formed can show its action under various regimes of friction, like both a phosphide, and a sulfide film. By this is explained more the active action of additives of trialkyltrithiophosphites as compared to trialkylphosphites.

5. Hydrocarbon radicals of trialkylphosphites and trialkyltrithiophosphites under thermal influence split off, forming unsaturated hydrocarbons, and, thus, do not participate in chemical reaction with metal. Hydrocarbon radicals ensure solubility of phosphite in hydrocarbon medium — oil — and depending upon structure can in this or that degree increase total surface activity of molecule of phosphite which has a value during adsorption of phosphite onto surface of metal.

6. Additives of other types than trialkylphosphites will undergo other chemical transformations on a metallic friction surface. However, common for mechanism of action of additives of all types is the fact that all additives, including organic compounds of chlorine, sulfur, phosphorus, and also organic chlorophosphorous and thiophosphorous compounds, at increased temperatures in conditions of friction undergo chemical transformations (are decomposed) with formation of relatively simple compounds — chlorine, hydrogen chloride, sulfur, hydrogen sulfide, phosphine and others. During reaction with metals of the friction surface these compounds will form chlorides, sulfides, and phosphides of metals.

7. Study of the action of phosphorous organic compounds on wear during friction gives a basis for scientific approach to synthesis and selection of antiwear additives. Consequently, it is necessary to synthesize phosphorous organic (or other) compounds which would be decomposed in a definite temperature

range depending on conditions of friction, giving the above simplest compounds. Substances decomposed below this temperature range, especially at temperature of lubricating oil in the system, will react with the metallic surface, but simultaneously they will cause corrosion of metallic parts of the machine as a result of decomposition of the additive. Conversely, too stable substances will not be decomposed and, consequently, will not be active in conditions of increased temperatures of boundary friction.

Investigations of conditions of thermal decomposition of synthetic additives and mobility of separate atoms in a molecule of additive have to serve as the basis for synthetic works in this region.

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NEW METHODS AND RESULTS OF INVESTIGATION OF ANTIWEAR AND ANTIFRICTION PROPERTIES OF LUBRICATING MATERIALS

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Introduction

For a long time the lubricating action of petroleum oils has been explained exclusively by the presence in them of surface active materials which are able to be adsorbed on a metal -- oil boundary. The influence on lubricating ability of petroleum oils of hydrocarbon components, which are their basic component parts, and also in what measure they can generate substances active with relation to the metal -- oil surface, until recently have remained essentially uninvestigated.

Investigation of severe steel on steel friction conditions showed that surface active materials are not able to prevent the strongest damages of friction surfaces, developed as a result their gripping and the processes of seizing and fusing which are a result of this. Prevention of direct contact of metal with metal for the conjugate friction surfaces under high contact pressures turned out to be possible in the presence of substances containing chemically mobile atoms of sulfur, chlorine, and phosphorus. Study of mechanism of action of additives, preventing seizing, scoring, and fusing of surfaces of friction led to the

investigation of the reaction of chemically-active components of oils with metals. Friction can take place under significant local increases of temperature which leads to decomposition of additives and chemical reaction between additives and metal. It was determined that under heavy conditions of friction on the steel surface are formed layers of submicroscopic thickness of inorganic compounds of iron with chlorine, sulfur and phosphorus.

Although in implicit form, it is assumed that oil is only a carrier of the additives -- a medium from which they can be drawn out. It remains unclarified how active a role in these processes of chemical modification of friction surfaces is played by the actual hydrocarbon medium and in what measure is changed receptivity of oils to additives depending upon their nature and properties. With this is connected the more general and important question about what chemical processes take place in the hydrocarbon media during heavy friction conditions, how intense they are, and how they influence friction. Inasmuch as during friction of metals their juvenile surface is uncovered and the process of friction itself can be accompanied by significant thermal effects, there exist all prerequisites for different chemical reactions on the friction surfaces.

At present on the basis of the development of simple and effective methods of separation of petroleum oils into structural-group fractions there were opened wide possibilites for systematic investigations of the influence of the composition of oil products on their lubricating action.

Results of study of antiwear and antifriction properties of petroleum oils, their component parts and mechanism of action of antiwear additives are published by me, M. D. Bezborod'ko and colleagues in a number of articles. After our first works investigations of antiwear properties of petroleum oils and their structural-group fractions were conducted by K. I. Klimov and G. I. Kichkin. The simplest regularities were found in experiments which were conducted in the air with nonpolar naphthene-paraffin fractions of oils of different origin. It turned out

that with a high degree of reliability are recorded critical loads provoking seizing at friction of steel to steel in a medium of petroleum oils. These loads of seizing are lowered with transition from more viscous to less viscous oils (comparison during constant temperature) with increase of temperatures and rates of slipping. An immaterial distinction between average-viscous and high-viscous naphthene-paraffin fractions separated from various Baku oils was established. Naphthene-paraffin fractions of low-viscosity oils of different deposits, and also viscous oils separated from oils Ural-Volzhskoe deposits significantly differ from them. For these oil products is characteristic a less severe seizing and easing of the treatment of friction surfaces after seizing.

Investigation of structural-group fractions of petroleum oils enriched by aromatic compounds, showed that there is a decisive value in the presence of sulfur organic compounds in them. It was noticed that many low-viscosity oils and structural-group fractions separated from them differ by increased receptivity to additives. They occupy a special position with respect to the seizing process in them. On the one hand, after a very short time (tens of seconds) on seizing conditions the hydrocarbon medium is oxidized, and resinous substances are formed in zones of friction; on the other hand, in low-viscosity oils the seizing regime, extremely dangerous for friction surfaces, is quickly cut off and the regime is less severe than in the case of viscous oils. If the latter are highly purified, then the seizing immediately obtains the character of fusing of friction surfaces. Forcing and suppression of oxidation by blowing O_2 and Ar through the lubricating media showed that presence of O_2 in friction zones exceptionally strongly influences friction at high contact pressures.

Molecular oxygen and products of oxidation of hydrocarbon not only act in the same direction as sulfur organic additives to oils, but also strengthen one another's action.

Recently there were investigated antiwear and antifriction properties of mixtures of isomers of hydrocarbons and individual hydrocarbons. They showed that in experiments with them are observed the same phenomena, which earlier were studied on structural-group fractions of low-sulfur petroleum oils. It follows from this that the behavior of oil products under heavy regimes of boundary friction is determined first of all by flow of conjugate reactions of oxidation of hydrocarbons and steel. The present report gives a strict foundation of this position.

Experimental Method

Many of our works in which were studied the above questions, were carried out on an MT-2 friction machine with a friction unit through which it is possible to blow different gases. However, this installation does not ensure a sufficiently wide change of temperatures, rates of slipping, and contact pressures. In it is used an open friction unit which does not give the possibility to conduct experiments in strict conditions with inert and other pure gases; in it, it is impossible to conduct tests in a vacuum and to work with lubricating materials, which are obtained or are distilled outside contact with oxygen. Resolution of these problems was made on an MT-4 friction machine (construction of V. I. Drandin and A. A. Konstantinov). Machine MT-4 was adjusted by P. T. Pavlovskaya and Ya. Ya. Podol'skiy. In Fig. 1 is shown fundamental diagram of a vacuum high-temperature friction machine.

Loading the friction unit and change of load is carried out with the help of a standard piston manometer 1. Pressure from it is transmitted by oil filling pipeline 2, to piston 3 in load chamber 4. Cup with spheres and tested lubricant rests on piston 3 by means of ball and thrust bearings, among which is placed a thermoinsulating disk 5. Changeable piston 3 are used for expansion of range of axial loads; they have a cross section area of 7.5 and 15 cm^2. This allows axial loads of from 7.5 to 5000 kg on friction unit.

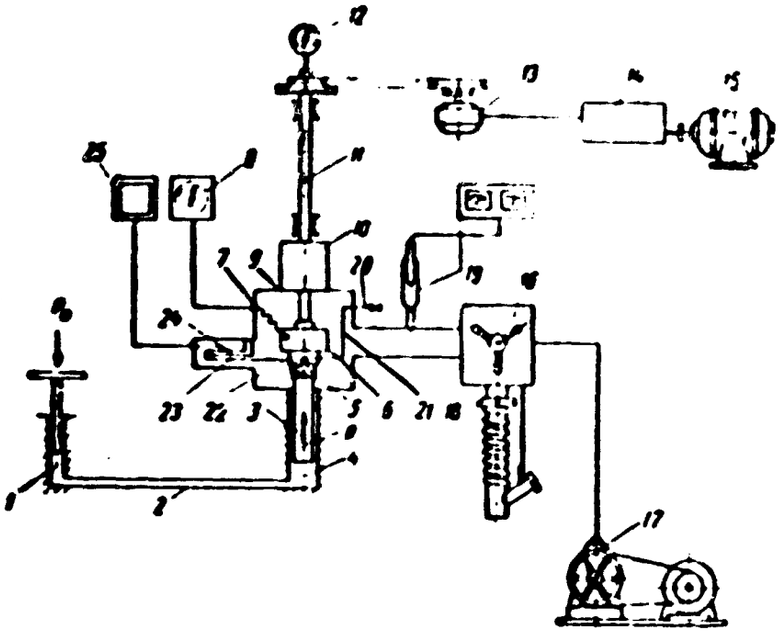


Fig. 1. Diagram of a vacuum friction machine.

In friction unit 6 is a cup with three spheres and the test lubricating material. To regulate it on the cup is put a jacket, through which with the help of a circulating thermostat, liquid is expelled. This makes it possible to conduct experiments at a temperature up to 180-200°. The regulating liquid enters the jacket surrounding the cup with spheres through flexible hoses, not shown in Fig. 1.

If it is necessary to conduct the test at higher temperatures, then a radiation furnace is used, which is significantly more effective and more convenient than the electric heater applied in the MT-2 friction machine.

Current to the heating spiral of the radiation furnace is brought in along flexible wires, insulated by porcelain beads from terminal 7 (second terminal in Fig. 1 is not shown). Heating of friction unit is regulated with the help of a pyrometric electronic potentiometer 8 of the type EPV11-2T, connected to the circuit of the heating spiral. Transducer for that potentiometer is a Chromel-Konel thermocouple, the hot joint of which is placed in lubricant.

The friction unit is in a hermetically closed chamber 9. A special sealing

device 10 hermetically seals revolving shaft 11 from coming loose from chamber 9. Speeds of its rotation at which it is possible to carry out of the experiments, are changed from 50 to 3200 rpm. They are measured by tachometer 12. Shaft 11 is set into rotation by a v-belt transmission with removable pulleys from hydromotor 13, which is fed by oil from hydraulic pump 14. Adjustment of speed oil feed makes it possible to change speed of rotation of shaft of friction machine in the necessary manner. The hydraulic pump works from induction motor 15 1.7 kilowatts in capacity at 1420 rpm. Instead of hydrodrive, electric drive may be used with success.

Chamber 9 is joined by vacuum cock 16 with fore pump 17 (type RVN-20) and high-vacuum pump 18 (type TsVL-100). With the help of cock 16 it is possible to switch on vacuum pumps and to connect closed chamber with atmosphere. The fore pump creates a vacuum to 10^{-2} mm Hg; a vacuum to 10^{-5} mm Hg is attained during operation of pump TsVL-100 for 5-7 minutes to measure the vacuum, vacuum gage 19 of the VIT-1 type is used.

In the chamber in which the friction unit is, can be created gas media of different composition. First a vacuum is created. Then is opened the valve closing off branch pipe 20, and through it into the chamber moves the appropriate gas. On the considered installation is foreseen the possibility of introduction into the friction unit of lubricating materials and additives to them, obtained or distilled in a vacuum and being in ampuls which prevents their contact with air.

It is possible not only to fill the chamber by gas of a definite nature, but also to blow the gas through the liquid lubricant which is in the friction unit. For that, introduction of tube 20 into the chamber is coupled with drilling in the cup in which are lubricant and friction body, with the help of flexible teflon tube 21. Gas blown through the friction unit emerges into atmosphere through cock 16.

Moments of friction are measured by tensometeric dynamometer. Cup 22, in which are spheres and test lubricant, is connected by bar 23 with dynamometric beam 24, on which are glued wire transducers connected to bridge circuit. Electromotive force and corresponding moments of friction are recorded by instruments 25. Self-recording potentiometer (type EPP-09), loop oscillograph, and cathode oscillograph ERU with afterglow screen are used.

Tests on friction machine MT-4 are carried out so that always at first a definite load is set, then the spindle with the upper sphere is set into rotation with the needed speed. The experiment is finished stopping the electric motor of drive. From experiment to experiment loads are increased by steps. They go from smaller to higher values. Coefficients of friction are recorded continuously during all experiments. Initial load of lubricating material is 3.7 ml.

The length of all experiments forming one test is 30 seconds. In the course of the test measurements of wear are not conducted; the balls do not turn. Experiments follow one after another with interruptions of 5 minutes. Experiments are conducted up to the start of seizing. Seizing is observed either prior to a strong decrease of frictional force (transition to regime of running-in), or as long as frictional force does not increase to critical values at which tensometric transducers can be damaged. To avoid this drive of friction machine automatically will be turned off. In many cases, after the first experiment in which seizing is observed, repeated experiments are conducted with the same or higher loads in order to determine presence or absence of inclination to develop running-in of friction surfaces.

For want of room, below are given only results obtained on balls from hardened (R_c-62) ball bearing steels at room temperature and a rate of slipping of 23 cm/sec. Tests were conducted by Liang-Kuo-lin and N. T. Pavlovskaya on naphthene-paraffin fraction (npf) of oil MS-20, obtained from a mixture of Surakhany and Karachukhurskoye oils. Blowing of gases was done at atmospheric pressure with a rate of 12 l/hour.

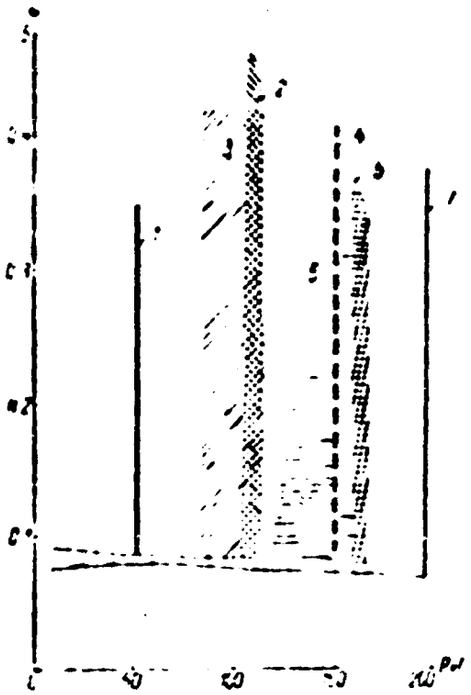


Fig. 2. Dependence of coefficients of kinetic friction on axial loads (naphthene-paraffin fraction of oil MS-20).
1) test in vacuum; 2) in presence of Ar (normal pressure); 3) while blowing Ar through oil; 4) in air without its blowing; 5) while blowing air through oil; 6) in an O_2 medium (normal pressure); 7) while blowing O_2 through oil.

In Fig. 2 is shown dependence of coefficient of kinetic friction μ on loads (P) pressing lower balls to upper ones. With loads lower than seizing load are used mean values of μ, recording during 30-second experiments. To seizing corresponds sharp increase of coefficients of friction, while on curves μ (P) are marked maximums fixed in seizing. In connection with the fact that in the interval of change of loads from 50 to 90 kg, curves μ (P) pass very closely one to another and their movement is smooth; on the graph are not shown the points by which they are constructed.

From Fig. 2 it is clear that all tests, conducted usually in air, are carried out in the presence of a very active antiscoring additive — molecular oxygen. Thus, tests of npf, conducted in a deep vacuum (residual pressure less than 10^{-4} mm Hg) and represented by curve 1, show that air (oxygen) dissolved in oil very strongly influences friction of steel against steel. In oil from which air was evacuated, seizing appears at lowest loads

Ar in experiments contained hundredths (less 0.05) of a percent of O_2. Therefore, experiments with Ar are essentially conducted in conditions of "sharp oxygen starvation" (Fig. 2). Upon blowing Ar through the cup with oil is observed a significant spreading of seizing loads. In Fig. 2 this is marked by shaded band 3, which includes a definite range of maximum values of μ, recorded during parallel tests in which seizing is observed.

Seizing loads in experiments with Ar are significantly larger than in a vacuum. This means that there are sufficient traces of oxygen in gas phase and in oil, so that conditions of friction sharply were changed and load of seizing is significantly increased.

Spreading of critical loads is connected with conditions of blowing the gas through the friction unit. Gas passes through liquid lubricating medium in the form of bubbles. The essential value of the passage of the bubbles was noted. If passage of bubbles directly precedes beginning of seizing, then it either does not occur, or is suppressed in the initial stage of its development.

Transition to experiments in air regularly leads to increase of seizing loads. Here always with special sharpness there appears strong influence of blowing air on spread of values of seizing loads. This is understandable, since air differs by significant oxidizing activity. At the moment of passage of bubble of air through the oil repeatedly there was noted a ceasing in the actual beginning of the seizing. Experiments conducted with pure oxygen show an increase of seizing loads which is still larger than in case of air.

Typical friction — time diagrams for experiments with loads lower than seizing loads are presented in Fig. 3. Every horizontal band on these diagrams corresponds to 5 sec. Coefficients of frictions are along the axis of abscissas. To decrease dimensions of diagrams, on them are shown only values of $\mu \geqslant 0.08$. Beginning of experiments is shown by arrows. Since starting of friction machine is done after seizing of load and compression of balls, in the beginning of the experiments static friction is surmounted. Moment of stop of friction machine (switching on of electric motor in drive system) after its 30-second run is marked by pointers with circle. In every test to experiments 1, 2, 3, 4 corresponded axial loads of 52.5, 60, 67.5, 75 kg. (To decrease dimensions of figure, intervals of time between separate experiments are shown significantly small than in reality.)

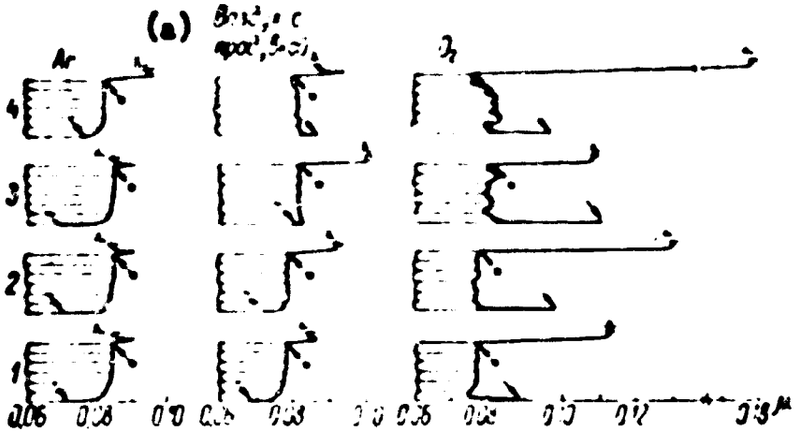


Fig. 3. Friction -- time diagrams with loads lower than seizing loads.
KEY: (a) Air with blowing.

Let us consider first the results of experiments with Ar. After the beginning of the first experiment for 2-3 sec there occurs an acceleration of the spindle with upper revolving sphere. During constant speed of rotation small changes of coefficient of friction are observed. When drive motor is stopped there occurs a very rapid slowing down of the upper sphere as a result of friction against the lower spheres. These spheres together with the cup are attracted by the upper sphere in direction of its rotation. On the friction -- time diagram this increase of frictional force during slowing down of upper sphere is marked as a jump of coefficients of friction.

The dynamometric brake, connected with cup in which are three lower spheres, tends to turn it in the direction reverse to the rotation of the upper sphere. As a result there occurs a drop of coefficients of friction to certain of their limit value which then can be kept any amount for a long time. To decrease dimensions of the figure decrease of μ after stop of electric drive motor is shown by lines with a break. Vertical sections of these lines give limit values of μ. At a given force deforming the dynamometer, transition to higher load is equivalent to a decrease of coefficient of friction. Therefore, on the following diagrams

of friction, in the beginning of every given experiment is marked a lower value of μ than the limit μ at the end of the preceding.

Limit values of μ are determined by characteristics of dynamometric brake and essentially depend on conditions of setting up the experiment. Using the same dynamometric brake, under identical conditions of setting up the experiments with respect to temperatures of lubricating medium, rates of slipping and loads, the limit values of μ characterize static friction.

In experiments with Ar with an increase of loads, static friction, although somewhat increased, in general remains insignificant.

In experiments with the blowing of air, first, with increase of P variations of coefficients of kinetic friction are revealed; secondly, static friction strongly increases. Already in the third experiment at P = 67 kg stop of drive motor entails significant deformation of dynamometric brake, since lower spheres are attracted with force by the upper sphere in the direction of its rotation. Here there exists a decrease of frictional force after its maximum increases, i.e., after termination of experiment frictional force remains at a limiting high level, attained at the moment the motor is stopped. When the motor starts anew, first frictional force sharply decreases, then it decreases slower, while continuous fluctuations of it are observed.

In experiments with blowing O_2 through friction unit, static friction turned out to be exceptionally high. Upon starting the friction machine with loaded friction unit, the frictional force is lowered 1.5 - 2 times. At established speed of rotation strong fluctuations of coefficients of friction are observed.

Strengthening of conjugate reactions of oxidation of steel and hydrocarbon lubricating substances worsens the antifriction properties of these media at relatively low loads. Increase of intensity of oxidation leads to growth of static friction and to fluctuation of coefficients of kinetic friction at a constant rate of slipping. It is possible to assume that this is connected with formation of

thick and friable oxidized layers, easily destroyed during friction. During their abrasion the seizing of the friction surfaces and closing up of the places of seizing are continuously alternated. This is accompanied by intensive wear of friction surfaces.

Consequently, optimum conditions of friction at relatively low contact pressures appear in an inert gas media containing traces of oxygen. A required condition here is intense mixing of lubricating medium.

Development of seizing in experiments with npf MS-20 considered here is illustrated by friction diagrams represented in Fig. 4. Every horizontal band corresponds to a time of 5 sec. Beginning of experiments is marked by arrows; end of experiments is shown by pointers with circles. Fat arrows show that after stop of drive motor coefficients of friction drop (their limit decrease is not given). Diagram 1 describes seizing in high vacuum at P = 45 kg. The shown decrease of coefficients of friction in the course of seizing forced us to assume that even in hydrocarbon medium from which air is removed, are contained substances of antiscoring character. This assumption was all the more so probable that oil from which air is removed showed a rather high load of seizing (45 kg). Since the investigated npf was in prolonged contact with air, although in darkness and in hermetic packing, one should have assumed the presence of products of oxidation in it. This will agree well with data of our other works.

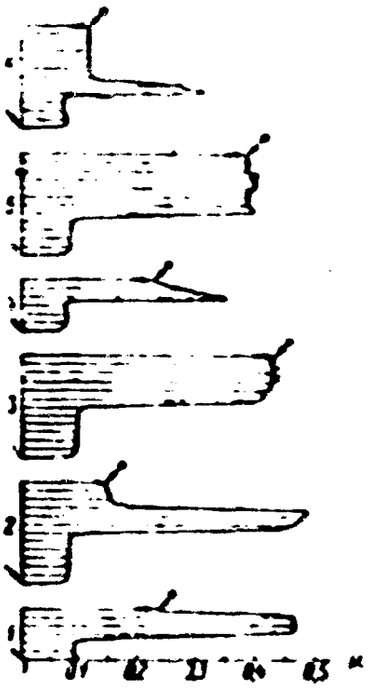


Fig. 4. Friction — time diagrams on regimes of seizing.

An experiment with Ar, blown through oil (diagram 2), was conducted at 97.5 kg. In this case there was shown a rapid ceasing — termination of seizing. These experiments with oil from which air is removed, and with blowing Ar through it showed that at low loads traces of oxidation products of hydrocarbons, which can assist in hydrocarbon lubricating media, act as effective antiscoring additives. Ease of termination of seizing and running in of damaged friction surfaces which is observed in the considered experiments with blowing Ar, will agree well with the purpose that was marked in an earlier works published by us. In inert gas media containing traces of oxygen, carburization of surface layers of steel and formation in them of iron carbides and alloy components due to decomposition of hydrocarbons take place with special ease. This leads to a significant increase of hardness of surface layers of steel and increases, thereby, the antiscoring action of oxidized layers.

In experiments in air (without blowing it with which corresponds diagram 3 (see Fig. 4), obtained at P = 150 kg, is observed a sharply expressed prolonged period of seizing. Intensity of seizing in this case is determined by the fact that at high loads is required a rather rapid feed of oxidizers to the zone of friction, which was not realized.

Very characteristic is the comparison of friction diagrams on seizing regimes in conditions of blowing air through friction unit at P = 120 kg (diagram 4) and P = 165 kg (diagram 55). In the first of these two cases occurs a rapid termination of seizing. In the second case is observed a prolonged period of seizing. This is explained by the fact that in the last case feed of friction zone substances oxidizing steel is insufficient for rapid healing of friction surfaces and transition to conditions of running-in of damaged surfaces.

Diagram 6 shows how the experiment took place with blowing O_2 through oil at P = 195 kg. It turned out that in spite of high initial contact pressure, there occurs a very fast termination (degeneration) of seizing and running in of friction surfaces.

The assumption that traces of products of oxidation (not revealed by the usual qualitative analytic samples) can strongly affect steel to steel friction was checked by direct experiments during tests of hydrocarbon media, on one hand, located prior to these experiments in contact with air, and on the other hand, distilled in vacuum in a current of clean Ar. These tests were conducted on npf (temperature of boiling 140-200° at 2 mm Hg) kerosene from Romashkinskiy oil, and also on npf (temperature of boiling 160-210° at 2 mm Hg), driven off from wide npf oil MS-14, obtained from a mixture of Surakhany and Karachukhur oils.

In Fig. 5 are presented results of test of npf heavy kerosene. Line 1 shows seizing during two parallel tests in vacuum (pressure less than 10^{-4} mm Hg) of a product which was not in contact with air after its distillation in vacuum in an Ar stream. Curve 2 pertains to experiments in vacuum with npf from which although air was removed, before introduction into vacuum chamber on short time interval was put into contact with air at atmospheric pressure. Curve 3 pertains to test in vacuum of undistilled npf. Curve 4 describes results of test of npf distilled and not in contact with atmospheric oxygen while blowing through it Ar containing traces of O_2. Experiments in air with npf fresh-distilled in vacuum and undistilled gave close results (curves 5 and 6). In the case of blowing O_2 through npf distilled in a vacuum curve 7 was obtained. Similar results turned out to be in the case (not shown in Fig. 5) of blowing O_2 through npf not distilled in a vacuum. Tests conducted with npf separated from MS-14 gave results analogous to those presented in Fig. 5.

During tests in vacuum of npf not formerly in contact with atmospheric oxygen, seizing sets in at the lowest loads which it is possible to give to a friction unit. Even brief contact with air noticeably increases load of seizing. In experiments with blowing Ar through npf not distilled in a vacuum frequently there are observed low coefficients of friction (with loads lower than loads of seizing). This will

agree well with low wear observed by us earlier in similar test conditions. It is very interesting that traces of products of oxidations present in undistilled npf render an action analogous to traces of oxygen which is contained in argon. A qualitative similarity of action of molecular oxygen and products of oxidation of hydrocarbons was repeatedly noted in our works recently.

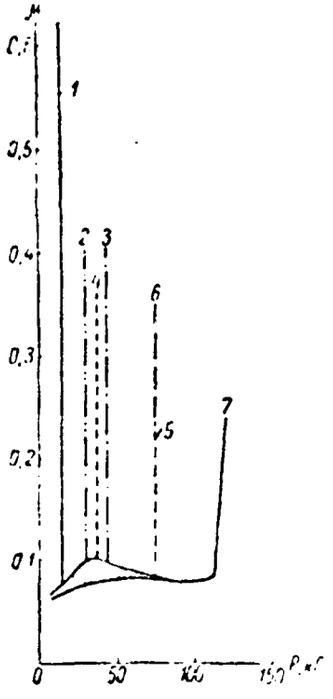


Fig. 5. Dependence of coefficients of kinetic friction on axial loads (naphthene-paraffin fraction of heavy kerosene).

In cases when tests are conducted in the presence of gas media active with respect to oxidation (experiments in air, with blowing of air and O_2, etc.), the influence of traces of oxidation products no longer renders a noticeable influence.

Experiments in vacuum and in Ar (without blowing it) with oil products distilled in a vacuum, are characterized by two peculiarities. First, after ceasing of experiments on conditions of seizing repetition of them with the same (and even larger) load again leads to seizing, which with increase of loads is all the more intensely and is accompanied by progressive growth of coefficients of friction. In these conditions is absent the running in of friction surfaces. Conversely, in experiments with blowing O_2 after degenerated seizing took place a very significant increase of loads is necessary in order to cause it again. Secondly, with loads lower than loads of seizing in experiments with media containing only insignificant traces of oxygen, an intense grabbing of friction surfaces is shown. This appears in the fact that, in spite of low loads, a stop of the drive motor is not accompanied by reduction of frictional force after completion of deceleration of spindle.

Thus, as during test of npf MS-20, in experiments with npf kerosene and MS-14 the static friction of steel against steel is increased with increase oxidizing activity of gas medium.

From considered data of test of npf of different oil products it is clear that although their nature influences the appearance and period of seizing and antifriction properties under heavy conditions of friction, however, the distinction among such extreme cases as residual oils and tail fractions of kerosene are not essential as compared to distinction of behavior of each of these objects depending upon intensity of conjugate reactions of oxidation of hydrocarbon media and steel.

To simulate action of oxidation products active in conditions of friction, into npf distilled in a vacuum was introduced 0.5% benzoyl peroxide. This leads to an increase of static friction which is shown in experiments in a vacuum. Load of seizing during test in vacuum and in an Ar atmosphere (without blowing it) extraordinarily increases.

In experiments with blowing O_2 through solutions of benzoyl peroxide in npf was shown a decrease by 2 times of the seizing load as compared to control experiment on initial npf. However, seizing here is very easily stopped. It is accompanied by insignificant wear. Further increase of load, more than by 2 times, does not lead to seizing and is not combined with noticeable growth of wear. Consequently, there are possible such cases when excessive forcing of process of conjugate oxidation of hydrocarbon media and steel lead not only to strengthening of chemical oxidizing wear under low loads, but also lowers load of seizing. At the same time under very high contact pressures actively effective oxidizing agents act just as well-known antiscoring additives, lowering wear and preventing seizing.

Introduction of inhibitors of oxidation of the type of pure 2.6-tert-isobutyl-4-methylphenol in npf of different oil products showed that in the presence of these inhibitors static friction and loads causing intensity of seizing or fusing of steel are lowered.

Conclusions

1. In the absence of oxygen and oxygen-containing compounds under boundary conditions of friction of steel, hydrocarbon (petroleum) oils constitute an ineffective or little effective lubricating media.

2. Oxygen dissolved in petroleum oils and products of their oxidation play the most important role of natural additives, preventing seizing of steel under boundary friction. Here traces of these substances essentially influence.

3. During transition from easy to heavier conditions of friction the relative role of boundary layers formed by organic compounds (soap and so forth) decreases, and the role of oxidized layers increases.

4. With strengthening of processes of oxidation is increased static friction and oxidizing wear, at the same time seizing degenerates (is accompanied only by brief, frequently relatively small increase of coefficient of friction), and seizing of high intensity is developed during very high contact stresses. Consequently, to every condition of friction correspond definite optimum concentrations of oxiders and intensity of oxidation.

5. Since petroleum oils are the media supplying oxygen to surface of steel, an important role must be played by conditions of transport to these surfaces of molecular oxygen and products of oxidation which can depend on viscosity of liquid lubricant, thickness of lubricating film covering body of friction, etc.

6. Oxygen and products of oxidation of petroleum oils act similarly to sulfur organic compounds utilized as antiscoring additives to oils.

7. Chemical organic compounds rich in oxygen have to differ in strong antiscoring action during friction of steel.

INVESTIGATION OF MECHANISM OF REACTION OF TRIBUTYLTRITHIOPHOSPHITE IN A HYDROCARBON MEDIUM LAYERS OF COPPER BY USING RADIOACTIVE INDICATORS

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For a comparative appraisal of effectiveness of different additives to lubricating oils an important value belongs to the study of the mechanism of reaction of these additives with metals. In view of the fact that the majority of additives are sulfur-, phosphorus-, or chlorine-containing compound or their mixture, a special value belongs to functional differentiation of action of individual compounds and atoms in molecule of additive reacting with metal, on the surface of which are formed protective layers possessing antiwear properties.

In recent years have been published works [1-3], dedicated to the investigation of the mechanism of reaction with metals of additions containing sulfur, phosphorus, or chlorine, and also the study of joint action of sulfurous and chlorine-containing compounds. In these works are fixed temperature boundaries of reaction of additions with metals. It is shown that with increase of temperature there sets in thermal decomposition of additions determining the upper limit of effectiveness of their action. In a number of works [4-8] are given results of investigation of mechanism and kinetics of reaction with steel and copper at

various temperatures of thio-, phosphorus- and organic thiophosphorous additives dissolved in a naphthene-paraffin fraction of oil MS-20. In these works radioactive tracers are used, possessing the high sensitivity necessary for detection of small quantities of products of reaction of additions or their components with metals. As additions there were used individual thio, phosphorus-, and organic thiophosphorous compounds, marked according to sulfur (isotope S^{35}) and according to phosphorus (isotope P^{32}).

In this report are given results of investigation of mechanism of reaction of tributyltrithiophosphite with films of copper in a hydrocarbon medium (naphthene-paraffin fraction of oil MS-20) by using radioactive tracers. Investigation of reaction of copper with the addition of tributyltrithiophosphite, marked according to S. P, or C, makes it possible to differentiate action of sulfur and phosphorus and to clarify role of hydrocarbon radical of additive.

Works published earlier were conducted with metallic surfaces subjected to machining of a different class of cleanness, not ensuring sufficiently good reproducibility during measurements of activity. In connection with this, for improvement of an earlier used method the reaction was studied of elementary sulfur with metal in a hydrocarbon medium on films of copper of a given thickness, obtained by evaporation of metal in vacuum and ensuring good reproducibility of quality of surface. Use of layers of different thickness also allowed estimation of depth of penetration of atoms of sulfur in metal (with formation of copper sulfide) according to thickness of applied layer during full chemical reaction of sulfur with copper.

Layers were applied on a thoroughly degreased glass lining (covering of glass), and their thickness was determined by weight method with accuracy up to 30A (weighing on microanalytical scales with accuracy up to $5 \cdot 10^{-6}$g).

The experimental method of determination of β-activity with the help of an end-window counter is presented in published works [4]. As an addition to

naphthene-paraffin fraction of oil MS-20 was applied elementary sulfur containing S^{35} (specific activity $3.5 \cdot 10^7$ imp/min g) in 0.5% concentration. Investigation of the reaction with copper of elemental sulfur in a hydrocarbon medium was carried out according to an earlier developed method [5] during intense mixing and thorough removal of oil from surface by petroleum ester in a Soxhlet apparatus. The sample of copper was placed in a glass holder which simultaneously acted as a mixer, was dipped into a vessel with oil containing sulfur, and was kept for a definite time in a thermostat at a temperature of 120°, corresponding to the energy reaction of sulfur with copper. Duration of experiment was established experimentally and constituted from 30 to 180 minutes.

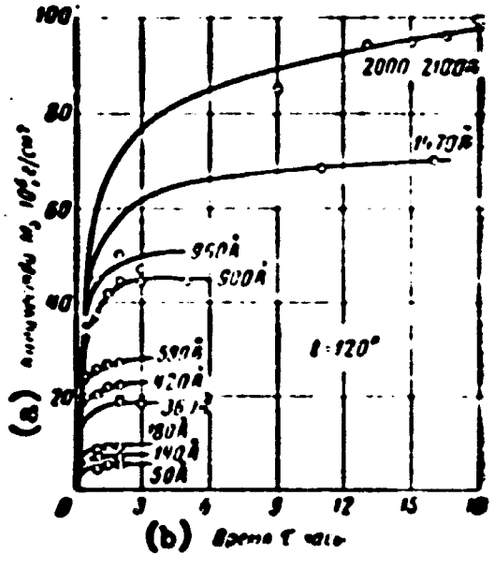


Fig. 1. Dependence of quantity of elemental sulfur combined with copper, on time for layers of different thickness (at constant temperature).
KEY: (a) Quantity $M_s \cdot 10^6$, g/cm^2; (b) Time τ hours.

In Fig. 1 is depicted dependence of activity, estimated with respect to quantity M_S, of sulfur combined with copper, on time τ for layers of different thickness at constant temperature (120°). On the figure it is clear that the reaction of copper with sulfur dissolved in oil, for the first 30-60 minutes is developed with great speed and further, gradually being delayed, ceases, which corresponds to a full ceasing of reaction of sulfur with all copper in the layer. Here the activity of the formed layer of copper sulfide in time is not changed. The limit value of activity of the layer is higher the greater the thickness of the initial layer of copper. In Fig. 2 is shown the dependence of limit quantity M_S sulfur combined with copper, on thickness h of layer of copper at constant to temperature (120°).

Inasmuch as this dependence carries a linear character, one may assume that all copper completely reacts with sulfur introduced into the oil, and that within limits of errors of measurements for the investigated interval of thicknesses (measurements were carried out for layers of copper up to 5000A thick) absorption of electrons in the layer does not have to be considered. Calculation of stoichiometrical quantities of sulfur and copper for experiments with layers of various thickness (various quantity of sulfur) shows that the compound of copper and sulfur which forms can be only sulfide of copper. Here was observed satisfactory coincidence of results of stoichiometrical calculation with experimental data obtained by weight method which can serve as proof of the formation of CuS during chemical reaction of sulfur with copper. This conclusion allows estimation of total thickness of layer and number of monolayers of copper sulfide.

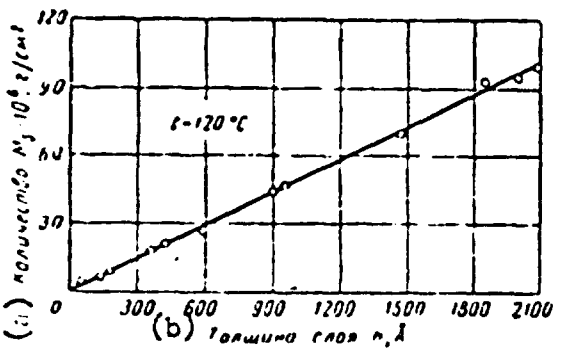


Fig. 2. Dependence of maximum quantity of elemental sulfur, combined with copper, on the thickness of the copper layer (at constant temperature).
KEY: (a) Quantity of $M_s \cdot 10^6$, g/cm^2; (b) Thickness of layer h, A.

Total thickness h_{CuS} of layer of copper sulfide equals

$$h_{CuS} = \frac{M_{CuS}}{S \varrho_{CuS}}, \qquad (1)$$

where M_{CuS} is mass of copper sulfide in a layer with area S and ϱ_{CuS} is density CuS. The number N_{CuS} of monolayers of copper sulfide may be approximately calculated from the relationship

$$N_{CuS} = \frac{M_{CuS}}{S \varrho_{CuS}} \sqrt[3]{\frac{N_0}{\mu_{CuS}}}, \qquad (2)$$

in which N_0 is Avogadro's number and μ_{CuS} is the molecular weight of copper sulfide.

This relationship is obtained from the assumption that the linear dimensions of a molecule of copper sulfide can be approximately estimated, considering the form of the molecule as cubic.

Mass M_{CuS} of copper sulfide in principle may be determined by three methods: 1) by means of calculation from results of weighing of layer of copper taking into account stoichiometrical relationship of copper and sulfur in CuS molecule; 2) by means of calculation from results of determination of quantity of sulfur on the basis of measurement of activity taking into account stoichiometry, and 3) direct weighing of layer of sulfide of copper.

Results of calculation of h_{CuS} and M_{CuS} by the first method and value of h_{CuS}/h_{Cu} ratio are given in the table; thickness h_{CuS} of layer of copper sulfide is calculated from relationship (1), in which mass M_{CuS} of copper sulfide is determined by the second method.

The h_{CuS}/h_{Cu} ratio may be calculated taking into account stoichiometrical relationships. For that case

$$\frac{h_{CuS}}{h_{Cu}} = \frac{\rho_{Cu}}{\rho_{CuS}} \cdot \frac{96}{64} \cdot \frac{8.94}{6.6} \cdot \frac{3}{2} = 2.92.$$

From Table 1 it is clear that the h_{CuS}/h_{Cu} value is close to its value obtained on the basis of stoichiometrical relation. The observed small divergence, apparently, is combined on the one hand with inevitable experimental errors during determination of activity, and on the other hand with inaccuracy of estimation of linear dimensions of CuS molecule.

On the basis of data obtained during the study of the reaction of elemental sulfur in hydrocarbon medium with layers of copper of different thickness, it follows that the quantity of copper sulfide estimated according to its activity, is proportional to the thickness of the layer. Thickness of layer of copper, estimated by weight method, will agree well with thickness determined with respect to activity proportional to thickness of layer. Thickness of layer of copper estimated by weight method, will agree well with thickness determined by activity of sulfur reacting with copper, which allows the use of radioactive tracers by β-radiation for determination of thickness of films of metallic coatings.

Determination of thickness of layer of copper sulfide by means of calculation and on the basis of experimental data gives satisfactorily coinciding results. Experimentally determined thickness of layers of copper sulfide turns out to be approximately 3 times more than thickness of layers of copper itself, which coincides with results of calculation on the basis of stoichiometrical relationship.

In [4,5] are given results of investigation of kinetics of reaction at various temperatures of tributyltrithiophosphite, marked with respect to S and P, with metals (steel and copper) whose surface which was subjected to machining.

Total Thickness of Layers h_{CuS}, Number N_{CuS} of Monolayers and ratio $\frac{hCuS}{hCu}$

Total thickness of layers h_{CuS}, A	Number of monolayers N_{CuS}	Ratio $\frac{h_{CuS}}{h_{Cu}}$	Total thickness of layers h_{CuS}, A	Number of monolayers N_{CuS}	Ratio $\frac{h_{CuS}}{h_{Cu}}$
444	136	3.17	2935	900	3.14
520	165	3.53	3045	933	3.19
594	182	3.30	4630	1415	3.15
1205	369	3.32	6130	1872	3.31
1383	423	3.29	6250	1910	3.12
1740	533	2.97	6660	2036	3.19
2900	887	3.18			

The below-mentioned results are obtained during the study of kinetics of reaction of tributyltrithiophosphite, labled by S, P, and C, with films of copper of different thickness, obtained by evaporation of copper in a vacuum. In all cases concentration of addition of tributyltrithiophosphite in oil constituted 0.1 mole/l, which corresponded to 1% of the content of sulfur in oil.

Results of investigation of kinetics of reaction of tributyltrithiophosphite, labled by sulfur $[(C_4H_9S^{35})_3P]$, at a temperature of 120° for layers of copper of different thickness from 200 to 800 A are shown in Fig. 3. In all cases activity estimated according to quantity M_S sulfur combinable with 1 cm^3 of copper surface,

attains maximum during the first 5-10 minutes and slowly drops in time, not reaching, however, zero. With increase of thickness of layer of copper the maximum value of activity increases.

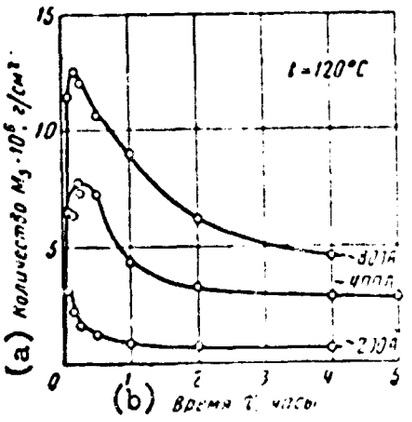


Fig. 3. Dependence of quantity of sulfur tributyltrithiophosphite, combined with copper, on time for layers of different thickness (at constant temperature).
KEY: (a) Quantity of $M_S \cdot 10^6$, g/cm^2; (b) Time τ, hours.

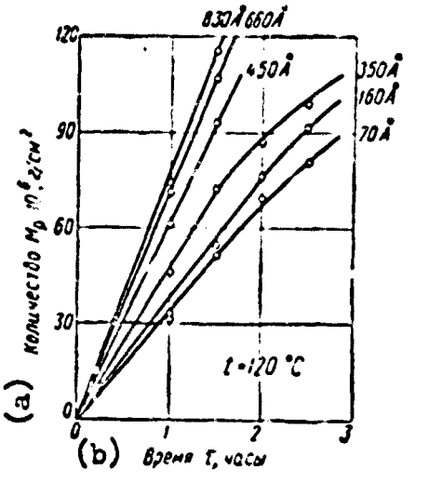


Fig. 4. Dependence of quantity of phosphorus tributyltrithiophosphite, combined with copper, on time for layers of different thickness (at constant temperature).
KEY: (a) Quantity $M_S \cdot 10^6$, g/cm^2; (b) Time τ, hours.

For tributyltrithiophosphite labled by phosphorus [$(C_4H_9S)_3P^{32}$], change of activity in time (Fig. 4) carries another character; there is observed a monotonic growth of activity in time, and with increase of thickness of layer of copper increases the speed of change of activity.

During research of kinetics of reaction of tributyltrithiophosphite labled by carbon [$(C_4{}^{14}H_9S)_3P$] (synthesized from butyl alcohol IC^{14}) with copper (thickness of layer 400 Å) at temperatures from 50 to 130°, it was revealed (Fig. 5) that increase of activity increases with increase of temperature. At all temperatures the kinetic curves possess maxima of activity. Maximum of activity increases with increase of temperature to 120° and at a higher temperature drops. Time of achievement of maximum value of activity sharply decreases with increase of temperature within limits to 130° and constitutes from 100-120 minutes

to several minutes. For tributyltrithiophosphite labled by carbon, with increase of thickness of layer of copper (within limits to 1000 A) maximum of activity at a given temperature increases approximately in proportion to thickness of the layer (Fig. 6). Here maximum value of activity is attained over several minutes.

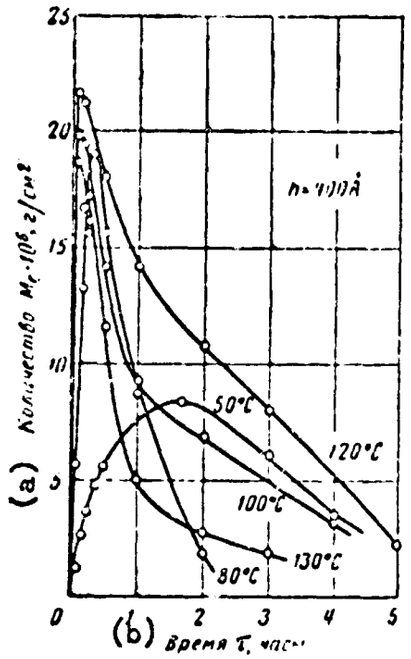


Fig. 5. Dependence of quantity of carbon tributyltrithiophosphite on time at various temperatures (for a layer of constant thickness).
KEY: (a) Quantity $M_c \cdot 10^6$, g/cm^2; (b) Time τ, hours.

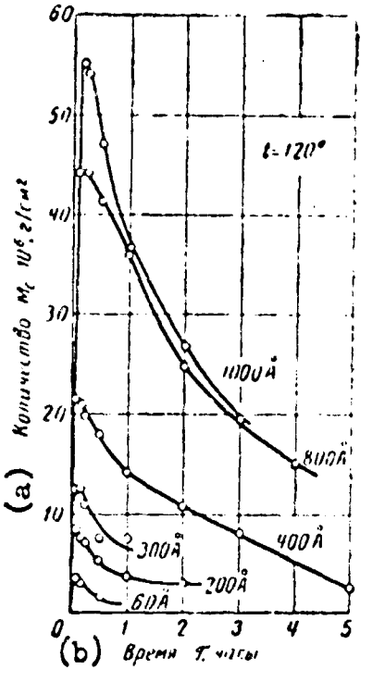


Fig. 6. Dependence of quantity of carbon tributyltrithiophosphite on time for layers of various thickness (at constant temperature).
KEY: (a) Quantity $M_c \cdot 10^6$, g/cm^2; (b) Time τ, hours.

In Fig. 7 are given curves characterizing kinetics of reaction with copper of sulfur, phosphorus and carbon in a molecule of tributyltrithiophosphite in the same conditions (temperature 120°, thickness of layer 400 A). From this graph it is clear that curves characterizing kinetics of reaction of tributyltrithiophosphite labeled by sulfur and carbon, carry an analogous character, but maximum value of activity measured according to the C^{14}, is higher than maximum value of activity measured according to the S^{35}.

In view of the fact that on all three curves shown in Fig. 7, there are initial sections for which $\frac{dM}{d\tau} > 0$, one may assume that in the beginning of the

reaction of tributyltrithiophosphite with copper will be formed a compound of phosphorus with copper and a sulfur organic compound. From the character of the curves $\left(\frac{dN}{d\tau}\right)_{\tau=0}$ for $(C_4H_9S)_3P^{32}$, $(C_4H_9S^{35})_3P$ and $(C_4{}^{14}H_9S)_3P$ (in the two last cases the presence of maximum and, consequently, presence of sections for which $\left(\frac{dN}{d\tau}\right)_{\tau=0}<0$) it follows that on surface of metal will be formed copper phosphide, whose thickness of continuously grows in time, and a chemically unstable sulfur organic compound (apparently, copper mercaptide), decomposed in time. Thus, it is possible to consider it established that the hydrocarbon radical of the addition participates in the reaction with metal*.

The obtained experimental results make it possible to express the following assumption about mechanism of reactions taking place during the reaction of tributyltrithiophosphite with copper at an increased temperature: tributyltrithiophosphite can be decomposed, for instance, with formation of phosphine and mercaptan by the reaction

$$8(C_4H_9S)_3P \rightarrow 2PH_3+9C_4H_9SH+15C_4H_8+3P_2S_5$$

analogous to the reaction considered in [9].

The mercaptan which is formed, reacting with copper (or with copper oxide), is turned into copper mercaptide $(C_4H_9S)_2Cu$, which at increased temperature can be decomposed with formation of copper sulfide, butylene and hydrogen sulfide by the reaction

$$(C_4H_9S)_2Cu \rightarrow CuS+2C_4H_8+H_2S.$$

Simultaneously with copper reacts phosphine, as a result of which there will be formed copper phosphide, for instance Cu_{32}. Consequently, during the reaction of tributylphosphite with copper can be formed copper phosphide, copper mercaptide, and copper sulfide.

*In [3] is contained the indication that during friction of steel surfaces in the presence of lubricating oil containing a thioorganic addition, on the surface of the metal can be formed iron mercaptide.

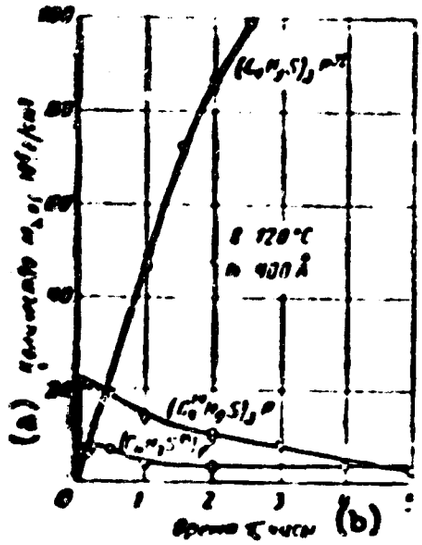


Fig. 7. Reaction of tributyltrithiophosphite, labled phosphorus and carbon, with copper in the same conditions (at constants thickness of layer and temperature). KEY: (a) Quantity $M_{S,P,C} \cdot 10^6$, g/cm^2; (b) Time τ, hours.

In view of the fact that activity of surface in the case of $(C_4H_9S)_3P^{32}$ continuously increases in time, one may assume that thickness of layer of copper phosphide is increased. At the same time for $(C_4H_9S^{35})_3P$ and $(C_4{}^{14}H_9S)_3P$ activity of surface after achievement of maximum drops: in the first case not to zero, but in the second — practically to zero. Increase of activity of surface and its subsequent decrease in the case of $(C_4H_9S^{35})_3P$ can be explained by the fact that, on the one hand, copper mercaptide is stored and, on the other hand, part of the sulfur of the copper mercaptide according to the above equation during prolonged heating leaves the surface of the copper in the form of hydrogen sulfide (H_2S^{35}) which as a result leads to decrease of activity to a level corresponding to the activity of the formed copper sulfide. Analogously the kinetics of reaction may be explained in the case of $(C_4{}^{14}H_9S)_3P$; increase of activity in the beginning of the reaction in this case is explained by formation of $(C_4{}^{14}H_9S)_2Cu$, and subsequent decrease — by decomposition of mercaptide and formation of butylene ($C_4{}^{14}H_8$). A higher value of maximum activity measured by C^{14}, as compared to value of maximum activity measured by S^{35}, is explained by the relatively large content of carbon in the $(C_4H_9S)_2Cu$ which forms, as compared to content of sulfur in this molecule and higher specific activity of initial preparation of $(C_4{}^{14}H_9S)_3P$ synthesized for these experiments as compared to specific activity of $(C_4H_9S^{35})_3P$*. With formation of butylene and

*Specific activities of synthesized preparations were equal to $3.08 \cdot 10^7$ imp/min g for $(C_4H_9S^{35})_3P$; $3.40 \cdot 10^6$ imp/min g for $(C_4H_9S)_3P^{32}$ and $3.75 \cdot 10^8$ imp/min g for $(C_4{}^{14}H_9S)_3P$.

its removal from the surface, activity, estimated using carbon, gradually decreases and practically turns into zero.

This presentation about reaction mechanism of the reaction of tributyltrithiophosphite with copper at increased temperature will agree with results obtained in the work of P. I. Sanin and A. V. Ul'yanova [9], in which it was shown that during thermal decomposition of tributylphosphite and tributyltrithiophosphite in the products of decomposition phosphine, hydrogen sulfide, and butylene are qualitatively revealed. During thermal decomposition of tributyltrithiophosphite $(C_4H_9O)_3P$ in the presence of copper phosphide will be formed.

It is necessary to note that reaction mechanism of the interaction of additions of the type of phosphites with metals still requires further study.

Conclusions

1. The developed method of studying kinetics of the interaction of elemental sulfur in hydrocarbon medium with films of copper using radioactive tracers, makes it possible to estimate thickness of protective layer of copper sulfide.

2. Determination of thickness of layer of copper sulfide from stoichiometrical considerations and on the basis of experimental data on activity gives satisfactorily coinciding results.

3. During reaction of addition of tributyltrithiophosphite (labled by sulfur, phosphorus, and carbon) with copper in a hydrocarbon medium there are formed sulfide, phosphide, and copper mercaptide. Thus, one should consider that the hydrocarbon radical of the addition reacts with metal.

4. On the basis of studying kinetics of interaction of tributyltrithiophosphite (labled by sulfur, phosphorus, and carbon) with copper in a hydrocarbon medium the assumption is expressed about decomposition of copper mercaptide at an increased temperature with yield of butylene and hydrogen sulfide.

5. The presentation about mechanism of reaction of tributyltrithiophosphite with copper at increased temperature, presented in this work, will agree with results obtained during the study of thermal decomposition of tributyltrithiophosphite.

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ANTISCORING ADDITIVES TO OILS FOR AUTOMOBILE TRANSMISSIONS AND MECHANISM OF THEIR ACTION

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VNII NP*

Due to a shift of large part of automobiles to hypoid transmission, and also decrease of margin of safety of parts and boosting of operating conditions of transmissions it is necessary to apply widely antiscoring and antiwear additives to transmission oils.

The present trend is creation of additives effective during all operating conditions of automobile transmissions, i.e., possessing a definite universality; this leads to necessity of use of complicated compositions of different substances [1; 4]. Principles of selection of these compositions will be clear from the following text.

For lowering of friction and wear are applied:

a) saponified fatty oils, fatty acids or their esters;

b) organic compounds of sulfur and halides (most frequently chlorine), organic compounds of phosphorus and nitrogen;

c) different compounds of metals (plumbic soaps, oxidized and sulfurous compounds of molybdenum and tungsten, compounds of zinc and others).

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All the enumerated types of compounds possess the ability to lower friction and wear or to prevent seizing of surfaces, but in a different degree, depending on their chemical activity, adsorptive properties, and on physical properties of surface layers obtained as a result of reaction of metal with lubricant.

Additives containing fatty acids or their esters, basically are antifriction; their action is based on adsorptive effect of polar-active molecules. Such additives have been recently used as one of the components of an additive to oils for hypoid transmissions for the purpose of stabilization of moment of friction in mechanisms of interlocking gears of differentials lubricated by the same oils [2, 3].

Additives containing organic compounds of sulfur, chlorine, or phosphorus, act, entering into chemical reaction with surface of metal at high temperatures of friction, and create surface layers with modified physical and mechanical properties [5-8]. By their antiscoring properties these additives are the most effective, however sulfur- and chlorine-containing additives often turn out to be corrosively aggressive; the difficulty during development of such additives is combining maximum antiscoring properties with anticorrosive properties.

Additives containing metallic derivatives, with the exception of plumbic soaps only recently have begun to be used in oils for heavily loaded gear transmissions; the mechanism of their action has not been studied at all.

In VNII NP there were investigated and tested certain additives of the second and third types, presented in Tables 1, 2.

Of additives containing one active element, the highest antiscoring properties were possessed by disulfides and polysulfides with sulfur in the chain: dibenzyl-sulfide and xanthogenates, where atoms of sulfur in middle of chains are divided by CH_2 group. Esterfied compounds of this type (xantho) are significantly less active which, in the opinion of the authors of this additive, is combined with their high thermal stability [9].

Sulphurized vegetable oils and animals fats, as a rule, with respect to antiscoring properties yield xanthogenates and sulphurized aromatic hydrocarbons, but have ability essentially to lower friction. According to source material they also possess good anticorrosive properties both with respect to nonferrous metals and also to steel [10, 11].

The majority of opinions is inclined to say that the antiscoring action of additives containing sulfur is explained by formation of metal sulfides having a lowered durability on the friction surface, [8, 12, 13]. This promotes easy destruction cohesion points. Apparently this can explain why in a number of cases strong antiscoring sulfuric additives give increased wear during moderate operating conditions of surfaces.

Of a number of additives containing chlorine, the most active are the lowest chlorinated hydrocarbons, then compounds with chlorine in a chain, and the least active are compounds with chlorine in a ring. According to antiscoring properties chloric additives, as a rule, yield sulfuric.

A drawback of chloric additives is their corrosive aggressiveness, especially in combination with sulfuric additives. Corrosion under the action of chloric additives is difficult to show by the existing standard method of corrosion test (All-Union Government Standard 2917-45). This method of testing is not very useful for oils with additives containing compounds of chlorine, since in this case corrosion of steel surfaces appears, as a rule, only after condensation of moisture from air on them. Practically, during use of automobiles this occurs when the automobile must stand. In connection with this we used the Swiss method of testing, which showed the possibility of sufficiently accurately fixing the boundaries of the additives and giving a quantitative evaluation of their corrosivity [14]. In this method steel plates are first kept for 3 days at 120° in oil with the tested additives, and then after washing in a solvent they are kept 7 days in an atmosphere of humid air in an exsiccator. Corrosion is determined by increase of weight of plates after the test, which should not exceed 5 g/m^2.

Table 1. Characteristics of Experimental Single-Component Antiscoring Additives and Results of Their Tests in Oil DS-14

Additive	Chemical characteristic of formula	Content of active elements in additive	Results of tests of oil with additives: Additive, in oil, %	Corrosion of [illegible] steel, g/m²	Test on Four-ball machine ChSMI-2: OF, kgs	P_K	P_{CB}
Dibenzyldisulfide, technical (Czechoslovakia)	$(C_6H_5CH_2-S)_2$	26%, S	5	0.0	77	220	1001
LZ-4/9	Dibutylxanthogenate $(C_4H_9OC(=S)-CH_2)_2$	29%, S 8.5%, Cl	5	0.1	70.5	192	304
[illegible]	Dioctylxanthogenate $(C_8H_{17}OC(=S)-S)_2$	43% S	5	1.3	81	182	794
LZ-19	Diisoamylxanthogenate $(C_5H_{11}OC(=S)-S-CH_2)_2$	33%, S 3% Cl	5	1.0	76	235	447
LZ-23	Diisopropylxanthogenate $(C_3H_7OC(=S)-S-CH_2)_2$	42.7%, S 0.5% Cl	5	1.0	73	200	447
LZ-20	Diisoamylxanthol $(C_5H_{11}OC(=S)-S-CH_2-CH_2)_2O$	29% S 2.8% Cl	10	0.2	62	238	316
LZ-21	Dibenzylxanthol $(C_6H_5OC(=S)-S-CH_2-CH_2)_2O$	20.3%S 4.2% Cl	10	0.4	62	235	308
Sulphurized terpene	–	25% S	5	–	56	200	224
NDS	$\beta\beta'$-mercaptoethyl ester $(HOOCCH_2-CH_2-S)_2$	19%, S	10	–	48	80	282
Nami-4-122**	Chlorinated paraffin From $C_{12}H_{25}Cl$ to $C_{18}H_{37}Cl$	40%, Cl	10	7.8	70	120	316
Nami-4-122 + ZS vnii ap-371	The same	40% Cl	10	0.4	62	200	346
Anmi-9	Chlorinated naphtha	25% Cl	5	0.3	68	70	355
Hexachloroethane		90% Cl	5	15.0	68	200	355
Chlorinated biphenyl	Mixture of tetra- and pentachlorodiphenyl	49% Cl	5	0.3	61	85	224
VD-2	Dichlorodiphenyltrichloroethane	45% Cl	5	0.8	61	70	200

*Tests were conducted by the method of All-Union Government Standard 9490-60.

**Abbr. Note: Nami = NAMI = State All-Union "Order of Labor Red Banner" Automobile and Automobile Engine Scientific Research Institute; Vnii ap = VNII NP = = All-Union Scientific Research Institute of the Petroleum Industry; Anmi = AzNII = = Azerbaydzhan Scientific Research Institute. The additives are named after the research institutes.

***Abbr. Note: OFI = Generalized Wear Index

Table 2. Characteristics of Antiscoring Additives Containing Several Active Elements, and Results of Their Tests in Oil DS-14

Additive	Characteristics or chemical formula	Content of active element in additive	Results of tests of oil with additives: Additive in oil, %	Corrosion, g/dm²	Tests on four-ball machine ChShM-3*: OPI	P_K	P_{cb}
Chlorophosphorous additives							
Chloreth-60	Butyl ester of trichloromethylphosphine acid $CCl_3PO(OC_4H_9)_2$	31% Cl, 10% P	2	0.9	88	158	562
Chlorophosphorous additive	Isoamyl ester of trichloroacetoxyphosphine acid $(C_5H_{11}O)_2P(O)-CHCCl_3$, $OCOCH_3$	21.8% Cl, 6.8% P	2	1.08	86.5	158	557
Cloreth-15	Butyl ester of monochloromethylphosphine acid $ClCH_2PO(OC_4H_9)_2$	14.5% Cl, 12.4% P	2	1.08	53	126	200
Sulfur-chlorine and sulfur-chlorophosphorous additives							
Hexachlorosulfide		55.8% Cl, 8.4% S	4	0.77	83.9	100	631
Hexachloride and DF-11		31.8% Cl, 9.1% S, 2.0% P, 2.1% Zn	7	0.32	95.2	141	631
Additives, containing molybdenum and sulfur							
LZ-6/9 and molybdenum blue		11.7% S, 6.15% Mo	5	1.73	88.8	126	447
Sulfur-phosphorous additives							
EPO in oil from extracts of phenol purification SF-2	Residual extract, treated by phosphorous pentasulfide	7% S, 2.5% P	10	—	48	100	251
SF-2	Still residues of distillation of alkylate for additive Ionol, treated by phosphorous pentasulfide	3% S, Phosphorus is not determined	5	—	55	112	282
LZ-30	Dithiophosphate—obtained by means of treatment of alkylphenol by phosphorus pentasulfide	6% S, 2% P	6	—	49	112	200

*Tests were conducted by the method of the All-Union Government Standard 9490-60.

The role of chloric compounds in friction consists in formation of films of iron chloride, which can appear during direct interaction of chloric compounds with metal or as a result of reaction of iron with the hydrogen chloride appearing during decomposition of chlorine-derivatives in conditions of friction [7, 15]. In the second case chloric additives are especially corrosively aggressive.

However, it is possible to select special additives which protect steel from corrosion in the presence of chloric component of additives. Such an effective anticorrosive additive turned out to be the additive vnii np-371, a product of formaldehyde condensation of barium alkylphenolate. The most cheap and long-term chloric additive is chlorinated paraffin, which is industrially manufactured.

Single-component phosphorous additives are usually esters of phosphorous and phosphine acids. These additives insignificantly increase antiscoring properties of oils; however, they promote improvement of friction conditions of surfaces and in a number of cases possess anticorrosive properties.

Films of iron phosphides appear at comparatively low temperatures (near 200°), at which there occurs decomposition of phosphorous compounds and formation of phosphine, reactive with respect to metal [16]. The ability of iron phosphides to etch leads to a significant increase of actual area of contact in conditions of high loads which determines a sharp grasping of surfaces with a great deal of deep destruction of them [6, 18].

Work done abroad on creation of universal oils for hypoid automobile transmissions, equally effective both in conditions of high torque and medium speeds characteristic for trucks, and also in conditions of high speeds with sharp shock braking characteristic for the passenger automobiles in big cities, showed that in this case it is necessary to use additives containing simultaneously a number of active elements: sulfur, chlorine, phosphorus, nitrogen, zinc, lead, or other metals. In this case the content of additives in oil reaches sometimes 15% [19].

Especially effective in antiscoring properties are additives containing simultaneously sulfur and chlorine. It is proven that in this case sulfur not only acts independently, but is also a catalyst in the formation of films of iron chlorides during friction [7].

In Fig. 1 is shown dependence of OPI index characterizing movement of curve of dependence of spot of wear from load (during test on four-ball machine*) on the concentration of additives of sulfur and chlorine in oils DS-14. In the left part of the diagram antiscoring properties of oil are increased due to increase of concentration of chloric component (from 0 to 10%) in oil (chloroparaffin, chlorinated biphenyl hexachloroethan). In the right part of the diagram is represented dependence of OPI index on concentration of sulfuric additive (dibenzyl-disulfide, LZ-6/9), changing from zero to 10% in oil. In the middle of the diagram the total concentration of additive remains constant. Content of sulfur and chlorine components changes so that with decrease of one the quantity of the other component correspondingly is increased.

From this diagram it follows that an increase of concentration in oil of single-component sulfur and chlorine additives over 5% (left and right side of diagram) little affects antiscoring properties. The antiscoring properties of chlorine additives are worse than those of sulfur additives due to large discontinuities in wear of spheres during seizing in the first case (Fig. 2). Antiscoring activity of chlorine additives depends not only on chlorine content in them, but in an even larger degree on their chemical structure: with an equal content of chlorine, the chlorinated biphenyl, where chlorine is in a ring, is significantly lower with respect to antiscoring activity than chlorinated paraffin. At the same time chlorinated aliphatic hydrocarbons - chlorinated paraffin and hexachloroethane, — are clearly excellent with respect to chlorine content in

*Method of test according to All-Union Government Standard 9490-60.

molecule (40% Cl and 90% Cl), and are distinguished with respect to antiscoring properties only as long as content of chlorine in oil does not attain 2%. With a higher chlorine content in oil hexachloroethane does not have advantages with respect to antiscoring properties as compared to chlorinated paraffin.

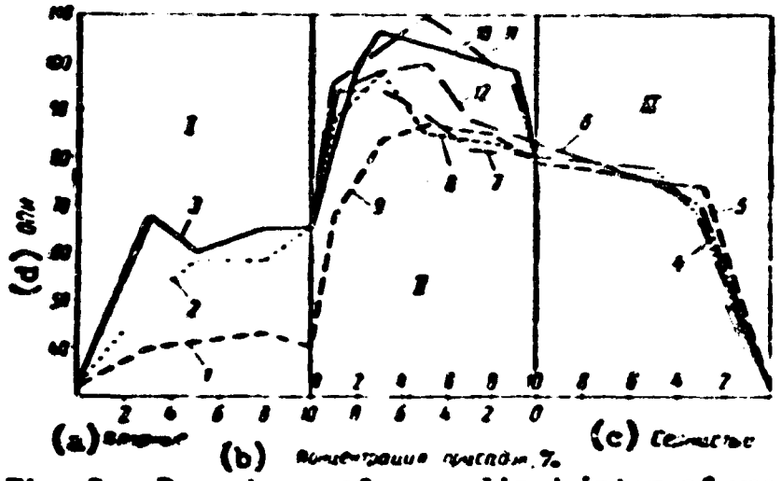


Fig. 1. Dependence of generalized index of wear (OPI) on concentration of sulfur and chlorine additives in oil DS-14.
I) chlorine additives; II) sulfur-chlorine additive; III) sulfur additives; 1) chlorinated biphenyl; 2) chlorinated paraffin; 3) hexachloroethane; 4) dibenzyldisulfide; 5) LZ-6/9; 6) sulphurized terpenes; 7) dibenzyldisulfide + chlorinated paraffin; 8) LZ-6/9 + + chlorinated paraffin; 9) LZ-6/9 + chlorinated biphenyl; 10) LZ-6/9 + hexachloroethane; 11) hexachloroethane + + sulphurized terpenes; 12) chlorinated paraffin + sulphurized terpenes.
KEY: (a) Chlorine; (b) Concentration of additives, %; (c) Sulfur; (d) OPI.

Upon introduction into oil of sulfur and chlorine components, the addition of a small quantity of sulfur additive to the chlorine component sharply increases antiscoring properties of the oil (middle of diagram of Fig. 1). Maximum effect is attained approximately with a ratio of 70% chlorine component and 30% sulfur component of additive and, apparently, almost does not depend on concentration of sulfur in sulfur component of additive (Fig. 3).

On the basis of the results obtained it is possible to more or less confidently recommend a ratio of sulfur and chlorine components in combined additives. In combination with anticorrosive additive vnii np-371 combined sulfur-chlorine antiscoring additives are not corrosively aggressive and are very effective.

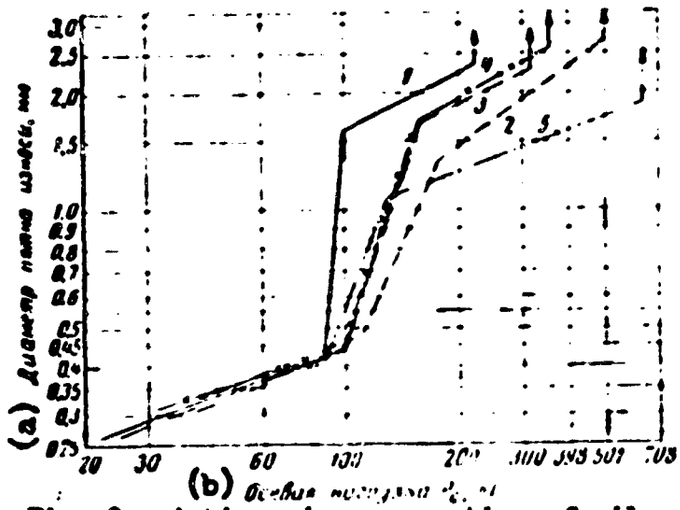


Fig. 2. Antiscoring properties of oil DS-14, containing sulfur and chlorine additives in 5% concentration.
KEY: (a) Diameter of spot of wear, mm; (b) Axial load P_o, kg.

No. sample	Additive	Antiscoring properties		
		OPI	P_K	P_{cb}
1	Chlorinated biphenyl..	40.8	89	224
2	LZ-6/9.....	76.6	112	501
3	Chlorinated paraffin..	58.2	100	316
4	Hexachloroethane.....	66.0	100	355
4	Dibenzyldisulfide.....	77.1	89	631

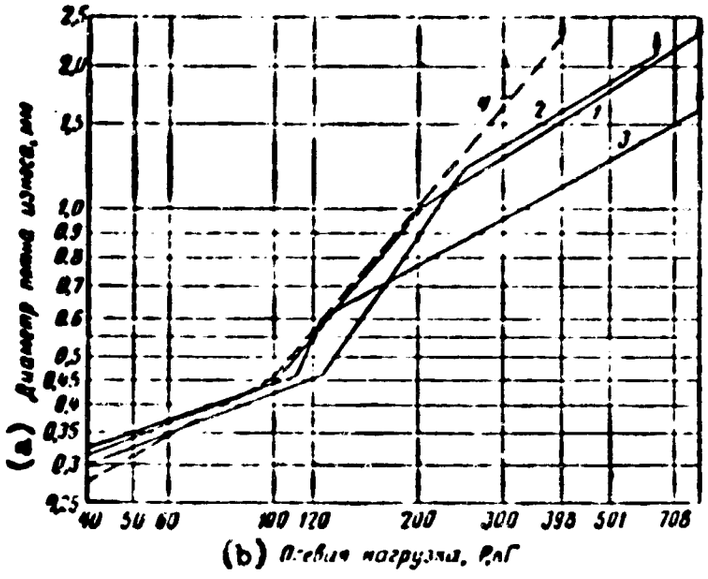
Possessing high antiscoring activity, sulfur-chlorine additives at the same time can increase wear of friction surfaces under moderate operating conditions. Therefore, improvement of antiscoring additives was in the direction of development of three-component sulfur-chlorine-phosphorous additives. Phosphorus promoted not only lowering of friction and wear, but also certain a impairment of antiscoring properties as compared to two-component sulfur-chlorine additives.

Very effective for reducing wear of surfaces are zinc dithiophosphates, and, in particular, additive DP-11.

Similar additives in combination with sulfur and chlorine components at present are applied in the USSR and abroad in universal oils for hypoid transmissions. A valuable property of zinc dithiophosphates, besides reducing wear,

is the fact that they do not lower effectiveness of active antiscoring additive in oils.

The VNII NP has proposed a strong additive, containing four active elements: sulfur, chlorine, phosphorus, and zinc, introduced in oil in 7% quantity. The additive has also good antiwear properties and is obtained from accessible raw material.



(a) Диаметр пятна износа, мм

(b) Осевая нагрузка, R, кг

Fig. 3. Antiscoring properties of oil DS-14, containing two-component sulfur-chlorine additive.
KEY: (a) Diameter of spot of wear, mm; (b) Axial load, R, kg.

No. sample	Additive		Antiscoring properties		
	Designation	Concentration, %	OPI	P_K	P_{cb}
1	Chlorinated paraffin and dibenzyldisulfide.....	7 3	96	100	794
2	Chlorinated paraffin and LZ-6/9.....	7 3	94.8	126	631
3	Hexachloroethane and LZ-6/9.....	7 3	108.8	112	794
4	Chlorinated benzyl and LZ-6/9.....	7 3	84.2	100	398

Very effective are additives of chloroalkylphosphine acids and their esters. The additive Chloreth-40 (butyl ester trichloromethylphosphine acid) showed itself sufficiently effective upon addition to oil in 2% quantity. It is possible without doubt to recommend it for wide use in spiral-conical automobiles transmission; however, as yet the possibility of its use in oils for hypoid transmissions remains still vague due to its instability at temperatures higher than 130°, which can be developed in these conditions.

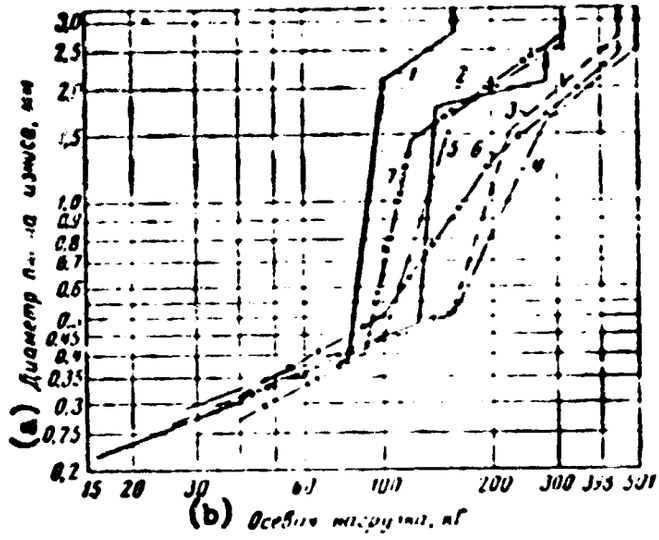


Fig. 4. Antiscoring properties of oil DS-14, containing compounds of molybdenum.
KEY: (a) Diameter of spot of wear, mm; (b) Axial load, kg.

No. sample	Additive: Designation	Additive: Concentration %	Antiscoring properties: OPI	Antiscoring properties: P_K	Antiscoring properties: P_{cb}
1	—	—	37.5	79	158
2	Molybdenum blue.....	1.5	56.1	126	282
	" "	1.5			
3	LZ-6/9.....	3	88.8	158	447
	Molybdenum blue.....	1.5	97	158	501
4	Chlorinated paraffin....	5			
5	" "	5	58.2	100	316
6	LZ-6/9.....	3	74	100	447
7	MoS_2.....	10	52	89	316

Sulfur-phosphorous antiscoring additives are simultaneously anticorrosive and antioxidant; however, according to tests on four-ball machine of additives SF-2, LZ-30, vnii np-353, and EPO they yield with respect to antiscoring properties sulfur-chlorine and chlorine-phosphorous additives. Nonetheless, certain data of bench tests of sulfur-phosphorous additives in hypoid transmissions shows that they are effective in a wide range of operating conditions [19]. Here, probably, there is a possible non-correspondence between behavior of additives on friction machines and in actual gears, or structural distinctions between additions, since it is found that the biggest effect of thiophosphoric compounds is in the presence of relatively low mobile phosphorous and high-mobile sulfur [5, 20].

Additions containing metallic derivatives, apparently, act by various means, depending on character of these compounds.

Plumbic soaps are applied in oils in combination with active sulfur and are effective for running in of surfaces of gear teeth in the first period of operation. Action of these additives is based on the reaction between the film of plumbic soaps adsorbed on the surfaces, sulfur and oxygen, leading to formation of lead sulfate, which during further thermal effect changes into lead sulfide. Lowering of friction is obliged by formation of eutectic alloys FeS and PbS with a reduced melting point (970°) [21].

The additive molybdenum blue, consisting of a complex oxidized form of compounds of molybdenum is of interest According to available assumption [20], additions of this type can act only in the presence of a sulfur component; under the action of temperatures on friction surfaces there occurs decomposition of the complex compound of molybdenum blue and molybdenum disulfide will be formed, ensuring an easy shift of shells between atoms of sulfur.

Meanwhile tests of molybdenum blue and molybdenium disulfide in oil DS-14 showed that molybdenum blue in pure form is a stronger antiscoring additive than MoS_2. Molybdenum blue in combination with chlorinated paraffin possess higher

antiscoring properties than in combination with sulfuric addition LZ-6/9 (Fig. 4). Investigation of electron diffractions, conducted by the VNII NP jointly with NIIKhIMMASh [Scientific Research Institute of Chemical Machinery], showed that lines characteristic for molybdenum disulfide are absent in the diffraction pattern after test of molybdenum blue with LZ-6/9, but are revealed on surfaces after tests of oil with additive MoS_2. This indicates that mechanism of action of molybdenum blue is different than action of molybdenum disulfide.

A qualitative reaction to an ion of molybdenum and to sulfide after test of friction surfaces shows that in the presence of a sulfur addition the reaction to molybdenum weakens, and in the presence of molybdenum blue the reaction to sulfur is strengthened. This indicates catalytical action of complicated oxidized complexes of molybdenum, strengthening the reactivity of sulfur compounds. Apparently, complex oxidized form of molybdenum compound with variable valence possesses high surface activity and reactivity with second active element of additive. High surface activity ensures independent effect of additive of molybdenum blue, simultaneously reacting with sulfur and chlorine with formation of compounds various according to character. Such reactive films strongly increase antiscoring properties of surfaces.

The problem of creation of high-quality oils for automobile transmissions is rather complicated. Besides the basic requirement of high antiscoring properties, additives in oil have to be selected in such a manner that they do not cause increased wear of surfaces during moderate conditions of friction and corrosion of metallic surfaces; they have to be dissolved in oil and to be stable in solution; they should not decompose in oil under the influence of increased temperatures and only by temperature-selective means in local points - on micro-contacts; last, they should not worsen the remaining physico-chemical properties of oils.

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INFLUENCE OF CATALYST OF OIL OXIDATION ON ANTICORROSIVE EFFECTIVENESS OF ADDITIVES CONTAINING VARIOUS FUNCTIONAL GROUPS

K. S. Ramayya and R. Kh. Sil's
NAMI*

Corrosive aggressiveness of motor oils and anticorrosive effectiveness of additives to them in the USSR are estimated according to loss of weight of lead plates in oil subjected to oxidation by oxygen. In these methods the catalyst of oil oxidation is not applied; meanwhile in conditions of work of internal-combustion engine in oil, various metals capable of catalytically affecting oxidation of oil are present or are in contact with it. Furthermore, additives applied in motor oils contain components having both a negative, and also positive catalytical action on oxidation of oil. Metallic catalysts can react with these components just as with the natural oxidation inhibitors assisting in motor oils which affects corrosive properties of oils with additives. The present investigation was conducted for the purpose of obtaining certain information on these questions. There were no attempts to reproduce catalysts which are in the motor as was done by other authors.

Experiments were conducted in a DK-2 NAMI instrument at 140° with standard lead plates. In order to obtain an idea about progress of corrosion with respect

*State [illegible] on "Order of Labor Red Banner" Automobile and Automobile Engine Scie[illegible] Research Institute.

to time, plates were weighed during the test through various intervals of time.

In Fig. 1 are given results of investigation of the influence of five catalysts — copper stearate, iron oleate, cobalt naphthenate, copper-iron, and copper-cobalt on corrosion of lead in two typical base oils (MKZ). Oil DS-8 from sulfur oils in the absence of a catalyst is little aggresive as compared to industrial oil 50; its corrosion is 7 g/m^2 against 90 g/m^2 for industrial oil 50 after a 25-hour test. Such a difference in corrosivity of two oils having almost identical viscosity is explained by presence in oil DS-8 of a more effective natural inhibitor of oxidation. In the presence of a catalyst of oxidation this difference practically disappears which one may clearly see during application of catalyst of a copper stearate (curves 2 and 8, Fig. 1). After a 25 hour of test with catalyst copper stearate (0.02%) in both samples of oils corrosion was equal to 185 g/m^2; this indicates, in all probability, that the catalyst poisons the natural inhibitors of oxidation and that hydrocarbons of these two oils, obtained from various oils, are oxidized, therefore, in identical degree.

To check the assumption about presence in oils from sulfur oils of compounds effective as inhibitors of oxidation, separate experiments were conducted, whose results graphically are depicted in Fig. 2.

On the figure curve 1 pertains to oil from sulfur oils (AS-9.5), and curve 2 to industrial oil 50; in both cases to the oil is added olein acid in a concentration of 1 milligram KOH/g oil. For 50 minutes of the experiment the magnitudes of corrosion in both oils are practically identical. The small difference obtained is the result of differences of viscosity of these oils. Consequently, under conditions, practically excluding oxidation of oil, inhibiting compounds in oils from sulfur oils do not affect corrosion. On the same figure are given results of 30-minute experiments with samples of oil AS-9.5 (MKZ), containing different concentrations of olein acid in the presence of a catalyst (copper stearate) and without it. In the absence of oxidation, influence of copper stearate also is not observed.

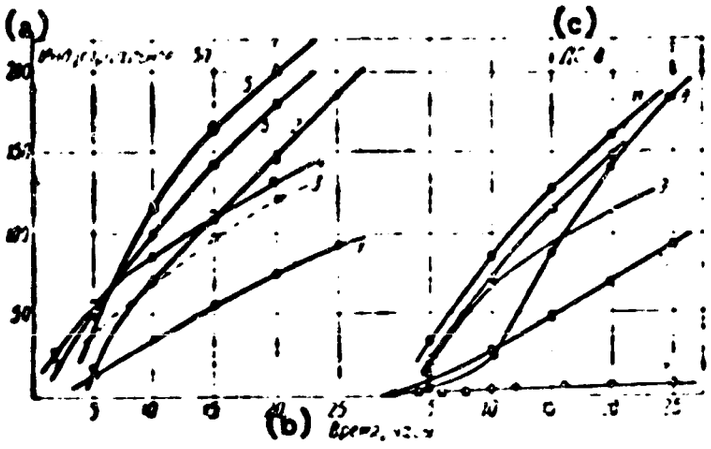


Fig. 1. Influence of catalysts of oxidation: salts of copper, iron, cobalt on corrosion of lead in industrial oils 50 and DS-8.
1) industrial oil 50 without catalyst; industrial oil 50 + additive: 2) copper stearate (0.02%); 3) iron oleate (0.02%); 4) cobalt naphthenate (0.02%); 5) copper stearate (0.01%) + + iron oleate (0.01%); 6) copper stearate (0.01%) + cobalt naphthenate (0.01%); 7) oil DS-8 without addition; oil DS-8 + additive; 8) copper stearate (0.02%); 9) iron oleate (0.02%); 10) cobalt naphthenate (0.02%); 11) copper stearate (0.01%) + iron oleate (0.01%); 12) copper stearate (0.01%) + cobalt naphthenate (0.01%).
KEY: (a) Industrial oil; (b) Time, hours; (c) DS-8.

Thus, data shown in Figs. 1 and 2 show that the low corrosive aggressiveness of oils from sulfur oils is the result of the presence in them of compounds which are natural inhibitors of oxidation, and that metallic catalysts of oxidation almost completely destroy action of compounds, the antioxidant and anticorrosive action of which is not combined with formation of protective film on metal.

Also it is clear that with application of a metallic catalyst it is possible to significantly reduce the time of testing oils on corrosivity. In Table 1 are given results of 10-hour tests of two samples of Baku oils and two samples of eastern oils with various additives without catalyst and in the presence of the catalyst of copper stearate (0.02%). Data of this table show that in the presence in oil of an anticorrosive additive the catalyst can significantly strengthen corrosion after 10 hours of tests. Such additives as azniI-5, in which anticorrosive action is attained by introduction of elemental sulfur, and also additives

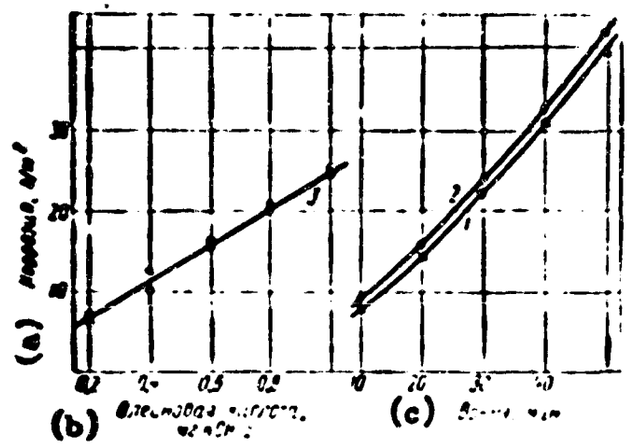


Fig. 2. Results of experiments on corrosion in the absence of oxidation. Catalyst is copper stearate. 1) oil AS-9.5 (NKZ) without catalyst + + olein acid (1 milligram KOH/g); 2) industrial oil 50 + olein acid (1 milligram KOH/g); 3) curve obtained with constant time (30 minutes); -- AS-9.5 (NKZ) without catalyst; AS-9.5 (NKZ) with catalyst (0.02%).
KEY: (a) Corrosion, g/m^2; (b) Olein, acid, milligram KOH/g; (c) Time, minutes.

Table 1. Influence of Catalyst Copper Stearate (0.02%) on Corrosion of Lead in Oil with Additives

Additive (3%)	Corrosion of industrial oil 50 (Baku), g/m^2			Corrosion of oil AK-10 (Baku), g/m^2			Corrosion of oil AS-9.5 (NKZ), g/m^2			Corrosion of oil DS-11 (NKZ) g/m^2		
	Without catalyst	With catalyst	Equivalent hours	Without catalyst	With catalyst	Equivalent hours	Without catalyst	With catalyst	Equivalent hours	Without catalyst	With catalyst	Equivalent hours
Without additive..	55	120	5.2	1.7	96	7.9	2.7	17	0.6	2.7	97	3.8
Tsiatim-339*.....	9.0	58	6.0	16	82	5.5	5.5	45	6.2	6.6	55	6
Aznii-7*.....	0.3	50	3.0	0.8	38	4.0	10.0	31	1—2	0.2	29	2
Aznii-5.....	11.0	140	2.0	46	76	8.0	1.6	56	4.0	9.6	69	5
Aznii-8.....	0.3	85	1.0	5.0	43	5.0	0.1	58	2—3	0.0	60	2
Paranox-56.....	0.7	1.6	—	0.8	10	6.0	0.8	0.3	—	2.0	2.0	—
DP-1.....	+0.2	0.6	—	0.1	0.7	6.0	0.1	0.9	~3	0.2	0.3	—

*Ed. Note: Tsiatim = Central Scientific Research Institute of Aviation Fuels and Lubricants; Aznii = Azerbaydzhan Scientific Research Institute. The Additives are named for the research institutes.

tsiatim-339 and aznii-7, in which, in all probability, the anticorrosive component is the disulfide group, during the 10 hours of the test almost completely lose their effectiveness.

A catalyst little affects effectiveness of additive Paranox-56, and the additive DF-1, containing the thiophosphoric functional group, actually does not yield to influence of a catalyst. The equivalent time (in hours) in Table 1 is the time necessary for obtaining in the presence of a catalyst the degrees of corrosion equal to corrosion after 10 hours of testing in the absence of a catalyst. It is significantly different for oils of various origin and oils containing various additives. It seems to us that clarification of anticorrosive effectiveness of additives in the presence of a catalyst under conditions of a sufficiently lengthy time of oxidation is a question in principle more important than reduction of time of standard tests.

In Table 2 are given results of 25-hour tests of oils with thiophosphoric additives in the presence of the catalyst copper stearate (0.02%). Additives DF-1 and Barthiol* are barium salts, but DF-11, Lubrisol-1060 and Zinthiol* are zinc salts of thiophosphoric acid. The additive Gintset* is a mixture of dithiophosphate of zinc with sulfonates of calcium and barium; additive vnii np-360 is a mixture of dithiophosphate of zinc with barium alkylphenolate. In industrial oil 50 all these additives almost completely inhibit corrosion. Even additive Gintset in this oil after 25 hours gives a corrosion of 7 g/m^2, which is 40 times less than in oil without additive. In sulfur oil DS-11 (NKZ) after 25 hours these additives are somewhat less effective than in industrial oil 50, but their effectiveness is sufficiently great, since they decrease corrosion from 25 to 100 times. This once again shows that in the presence of a catalyst of oil oxidation from sulfur oils in corrosivity there are no advantages over oils from low-sulfur oils.

*Additives Barthiol, Zinthiol obtained from the Czechoslovakian Republic; Gintset — from the German Democratic Republic.

Table 2. Anticorrosive Effectiveness of Thiophosphoric Additives in the Presence of Copper Stearate

Additive	Corrosion of industrial oil 50		Corrosion of oil DS-11 (NKZ), g/m^2	
	10 hours	25 hours	10 hours	25 hours
Without additive	140	270	97	206
DF-1 (3%)	0.2	0.4	—	—
DF-1 (5%)	—	—	0.0	3.6
Barthiol (3%)	0.2	1.2	0.7	8.2
Lubrisol-1060 (0.7%)	+0.7	+0.5	—	—
Zinthiol (3%)	+0.7	+0.1	0.7	5.4
DF-11 (2%)	0.8	2.2	—	—
Gintset (5%)	0.1	7.0	0.5	1.8
Vnii np-360* (5%)	0.3	1.6	0.6	178
Oil AS-9.5 (NKZ)				
Without additive			7.0	245
Component of additive Vnii np-360	Vnii np-350 (1%)		70	214
	Vnii np-354 (1%)		+0.4	3.5

*Ed. Note: Vnii np = All-Union Scientific Research Institute of the Petroleum Industry. The additive is named after the research institute.

In oil DS-11 with additive vnii np-360 and with catalyst after 10 hours of testing corrosion was not observed, but after 25 hours corrosion constituted 178 g/m^2. This is the result of the presence in this additive of a large quantity of barium alkylphenolate (vnii np-350), which is clear from results (placed at the end of Table 2) of test of sulfur oil (AS-9.5) with separate components of this additive. The thiophosphoric component of the additive (vnii np-354), taken separately, even in a concentration of 1%, practically completely protects lead from corrosion during 25 hours of testing.

In Fig. 3 curves 3, 4 illustrate influence of barium alkylphenolate (vnii np-350) on corrosion of lead without a catalyst and with one. In the absence of a catalyst for 11 hours the addition barium alkylphenolate completely stopped corrosion as compared to oil without additive (curves 1 and 3). Anticorrosive

effectiveness of barium alkylphenolate in the first hours of the test, obviously, is result of its neutralizing property.

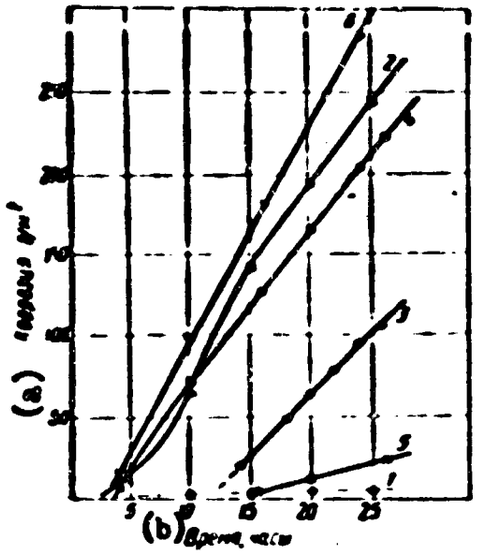


Fig. 3. Influence of catalyst — copper stearate (0.02%) — on corrosion of lead in oil AS-9.5 (NKZ) with additives.
1) oil without additive and without catalyst; 2) oil without additive + + catalyst; oil AS-9.5 + additive; 3) vnii np-350 (1%) without catalyst; 4) vnii np-350 (1%) + catalyst; 5) vnii np-361 (1%) without catalyst; 6) vnii np-361 (1%) + catalyst.
KEY: (a) Corrosion g/m^2; (b) Time, hours.

The alkylphenol liberated here, in all probability, turns out to be corrosively aggressive. In all these experiments all additives were taken in a 1% quantity.

In the presence of a large quantity of barium alkylphenolate in the oil, the alkylphenol liberated in the process of oxidation of oil can turn out to be sufficiently corrosively aggressive to counteract even the influence of effective thiophosphoric components of the additive. The high anticorrosive effectiveness of thiophosphoric components of additives vnii np-360 and 361 (vnii np-364 and vnii np-353) is conspicuous from the following data.

After 25 hours of testing oil with additive vnii np-353 in a 1% quantity gave a corrosion of 4.8 g/m^2; with additive vnii np-353 + catalyst 1.5 g/m^2; with additive vnii np-354 7.4 g/m^2 and with additive vnii np-354 + catalyst (0.02%) 2.8 g/m^2. It is remarkable that these components are more effective in the presence of a catalyst than without one. This phenomenon is frequently observed with thiophosphoric additives during their application in pure form.

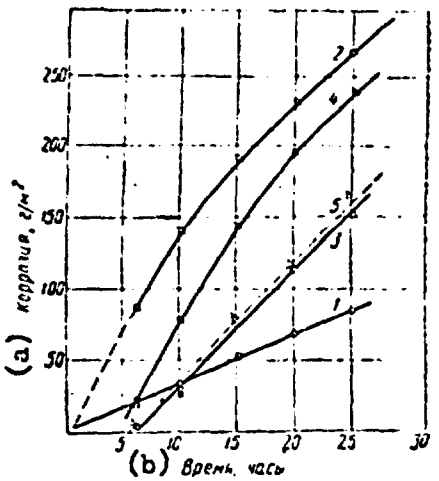


Fig. 4. Influence of catalyst -- copper stearate (0.02%) on corrosion of lead in industrial oil 50 with sulfonate additives. 1) oil without additive and without catalyst; 2) oil without additive + catalyst; industrial oil 50 + additive; 3) barium sulfonate (component aznii-5; ash 1.5%) without catalyst; 4) barium sulfonate (component aznii-5) + catalyst; 5) SB-3 (ash 1.5%) + catalyst. KEY: (a) Corrosion, g/m^2; (b) Time, hours.

For an example of additives SB-3 and component of additives aznii-5 (barium) in industrial oil 50 (Fig. 4) is illustrated the behavior of sulfonate additives with respect to corrosion of lead in oil. Low-ash barium sulfonate -- component of aznii-5 (curve 3) completely inhibits corrosion in industrial oil 50 over 6 hours, but after that period in its presence corrosion progresses at a higher rate than in industrial oil 50 without additive (curve 1). High-ash sulfonate SB-3 in the absence of a catalyst inhibits corrosion over 25 hours (1 g/m^2), but after additive of catalyst this sulfonate protects lead only over 5-6 hours. After that period corrosion in industrial oil 50 from this additive proceeds at a faster rate than in oil without additive. Path of curves for oils with both sulfonate additives shows that they can be anticorrosive only due to the presence in them of excess alkalinity, but actual neutral sulfonates, apparently, are corrosional-aggressive with respect to lead ratio.

Conclusions

1. Organic salts of metals: copper, iron and cobalt as a result of catalytical action on oxidation of oil, accelerate corrosion of lead in oils.

2. In the presence of a catalyst of oxidation, oils from sulfur-bearing oils containing natural inhibitors of oxidation, with respect to their corrosive

aggressiveness approach low-sulfur oils from Baku oils.

3. Additives containing as anticorrosive component compounds obtained by direct treatment of oil products of elemental sulfur or compounds of the disulfides type are not very effective in the presence of a catalyst. The thiophosphoric group in an additive is highly effective and protects lead from corrosion over a prolonged time both in the presence of a catalyst of oxidation and also without one.

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MECHANISM OF ACTION AND EFFECTIVENESS OF ADDITIVES INCREASING LUBRICATING ABILITY

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NIIchimprom*

Friction And Lubricating Ability of Oils

It is obvious that opinions on mechanism of action of additives have to result from physical and chemical presentations about phenomena regulated by additives. This in full measure pertains to additives increasing lubricating ability. Known difficulties and inconsistencies in treatment of their actions are combined with unequal role of lubricating oil under different conditions of friction. Consideration of regularities of lubricating action of oils is simplified if one separates types of friction proceeding from thickness of layer of oil in gap between surfaces of connected parts. By this criterion are distinguished three basic cases: 1) thickness of layer exceeds 0.4-0.6μ; 2) thickness of layer <0.3-0.4μ; 3) thickness of layer equals zero (oil was not kept on effective surface of friction).

In the first case friction is determined by viscosity of oil (hydrodynamic or liquid conditions of lubricant). Equilibrium thickness of butyric layer is a

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function of external factors (speed of shift, pressure, and so forth) and does not depend on properties of oil. Lubricating ability and, correspondingly, additives affecting it, do not have practical value.

Lubricating ability of oils in full measure appears in the second case. Analysis of a number of investigations leads to the conclusion [1, 2] that lubricating ability is a surface property of liquids, thanks to which they lower resistance to mutual shift of contacting solid bodies and simultaneously prevent approach of these bodies. Simultaneous development of both effects is an obligatory condition, since existence of only one of them cannot be considered as lubricating ability. If we artificially maintain a gap between parts of around 0.1 μ, then resistance to their shift in benzine will be lower than in best oils; on the other hand, elastoplastic films of polymers show a significantly higher resistance to approach of parts than oil, but they may cause an exceptionally high resistance to shift. In the considered case lubricating ability of oils essentially influence both static and also kinetic friction, but in kinetic conditions the effect is complicated by accompanying influences: deformation, dynamic, temperature.

Not going into a detailed discussion of the nature of lubricating ability (for different opinions on this question, see [1-10]), let us note that this property is caused by adsorption and orientation of linear molecules of surface active materials almost perpendicular to the surface of the solid body. In literature there are no conventional ideas about the distance to which the orienting action of the surface spreads, and, thereby, about thickness of layer of oil determining its lubricating ability, and about character of adsorptive interaction of molecules of oil with solid body. Bowden and his school [4] and certain other authors consider that the effect wholly or almost wholly is determined by a monomolecular layer. This point of view is in accordance with the known experiment of Langmuir [11] on measurement of coefficient of friction of glass

covered by a monomolecular layer of fatty acid. On the other hand, direct X-ray structural and electron diffraction investigations [12, 13] showed that orientation of molecules spreads to a depth of tens of molecular layers. Investigations conducted by B. V. Deryagin [3], A. S. Akhmatov [5] and certain other authors by methods of tribometry and molecular physics lead to the same conclusions. Our preceding measurements [1, 2, 14] also showed that the boundary layer of oil is polymolecular, and revealed certain factors determining its thickness and durability. In this report will be given further proofs of polymolecularity of the boundary layer.

It is impossible not to note an essential distinction between first layer of adsorbed molecules, directly combined with surface of solid body, and subsequent molecules of boundary layer.

First, the bonding energy of monomolecular layer with surface of solid body is not only considerably higher than for any subsequent layer of molecules, but, if one were to judge by certain indirect data (for a discussion of this question in connection with hydration, see [15]), it is significantly larger than for all the remaining part of the boundary layer. From this it follows that the coefficient of friction with a monomolecular lubricant should be higher than with a polymolecular lubricant.

Secondly, the nature of the interaction of molecules in boundary layer may be unequal. It has been proven [4, 6] that in a number of cases the first layer of surface active molecules of oil chemically interacts with metals (chemisorption), forming surface compounds; for instance, fatty acids form soaps. Interaction of molecules of the following layers carries a physical character. However, these experiments do not give a basis for dividing the boundary layer into chemisorbed and adsorbed in all cases. There exists sufficient bases to consider that interaction of solid bodies with monomolecular layer of even polar substances (halogenated organic compounds, esters, nitro derivative cyanides [16], fatty acids [17]

can have the nature of physical adsorption. A hydrogen bond, which also plays an important role, appears between carboxyl groups of acids inside the boundary layer and among these groups and such solid bodies as silicate glass and quartz.

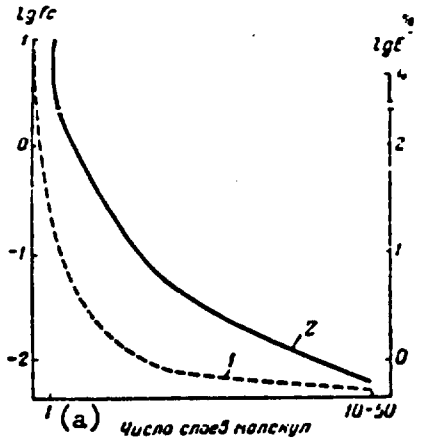


Fig. 1. Change of coefficient of friction and resistance to refinement of boundary layer of oil as function of its thickness.
1) $f_c = \varphi(n)$ (results of measurement of friction in four-ball friction gage); 2) $E = \varphi(n)$ (generalized result of measurement in instrument with plane-parallel disks).
KEY: (a) Number of layers of molecules.

Last, orientation of molecules of first layer is stabler than subsequent layers, where disorientation characteristic for volume of oil gradually grows. Longitudinal bond in monomolecular layer is determined by fixation by motionless molecules of solid body and interaction of molecules with each other, when in polymolecular layer the last factor has predominant value; but the bond with the solid body is realized only through molecules of monomolecular layer.

In Fig. 1 is schematically represented the change of coefficient of friction and resistance to refinement of boundary layer of oil, dividing conjugate flat surfaces of parts. The right side of the curves is the generalized result of measurement in instrument with plane-parallel disks [2, 17]; the left part has a hypothetical character, but is based on extrapolation and results of measurement of friction in four-ball friction gage [19].

When contact pressure and temperature attain limit high ("critical") value, the boundary layer "breaks through" and there develops direct contact of conjugate surfaces. However, such contact is never developed over the entire surface. Even in conditions of dry friction the true area of contact constitutes small part of the nominal area [20, 21]. The strength of the bond of monomolecular layer with

metal frequently is so significant that there occurs plastic flow of projections of microrelief of surface with preservation of this layer on them [22] (this is proven also in case of oxide films during cold welding [23]). Moreover height of the roughnesses considerably exceeds the length of molecules of oil and additives*. Consequently, under high loads friction on separate sections has the nature of dry friction, on others is threshold friction with monomolecular or polymolecular thicknesses of butyric layer.

Summarizing what has been presented, it is possible to express static friction of lubricated parts in the following manner:

$$F_c = \alpha S q_m + \beta S q_w + \gamma S \bar{q}_m$$

where S -- nominal area of contact; α, β and γ -- parts of it on which are developed accordingly direct contact of solid body mono- and polymolecular threshold lubricant; q_m — shearing strength of solid body per unit of surface area; q_w -- the same after covering by monomolecular layer of lubricant; $\bar{q}_m$ -- average resistance to shift in polymolecular boundary layer, pertaining to unit of area.

$q_m \gg q_w > \bar{q}_m$, but since $\alpha > \beta > \gamma$, then during the analysis of friction in conditions of incomplete)"ruptured") boundary layer all three component equations have to be considered**. Let us note that in distinction from friction, wear is combined mainly with magnitude αS and a small decrease of friction can lead to a significant drop of wear.

Analysis of the physical meaning of lubricating ability leads to the conclusion that additives which increase lubricating ability are all additives to oils (or other liquids) which ensure lowering of resistance to mutual shift (friction) of contacting solid bodies and increase of resistance to thinning of the layer of oil

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*Average height unevennesses of surface of parts, brought by polishing to 12-th class of cleanness, is approximately 80 times more than the length of molecule of the classic additive which increases lubricating ability — stearic acid.

**Rabinowicz and Tabor [24, 25] showed that in the case of lubrication of copper by copper palmitate the component of frictional force, combined with direct contact of copper during high loads, does not exceed 20% of the total frictional force in static conditions even 5%). Application of a lubricant with low lubricating ability increases this magnitude.

dividing these bodies, or cause one of these effects during stabilization of the second of them. Addition to oils of additives of this type leads to displacement of curve 1 (Fig. 1) to origin of coordinates (downwards and to the left). Antifriction action of these additives is expressed in decrease of magnitudes q_m, q_s and q_n or in increase of γ due to β and β owing to α. Change of the ratio between α, β and γ is due to increase of resistance to refinement of boundary layer of oil.

If with this α approaches zero, then wear strongly is lowered. During relatively high speeds of mutual shift, when speed of deformation of projections of microrelief of surface is great, then decrease of γ owing to β also leads to decrease of wear. Additives increasing lubricating ability are one of the forms of antiwear additives, since they weaken molecular and mechanical interaction of rubbing bodies, but antiwear additives [8, 26] include substances also with other mechanisms of action (polishing [7, 27], anticorrosive [28, 29] and others [30]), which can be more effective in heavy conditions of friction and in aggressive media.

Charact of action of additives increasing lubricating ability, and their effectiveness, and correspondingly the principles of selection and methods of investigation of these substances using a polymolecular and monomolecular threshold lubricant and during contact of rubbing surfaces are unequal. To solve practical questions of selection of additives, it is not obligatory to test them on actual mechanisms, but it is important to consider thickness of layer of oil between parts, temperature, speed of shift, mechanical and chemical properties of surface of solid body, and composition of oil. Under complicated conditions of friction it can turn out to be expedient, as was already noted by Beek and co-authors [31], to simultaneously apply two or three additives with different mechanisms of increase of lubricating ability.

Additives in Polymolecular Threshold Layer of Oil

According to the hydrodynamic law Stefan-Reynolds gap h between plane-parallel

disks immersed in a liquid is expressed by the following relationship*:

$$h = \sqrt{\frac{3\pi r^4 \eta}{4F}\,t}.$$

where r — radius of disks; η — viscosity of liquid; F — contact pressure; t — duration of contact.

From this equation it follows that if t is sufficiently great, then h decreases to zero.

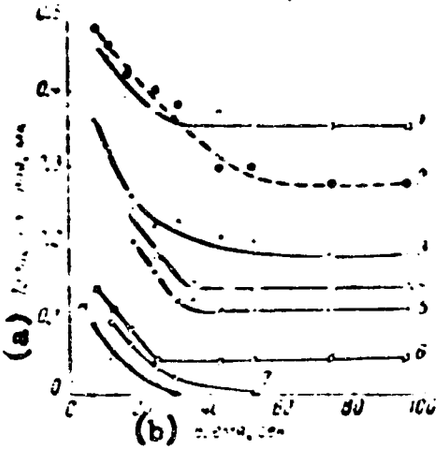


Fig. 2. Change of thickness of residual layer of hydrocarbons in gap between plane-parallel steel disks depending upon duration of action of load. 1) petroleum-paraffin fraction (npf) + 0.1% stearic acid, σ = = 4 kg/cm^2; 2) npf without additive, σ = 2 kg/cm^2; 3) the same, σ = 4 kg/cm^2; 4) isooctane + 0.1% stearic acid, σ = 1 kg/cm^2; 5) benzene + 0.1% stearic acid, σ = 2 kg/cm^2; 6) cyclohexane + + 0.001% stearic acid, σ = 0.2 kg/cm^2; 7) cyclohexane without additives, σ = 0.2 kg/cm^2; 8) benzene without additives, σ = 0.2 kg/cm^2.
KEY: (a) Thickness of layer, μ; (b) Time, sec.

This law is well observed in case of deep-purified lowest hydrocarbons. Investigation of mineral oils and lowest hydrocarbons with additives of fatty acids according to method [2, 17], shows that for such liquids the Stefana-Reynolds law is observed in gaps whose thickness exceeds 0.4-0.5 μ. From thinner gaps with contact pressures up to 25-30 kg/cm^2 these liquids are completely not squeezed (Fig. 2). They leave a residual layer whose thickness depends on contact pressure, nature of liquid, and additive (Table 1), and also on composition of surface of solid body and temperature.

*For greater detail, see [14].

Table 1. Residual Layer (in μ) 0.025% Solutions of Acids

Acid	Solvent	Steel UIOA		Ruby		Quarts	
		Contact pressure, kg/cm^2					
		0.2	2.0	0.2	2.0	0.2	2.0
Benzoic	Heptane	0.05	<0.02	—	—	~0.04	—
	Benzene	0.08	0.04	—	—	0.05	0.03
Valeric	Isooctane	0.08	0.06	0.07	0.05	0.05	0.03
Palmitic	"	0.16	0.11	0.14	0.10	0.12	0.08
	Benzene	0.11	0.07	0.08	0.06	0.04	<0.02
Phenylpalmitic	Isooctane	0.16	0.13	0.14	0.13	0.10	0.04
	Benzene	0.15	0.13	0.15	0.13	0.09	0.03
Adipic	Isooctane	0.06	0.04	0.05	—	0.03	—
Sebacic	Isooctane	0.06	0.04	0.05	—	0.03	—

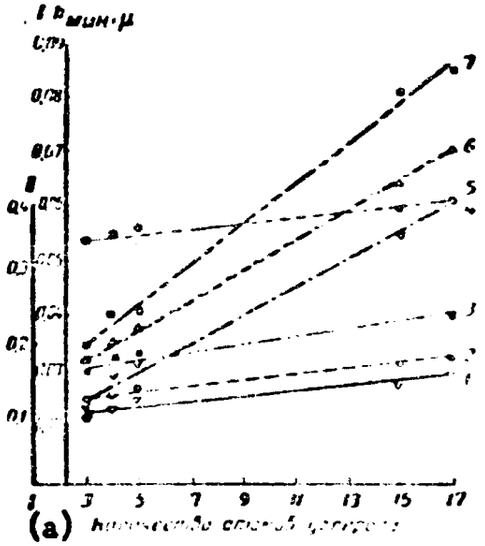
Thickness of residual layer of solutions of fatty acids in oils and lowest hydrocarbons turned out to be a linear function of the number of carbonic atoms of the hydrocarbon radical of the acid (Fig. 3):

$$h_{min} = K_1 + K_2 C_n,$$

where h_{min} — thickness of residual layer of liquid dividing conjugate surfaces; C_n — number of atoms of carbon in hydrocarbon radical of fatty acid; K_1 and K_2 are constants. It is interesting that K_1 equals thickness of residual layer of liquid without additive at a given contact pressure (in the case of lowest hydrocarbons $K_1 \approx 0$), and angular coefficient of slope of straight line K_2 depends on chemical composition of solvent (oil or other hydrocarbon liquid).

From the given data it is clear that effectiveness of additives of the fatty acids type with respect to their ability to increase resistance of polymolecular boundary layer to thinning is proportional to length of molecule of additive and

depends on relationship between structure of hydrocarbon radical of additive and molecules of solvent*. Benzoic acid is more effective in benzene than in isooctane, but palmitic acid is more effective in isooctane than in benzene. Phenylpalmitic acid acts almost equally both in paraffin and also in aromatic hydrocarbons (see Table 1). In dicarboxylic acids, in which hydrocarbon radicals are located, apparently, parallel to the surface of the solid body, the length of this radical does not affect thickness of residual layer, and consequently the resistance to its thinning.



(a)

Fig. 3. Dependence of thickness of residual layer of solutions of fatty acids in cable oil C-110 (curves 1, 2, 3, and 5), benzene (curves 4 and 7) and isooctane (curve 6) on quantity of atoms of carbon (C_n) in hydrocarbon chain of acid.
1, 2, 5, 7) pressure is 4.0 kg/cm^2;
3 and 6) pressure is 2.0 kg/cm^2;
4) pressure is 0.2 kg/cm^2.
Ordinate I — for curves 4, 6, 7;
Ordinate II — for curves 1, 2, 3, 5.
Key: (a) Number of atoms of carbon.

Action of the considered additives is explained by the fact that they create or increase disjoining pressure (for characteristics of this effect, see [33]) and give boundary layers an elastic (or quasi-elastic) property. Both disjoining pressure, and also strain hardening of the boundary layer increase with increase of length of adsorbed molecules which in turn depends on number of molecular bonds per unit of thickness of boundary layer and on increase of obstacles to relative rotation of molecules with increase of their length.

Within limits of boundary layer the resistance to mutual shift of plane-parallel disks (method [2]) decreases with increase of length of hydrocarbon radical of additive also according to the

*Preliminary experiments showed that this regularity also is observed for alcohols and nitro compounds of the normal aliphatic series and chlorine-substituted fatty acids.

linear law (Fig. 4). Consequently, in the case of solutions of additives in hydrocarbon liquids regularity is observed, established already by Hardy [3] during the investigation of threshold friction of surfaces lubricated by individual fatty acids and alcohols.

Both in experiments by Hardy and also during our measurements it remained vague how static friction is influenced by the molecular weight of fatty acids with more than 7-8 carbon atoms, inasmuch as shift in boundary layer is made along ends of hydrocarbon radicals of molecules oriented perpendicular to the surface, and a chain of 7-8 atoms of carbon is sufficient for shielding of carboxyl group. Actually, measurement of resistance to shift of surfaces in boundary layer of solutions of fatty acids with a strictly fixed gap (Fig. 5) shows that static friction practically does not depend on length of molecule of additive with more than 4-5 carbon atoms. Comparison of these data with data in Fig. 3 leads to the conclusion that the action of additives increasing their lubricating ability, within limits of the polymolecular boundary layer depends on their ability to maintain a gap between the rubbing parts, and at a given constant (but not too large) contact pressure this gap is increased in proportion to the length of a molecule of additive (within limits of compounds of one homologic series).

The "supporting power" of the polymolecular boundary layer, lying within limits 20-30 kg/cm^2 and above, is sufficient for many technical purposes but "temperature stability" of this layer is small. With increase of temperature, thickness of residual layer of solutions of additives in the beginning is not changed, but after a certain limit temperature, or more exactly, an interval of temperatures it decreases (Fig. 6) rather rapidly. Temperature of thinning of polymolecular boundary layer increases with decrease of its thickness (increase of contact pressure) and with increase of molecular weight of fatty acid, but it is significantly lower than temperature of fusing of corresponding soap or critical temperature limit of lubricating ability [6], pertaining to the monomolecular boundary layer.

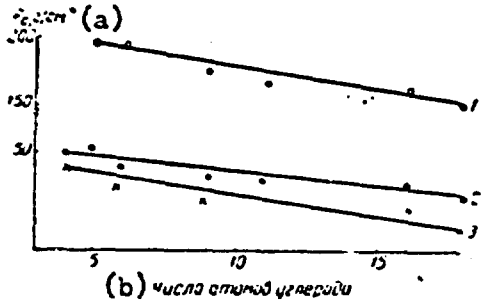


Fig. 4. Dependence of resistance to shift of plane-parallel disks on number of atoms of carbon in hydrocarbon chain of additive. 1) naphthene + 0.1% fatty acid, σ = 22 kg/cm^2; 2) naphthene + 0.1% fatty acid, σ = 6 kg/cm^2; 3) isooctane + 0.1% fatty acid, σ = 4 kg/cm^2. KEY: (a) g/cm^2; (b) Number of atoms of carbon.

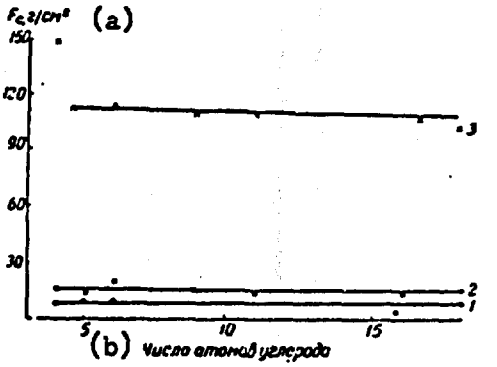


Fig. 5. Dependence of resistance to shift of surface of boundary layer of fatty acid solutions with a strictly fixed space on number of atoms of carbon in hydrocarbon chain of additive. 1) isooctane + 0.1% acid, h = = 0.10 μ; 2) npf + 0.1% acid, h = 0.30 μ; 3) the same, h = 0.10 μ. KEY: (a) g/cm^2; (b) Number of atoms of carbon.

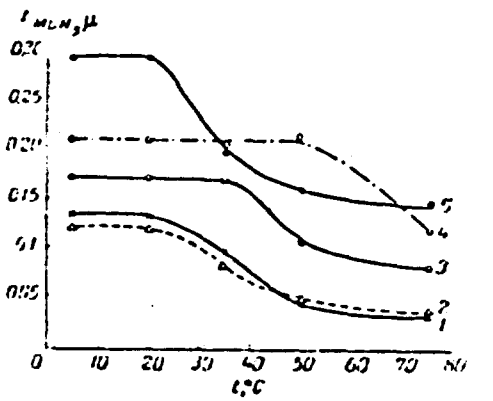


Fig. 6. Influence of temperature on thickness of residual layer of oil at a pressure of 2.0 kg/cm^2 between steel disks. 1) fraction of turbine oil η_{210} = 35.3 centipoise; fraction of transformer oil; 2) without additive; 3) the same + 0.1% caproic acid; 4) the same + 0.1% stearic acid; 5) naphthene-paraffin fraction MS-20.

From obtained data it follows that effectiveness of additives increasing lubricating ability, within limits of polymolecular boundary layer will increase with increase of length of molecule of additive, or more accurately — ratio of length to width. For this reason as additives of the considered type it is desirable to use diphenyl compounds of the normal series (without side chains), soaps with cations of a small radius (metals of first series of Mendeleyev' periodic system), molecules with rigid hydrocarbon chains. Flexibility of molecular chains is determined by potential barrier of

rotation of link of molecule near the bond, the higher it is the less flexible is the molecule. According to M. V. Vol'kenshteyn [35], potential energy of rotation of link of hydrocarbon chain near a triple bond is equal to approximately 500 cal/mole, near a double bond 1800 cal/mole, near a CH_3-CH_2 bond 3400 cal/mole, and near a ClH_2-CH_2Cl bond — more than 5000 cal/mole. With the selection and synthesis of effective additives, increasing lubricating ability, it is necessary also to consider that with increase of length even the most rigid molecules accumulate the possibility of rotation and oscillation of links, and therefore, there exists a limit of effective length of molecule of additive which increases lubricating ability.

Monomolecular Layer of Additives

When between surfaces of coupled parts there remain two layers of molecules of lubricating substance, the last one is not in a state of preventing mechanical interaction of solid bodies, but has a large influence on their molecular interaction. In particular, it prevents formation of metallic contacts (fusing) of surfaces [4, 10]. The monomolecular lubricating layer has a large value at high contact pressures (>40-50 kg/cm^2) and increased temperatures; therefore, to judge mechanism of action and effectiveness of additives it is important to clarify the nature and bonding strength of molecules of additive with metal or other solid body. This question was illustrated in literature [4, 6, 10], and we will be limited to only an indication of certain conclusions which follow from measurement of static frictions, conducted in our laboratory with the help of a four-ball instrument [19].

It turned out that fatty acids lower friction under very high contact pressures reaching the index of microhardness of metals (Table 2). It follows from this that with a slow load the contact surface of solid bodies is deformed without displacing the monomolecular layer of fatty acid from the space between them.

These results are in accordance with the work of Langmuir [36], which showed that for removal of the monomolecular layer of fatty acids from surface of metal it is necessary to heat the latter in a vacuum at a temperature higher than 340°, and from data of Bouden [4], revealing that fatty acids on the surface of metals form soaps. It is known also that surface active material are successfully used for easing of dragging and flattening of metals.

On the other hand, it was shown [4, 6, 38] that with an increase of temperature to a magnitude close to melting soap or another compound of additives with metal, in conditions of monomolecular lubricant there occurs a sharp jump of friction (and wear). This can be explained only by the fact that the additive, although still combined with metal, due to disorientation lost the ability to prevent molecular interaction of solid bodies (adhesion), leading to formation of a metallic bond.

Table 2. Coefficient of Static Friction of Solid Bodies at High Contact Pressures

Solid body		Lubrication by a 0.1% solution	Coefficient of static friction during contact pressure (kg/mm^2)		
Name	Microhardness according to method [37], kg/mm^2		100—300	750—900	1500—2000
Steel U10AV	850	Without lubricant	0.77	Permanent deformation of zone of contact	—
		Caproic in dioctylsebacinate...	0.15	0.14	—
		Stearic in dioctylsebacinate...	0.13	0.13	—
Quartz crystal	1500	Without lubricant.	0.80	0.78	Destruction of sample
		Caproic in naphthene-paraffin fraction MS-20.....	0.17	0.17	—
		Stearic in that same oil.....	0.14	0.14	0.20
Dark red ruby	2250	Without lubricant.	0.33	—	0.30
		Stearic in turbine oil.....	0.16	—	0.15
Leucosapphire	2400	Without lubricant.	0.33	0.31	0.29
		Stearic in turbine oil.....	0.17	0.18	0.20

Work of friction during a small speed of shift in conditions of monomolecular lubricant is expended mainly on plastic flow of projections of microrelief and only partially on their destruction. Additives like surface active materials promote deformation of metals [39], glasses [40] and other solid bodies, by which they can lower also the mechanical component of friction.

However, preservation of monomolecular lubricating layer is especially important for decrease of wear. In one of the preceding works [41] it was shown that for such high-hard bearing materials, as industrial jewels, there exists two forms of wear: brittle fracture of surface, to which corresponds a high coefficient of friction and catastrophic wear, and abrasion ("plastic wear"), at which takes takes place significantly slower and the coefficient of friction is essentially lower. Under high contact pressures for all materials represented in Table 2 in the case of dry friction the first form of wear was observed, with a monomolecular lubricant the second form was observed. Experiments revealing a mass transfer clearly showed that in the first case molecular (adhesional) interaction occurs, and in the second only mechanical interaction occurs. This graphically illustrates the role of additives increasing lubricating ability in conditions of a monomolecular lubricant.

Consequently, additives in the considered case have to be strongly bound with the friction surface. This follows, for instance, from comparison of lubricating ability of paraffin hydrocarbons with fatty acids equal to them in length of hydrocarbon chain. Reactivity of fatty acids may be increased by increase of dissociation of carboxyl group, for instance bonding of chlorine to neighboring atom of carbon.

However, energy of reaction of additives with metals and even oxides of metals and silicates does not limit effectiveness of the applied additives. In many cases a sufficient bond is provided by physical adsorption and in any case a hydrogen bond (see Table 2). Practically more important is an increase of temperature of

disorientation of monomolecular layer and increase of its thickness for more effective protection of rubbing bodies from adhesion. The first part of the problem is solved by using as additives substances forming on the surface high-melting compounds. Chemical principles of solution of the second part of the problem do not differ from those considered in the preceding division of the report.

One would think that in the case of a high speed of shift of rubbing surfaces it is expedient to increase energy of reaction of additives with them, in order to ensure rapid formation and reduction of monomolecular layer. But in this case the developed temperature of friction usually exceeds temperature of disorientation of monomolecular layer, and accumulation of heat in zone of friction finally leads to destruction of this layer.

Additives During Incomplete ("Broken") Threshold Layer

A general shortcoming of surface active materials like additives increasing lubricating ability is that boundary layers formed by them possess low temperature of "fusing". Up to now there are no known compounds of this type, which would form on metal boundary layers with a temperature of disorientation higher than 150°. Meanwhile under significant loads and speeds of shift in friction zone higher temperatures frequently are developed*. Due to this the boundary layer of the lubricant completely or partially breaks, and with rubbing of the surface zones of adhesion (fusing) or seizing appear.

Inasmuch as in such cases the physical and physico-chemical methods of lowering friction and wear are inactive, we resort to chemical modification of friction surface using sulfur-, chlorine-, phosphorus- and oxygen-containing additives.

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*A destroying action on the monomolecular boundary layer is rendered by temperature, but not by pressure. Above it was shown that this layer can sustain very high thermal stresses. Coming to us from American literature, the term "additive for super-high pressures" does not reflect the mechanism of action of these substances. It would be more correct to call them additives for high temperatures or additives for heavy friction conditions.

Shearing strength of compounds of metals with sulfur, oxygen, chlorine, and phosphorus is essentially lower than that of pure metals; they prevent formation of metallic bonds, and destruction of surface is localized in a thin surface, chemically modified layer. This leads to reduction of friction and prevents seizing. It is true, inasmuch as metal is covered by a less durable film of its compound, wear from abrasion can grow, but under heavy conditions of friction this form of wear, apparently, does not play a dominating role.

Mechanism of action and effectiveness of the considered additives were investigated in detail in the works of G. V. Vinogradov, P. I. Sanin, M. M. Kusakov, M. D. Bezborod'ko, Yu. S. Zaslavskiy, and others [26, 30, 18, 32]. Here we turned our attention to only one essential condition of action of the considered additives So that they be effective, it is necessary to guarantee the conditions of their reaction with metal. To develop the action of many of them it is sufficient to increase temperature (Table 3). During small speeds of shift and correspondingly low temperatures the effectiveness of the best of these additives may be lower than such substances as stearic acid (Table 3). Consequently, use of additives which change the property of the metal surface does not exclude use of surface active additives.

Basic requirement for additives modifying the surface is that compounds formed by them possess a lower shearing strength than corresponding metals. Unfortunately, this question is still studied very little. The second requirement follows from reactivity of additives. It should be sufficiently high that the protective layer is able to be restored in conditions of fast shifting, but at the same time too much metal does not have to be involved in the reaction. The theory of chemical interaction of additives with metal has only begun to be developed. Contemporary informations about this important and interesting regions are presented in quoted literature.

Table 3. Effectiveness of Additives in a Concentration of 6 Millimoles Per Liter in Dioctylsebacinate Under High Contact Pressures
Friction of Brass Against Steel in a Four-Ball Friction Gage [19].
Speed of Shift is 0.54 cm/sec

Contact pressure, kg/mm²	Temperature of oil, °C	Indices	Without additive	Stearic acid	$CH_3PO(OC_4H_9)_2$	$CCl_3PO(OC_4H_9)_2$	$(C_4H_9O)_3PS$*
89	25	Spot** of wear.....	129	115	144	174	242
		Coefficient of friction.....	0.20	0.16	0.24	0.25	0.25
	100	Spot of wear.....	135	130	132	119	175
		Coefficient of friction.....	0.20	0.17	0.18	0.18	0.19
246	25	Spot of wear.....	213	137	163	212	247
		Coefficient of friction.....	0.20	0.16	0.24	0.25	0.25
	100	Spot of wear.....	220	189	169	—	239
		Coefficient of friction.....	0.23	0.18	0.25	—	0.18
	150	Spot of wear.....	228	205	160	170	240
		Coefficient of friction.....	0.22	0.21	0.22	0.18	0.19

*Phosphorus-, chlorine- and sulfur-containing additives were given by P. I. Zamin.

**Diameter of spot of wear after 5 minutes, in microns.

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USES OF ANTIOXIDANT ADDITIVES TO POWER ENGINEERING OIL — NEW IN THEORY AND PRACTICE

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The phenomenon of negative catalysis during auto-oxidation of hydrocarbons was discovered in the first twenty years of the XXth century by the French chemists Moure and Dufraisse [1] and almost simultaneously and independently of them by B. G. Tychinin and N. A. Butkov in the USSR [2].

After 35 years, retarders of oxidation of hydrocarbons by molecular oxygen (antioxidants, inhibitors) found wide practical application in the most diverse areas of technology. In particular, they have long been used on a large scale as additives which inhibit the oxidizing aging of petroleum fuels during storage and of transformer and turbine oils during use [3, 4].

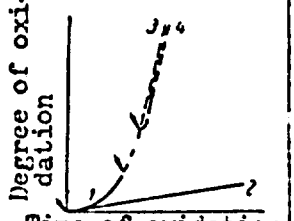
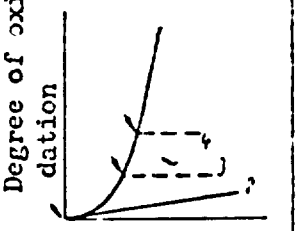
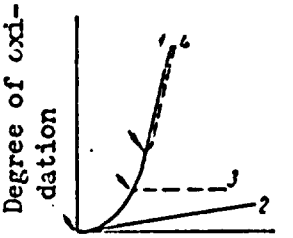
In spite of this, their mechanism of action has been little investigated. The first fundamental explanation of the inhibiting influence of antioxidants was obtained on the basis of the chain theory of the auto-oxidizing processes and combined with the ability of antioxidants to stop reaction chains [5, 6]. However, details of the chemical transformations undergone by the retarders, and also the question of the oxidizing stage on which their action appears were not studied.

[illegible] in recent years has there appeared new information shedding light on the chemical and kinetic side of the mechanism of action of auto-oxidation retarders.

Thus, in 1952-1955 for 2.6 — di-tert-butyl-4-methylphenol there was success in tracing the separate stages of chemical changes to which alkylphenol retarders are subjected in the course of inhibiting oxidation reactions and in confirming the radical nature of the reactions which developed [7, 8]. At the London 1958 symposium of the Institute of Oils, dedicated to insulating oils, in a number of works concerning antioxidants was reported experimental investigation marking significant distinctions in the chemism of action of antioxidant additives to these oils, which, besides the ability to stop reaction chains by means of capturing active organic radicals, as is peculiar to true antioxidants, can also act as a decontaminator or passivator of metals which are dissolved or washed by oil during use and accelerating of its aging [9].

In 1953, as a result of our laboratory investigation of the influence of antioxidants on kinetics of oxidation of petroleum oil hydrocarbons and reaction of these retarders with intermediate products of reaction, it was shown that differently built antioxidants, actively inhibiting the chain reaction of auto-oxidation in the period of its onset, do not equally affect the oxidizing process in the stage of its development [10]; the possibility of such phenomenon from the point of view of the chain theory in that same period of time was founded by N. M. Emanuel' [11]. We have experimentally proven that some inhibitors (group II) can vigorously inhibit oxidation which has already started, and others are not in the state to do this (group I), and lastly, a third group are able to stop the process only in its autocatalytic stage, but do not affect it in a later phase -- after achievement of constant speed by reaction (group III). It was shown that these observations, made on high-purified petroleum (white medical) oil, are confirmed also during action of the same substitutes on oxidation of normally purified commercially Baku transformer oil [12]. Further, it was found that these

Classification of Retarders of Auto-Oxidation of Petroleum Oils, Based on Their Action on Kinetics of the Process in Its Different Stages

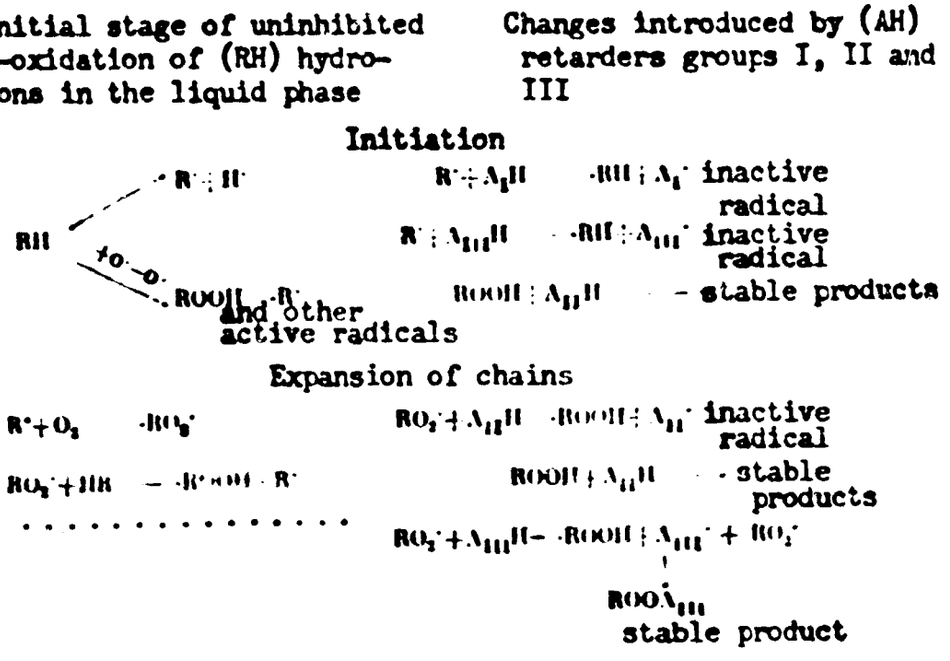
Group	Diagrams of influence on kinetics of oxidizing process*	Retarders	Concentration of retarder, weight %	Influence on thermal disintegration of hydrogen peroxide	Interaction with free R· and RO_2· radicals
I		diphenyl	0.017	Does not act	Reacts with R·
		Phenyl-β-naphthylamine	0.023-0.07		
		para-oxydiphenylamine	0.018;0.036; 0.072		
		para-oxyphenyl-β-naphthylamine	0.036		
		methyl aniline	2		
		dimethyl aniline	3		
		antipyrine	0.05		
II		α-naphthylamine	0.20	Actively promotes decomposition	Reacts with RO_2·
		α-naphthol	0.10		
		para-phenylene diamine	0.01		
		diethyl-para-phenylene diamine	0.008—0.017		
		para-aminophenol	0.010		
		hydroquinone	0.110		
		4.4-diamino diphenyl disulfide	0.003; 0.01; 0.025		
		para-tert-butyldiphenol	0.20		
		bezidine	0.036		
		ortho-tolidine	0.042		
III		β-naphthylamine	0.10	Moderately promotes decomposition	Reacts with R· and RO_2·
		β-naphthol	0.010, 0.30, 0.90		
		meta-phenylene diamine	0.010		
		diphenyl-para-phenylene diamine	0.026; 0.05		
		phenyl-α-napthylamine	0.07		
		di-α-napthyl-para-phenylene diamine	0.020		
		di-β-napthyl-para-phenylene diamine	0.020		
		ortho-aminophenol	0.016; 0.033		
		diethyl-ortho-aminophenol	0.07		
		resorcin	0.11		
		2.6-di-tert-butyl-4-methyl-phenol	0.022; 0.05; 0.11; 0.22; 0.44; 0.88		
		pyramidon	0.05		

*1) kinetics of oxidizing process; 2) retarder introduced into oil prior to beginning of reaction; 3) the same, in its autocatalytic period; 4) the same, after achievement of constant speed.

peculiarities of the action of retarders are combined with their ability to differently interact with intermediate products of the oxidation reaction — hydrogen peroxides of ROOH hydrocarbons [10] and free R· hydrocarbons and $RO_2^·$ peroxide radicals [13].

On the basis of these data was proposed a diagram of the mechanism of action of an inhibitor, explaining features of their influence on different stages of auto-oxidation of hydrocarbons [13] and classification of retarders, including 29 investigated compounds, possessing amine, phenol, disulfide and other functions, based on the above-stated kinetic criteria [12].

Diagram of Mechanism of Action of Inhibitors



In examining this classification it is possible to note certain features of the chemical structure of the retarders, determining to which separate kinetic groups they belong.

1. The very chemical nature of the functional group which is in a molecule of retarder still does not make it possible for it to belong to one or another kinetic group (in each of the latter are amines and phenols).

2. There is an important value, apparently, in the position of the functional group in a molecule of the inhibitor, since on it to a larger degree depends the direction of action of the investigated substances on the kinetics of oxidation of oil.

Thus, for instance, a distinctive feature of the structure of retarders of group II, belonging to the classes of aromatic amines, phenols, or aminophenols, is that the amine group in them has a primary character and is just as phenol hydroxyl, in active α- or para-positions (α-naphthylamine, α-naphthol, para-phenylene diamine, para-aminophenol, hydroquinone). Isomeric compounds, where these same functions assist in less reactive β-, and also ortho- and meta-positions, react like representatives of group III of inhibitors (β-naphthylamine, β-naphthol, meta-phenylene diamine, ortho-aminophenol, resorcin). When in antioxidant of group II — para-aminophenol — the active aminogroup loses its primary character as a result of introduction into it of phenol or naphthyl radicals, then the obtained phenyl-para-aminophenol or para-hydroxylphenyl-β-naphthylamine react as retarders of group I.

The results of theoretical research presented here, illustrating the kinetic mechanism of action of antioxidants, lead to two important practical conclusions. They make it possible:

a) to solve such questions as stabilization of the petroleum oils subjected to oxidizing aging (in the first place of transformer and turbine oils) not only in the fresh state but also during their use, i.e., already undergoing oxidizing changes, and also to reliably stabilize regenerated oils, in which there usually remains certain quantity of products of aging;

b) to use for stabilization of oils a mixture of antioxidants, fundamentally selecting the components of these mixtures.

Stabilization of Working and Regenerated Oils

In the stabilization of power engineering (transformer and turbine)oils, antioxidant additives until recently were introduced only into fresh oils, put into the aggregates for the first time. This was connected with the fact that the developed (at that time, by means of a purely empirical selection) effective additives, for instance, para-oxydiphenylamine and phenyl-β-naphthylamine proved to be incapable of stopping aging with had already started, and, consequently, were unacceptable for stabilization of working oils and the majority of regenerated oils. Moreover, these additives required for guarantee of maximum activity a certain repurification of fresh oils as compared to norms [14].

The above presentations about the kinetic mechanism of action of antioxidants allow a basic approach to selection of retarders for stabilization of working and regenerated power engineering oils. They make it possible to affirm that the most effective for inhibiting oils which have already starting aging have to be antioxidants of groups II and then III, and that retarders of group I(including para-oxydiphenylamine and phenyl-β-naphthylamine) are not useful for this purpose.

This position was confirmed during a wide check of it on commercial turbine and transformer oils not only in laboratory conditions (by artificial aging, All-Union Government Standard 981-55), but also during their use.

In tests under working conditions [15, 16], for the stabilization of working and regenerated turbine and transformer oils the additive VTI-8 (belonging to group II) and the additive Ionol (belonging to group III) were successfully used.

Advantages of Using Mixtures of Antioxidants

As a result of investigation of the interaction of antioxidants belonging to different kinetic groups, with intermediate products of auto-oxidation of hydrocarbons it was possible by direct experience to show that retarders of group I

($A_I H$) react only with free $R^\cdot$ hydrocarbon radicals and do not react with ROOH hydrogen peroxides and with free $RO_2^\cdot$ peroxide radicals; retarders of group II ($A_{II} H$) vigorously interact with hydrogen peroxides and $RO_2^\cdot$ and belong passively to $R^\cdot$ hydrocarbon radicals; retarders of group III ($A_{III} H$) react with $R^\cdot$ and $RO_2^\cdot$ and moderately, or not at all with hydrogen peroxides [13].

Considering this, it was possible to assume that simultaneous application of antioxidants of different groups (for instance, I and II, II and III, I and III) would cause mutual strengthening of their action and, consequently, would ensure maximum inhibiting of the oxidizing process.

In the case of joint application of retarder of groups I and II it is possible to imagnine, for instance that an antioxidant of group I will ensure the capture of a majority of $R^\cdot$ radicals appearing in the period of initiation, and those of them which will be kept will be turned into $RO_2^\cdot$, and will be deactivated by assisting antioxidant of group II.

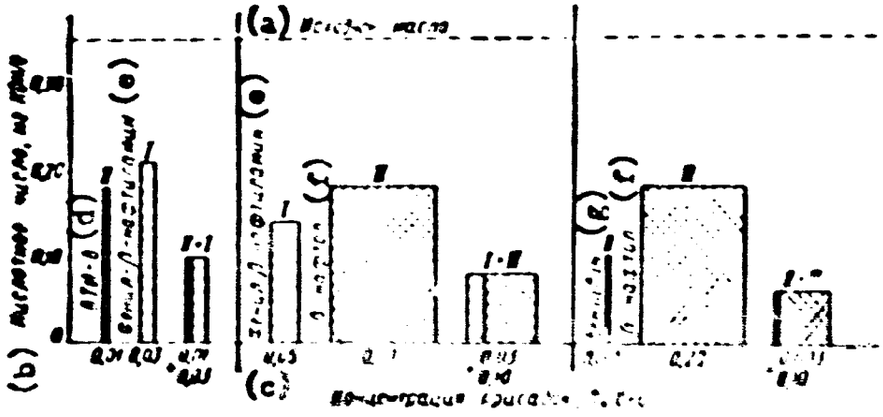


Fig. 1. Action of mixtures of antioxidants of different groups on stability of commercial transformer oil from Bezovoy oil.
KEY: (a) Initial oil; (b) Acid number, milligrams KOH/g; (c) Concentration of additives, weight %; (d) ViTI-8; (e) Phenyl-β-naphthylamine; (f) β-naphthol; (g) Benzidrine.

Opinions appearing in literature recently on the effectiveness of using mixtures of antioxidants for stabilization of petroleum oils are contradictory. Thus, on the one hand, G. Kennerli and W. Patterson, subdividing antioxidants into inhibitors (blocking free radicals of oxidizing chains) and destroyers of

Table 1. Influence of Antioxidants of Groups I and II and Their Mixtures on Stability of Power Engineering Oils (All-Union Government Standard 981-55)

Antioxidants			Stability of oil			
			Overall		Inclination to formation of water soluble acids in the beginning of aging	
Name	Group of classification	Concentration, weight % in oil	Acid number, milligrams KOH/g	Deposit, %	Nonvolatile acids, milligrams KOH/g	Volatile acids, milligrams KOH/g
Turbine oil (commercial, from butyric Balakhany oil)						
Oil without additive	—	0,00	0,28	0,02	0,003	0,006
para-oxydiphenylamine	I	0,02	0,13	0,02	0,001	0,007
VTI-8	II	0,02	0,07	0,01	0,002	0,001
para-oxydiphenylamine + VTI-8	Mixture I + II	0,01 + 0,01	0,01	0,01	None	0,003
Transformer oil (commercial from Emba butyric oils of the 1-st sort)						
Oil without additive	—	0,00	0,57	0,05	0,023	0,030
para-oxydiphenylamine	I	0,015	0,22	0,03	0,003	—
Phenyl-β-naphthylamine	I	0,02	0,27	0,03	—	—
α-naphthylamine	II	0,05	0,30	0,06	—	—
para-oxydiphenylamine + α-naphthylamine	Mixture I + II	0,01 + 0,05	0,12	0,06	0,005	0,007
para-oxydiphenylamine + α-naphthylamine	Mixture I + II	0,005 + 0,03	0,13	0,04	0,006	0,007
Phenyl-β-naphthylamine + α-naphthylamine	Mixture I + II	0,01 + 0,05	0,08	0,04	—	—
Transformer oil (experimental No. 1 from Tuymazy oil, content of sulfur 0.7%)						
Oil without additive	—	0,00	0,50	0,08	0,008	0,010
para-oxydiphenylamine	I	0,01	0,45	—	0,003	0,011
α-naphthylamine	II	0,05	0,45	0,13	—	—
para-oxydiphenylamine + α-naphthylamine	Mixture I + II	0,01 + 0,05	0,16	0,07	0,002	0,010
Transformer oil (experimental No. 2 from Tuymazy oil, content of sulfur 0.5%)						
Oil without additive		0,00	0,52	0,06	0,021	0,035
para-oxydiphenylamine	I	0,01	0,29	0,03	0,002	0,006
α-naphtol	II	0,05	0,18	0,03	0,002	0,012
para-oxydiphenylamine + α-naphtol	Mixture I + II	0,01 + 0,05	0,09	0,03	0,002	0,006

Table 2. Influence of Antioxidants of Group I and Their Mixtures on Stability of Transformer Oil from Butyric Balakhany Oil (All-Union Government Standard 981-55)

Antioxidants			Stability of oil			
Name	Group in classification	Concentration, weight % in oil	Overall		Inclination to formation of water-soluble acids in beginning of aging	
			Acid number, milligrams KOH/g	Deposit, %	Water-soluble acids, milligrams KOH/g	Volatile acids; milligrams KOH/g
Oil without additive	—	0,00	0,36	0,12	0,003	0,002
para-oxydiphenylamine	I	0,015	0,14	0,04	0,002	0,003
Phenyl-β-naphthylamine	I	0,020	0,17	0,05	0,003	0,003
para-oxydiphenylamine + phenyl-β-naphtyhlamine	Mixture I I	0,015 0,020	0,13	0,04	0,003	0,003

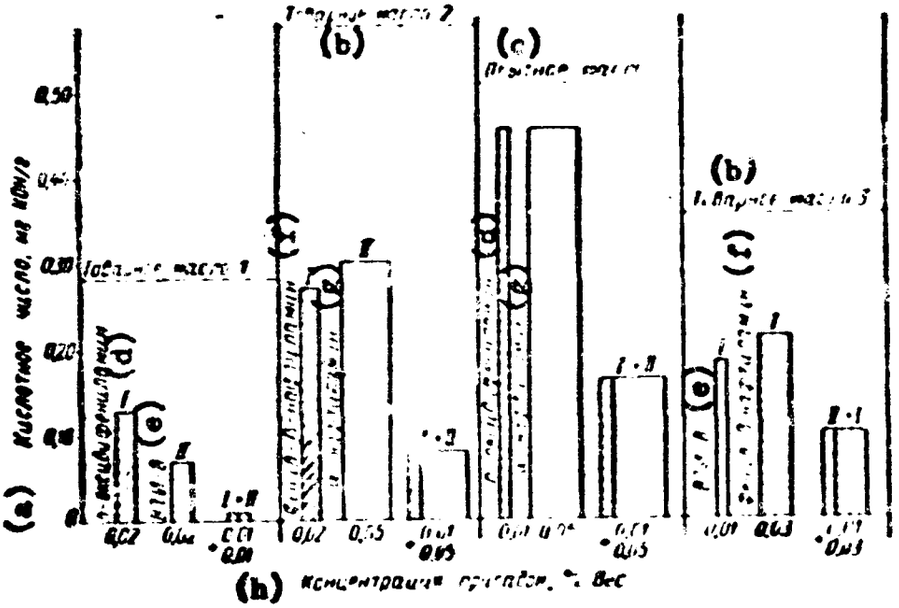


Fig. 2. Action of mixtures of antioxidants on stability of power engineering oils of different origin. Commercial oil 1) turbine commercial oil from butyric Balakhany oil; commercial oil 2) transformer commercial oil from butyric Emba oils; experimental oil — transformer experimental oil from Tuymazy oil (S = 0.7%); commercial oil 3) transformer commercial oil from Bazovny oil. KEY: (a) Acid number, milligrams KOH/g; (b) Commercial oil; (c) Experimental oil; (d) para-oxydiphenylamine; (e) VTI-8; (f) phenyl-β-naphthylamine; (g) α-naphthylamine; (h) Concentration of additives, weight %.

peroxides, note that mixtures of these substances in certain cases turn out to be more active than their components [17]. On the other hand, L. Massey and A. Wilsons present extensive experimental data indicating that mixtures of antioxidants investigated by them, act, as a rule, worse than each of them separately [9].

We conducted laboratory tests (Tables 1 and 2) and tests under operating conditions, showing that correct (from the point of view of positions expressed above) selection ensures an extraordinarily high effectiveness of the stabilizing action of mixtures of two additives on transformer and turbine oils, exceeding the effectiveness of each of them, even in those cases when the latter were taken (separately) in double concentration (Fig. 1 and Fig. 2). This can be considered as proof that we are dealing not with a simple addition of the influence of two antioxidants, but with a mutual strengthening of their activity, depending on their ability to seize on different stages of the process different active particles, provoking the onset and development of the chain reaction of auto-oxidation.

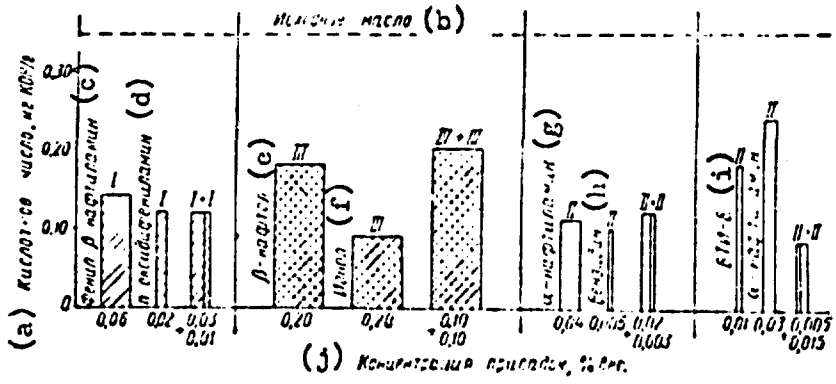


Fig. 3. Action of mixtures of antioxidants of analogous groups on stability of commercial transformer oil from Buzovny oil.
KEY: (a) Acid number, milligrams KOH/g; (b) Initial oil; (c) phenyl-β-naphthylamine; (d) para-oxydiphenylamine; (e) β-naphthol; (f) Ionol; (g) α-naphthylamine; (h) Benzidine; (i) VTI-8; (j) Concentration of additives, weight %.

The simultaneous use of a mixture of antioxidants belonging to the same kinetic group does not increase stabilizing action (Table 2, Fig. 3), with the exception of retarder VTI-8 containing sulfur, which, apparently, is connected with peculiarities of its chemical mechanism of action.

During the selection of such mixtures to be put into the butyric system of a turbine or into a transformer one should consider that one gain in stability is not sufficient and that it is necessary to check the influence of the selected mixture of additives on a whole series of other indices of the given oil both included and not included in technical conditions (All-Union Government Standard 932-56 and 32-53) for instance, corrosive properties, hygroscopicity, preservation of dielectric indices in the process of aging for transformer oils and others. Furthermore, it is important to be sure of the solubility of a given mixture of additives in oil, and also of the stability of this solution during storage. The latter is very important, since many paired additives tested by us in laboratory conditions, which were effective in their inhibiting action (for instance, a mixture of para-oxydiphenylamine with α-naphthylamine and with β-naphthol in eastern transformer oils) turned out to be practically unacceptable for this reason.

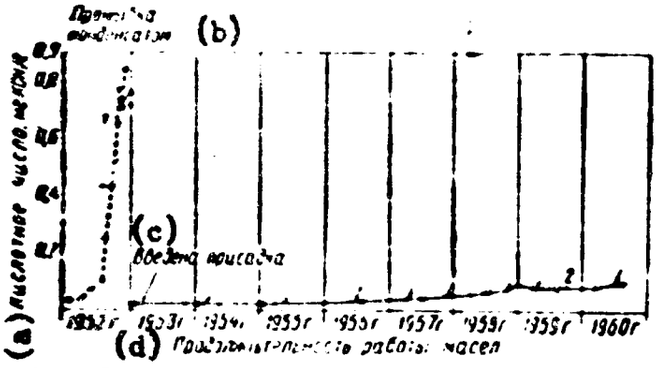


Fig. 4. Change of acid number of oils in a 6000 kilowatt turbine without additives and with a mixture of additives VTI-8 and VTI-1.
1) unstabilized oil in 1952; 2) stabilized oil in 1953 - 1960; □ --overhauling; Δ --acid reaction of aqueous extraction; ○--neutral reaction of aqueous extraction; ↓--addition of additives on additional oil fillings.
KEY: (a) Acid number, milligrams KOH/g; (b) Washing by condensate; (c) Additive is introduced; (d) Length of time the oils are used.

In Fig. 4 is given a graph illustrating work in a 6000 kw turbine of Baku oil stabilized by us in 1953 by a mixture of the additives VTI-8 (0.01%) and para-oxydiphenylamine (0.005%). For comparison, in the left part of the graph is shown the change of acid number of oil (not stabilized) used in a given turbogenerator prior to 1953. The use in this turbine of oil containing a mixture of the shown additives goes on continuously for 7 years without replacement with a neutral reaction of the aqueous extraction without use of an absorber.

Conclusions

1. Experimental investigations of the kinetic mechanism of action of retarders made it possible to establish that:

a) antioxidants of different structure, actively inhibiting the chain reaction of auto-oxidation in the period of its onset, unequally affect the process in the stage of its development;

b) these peculiarities of action of retarders depend on their ability to interact differently on various stages of the oxidizing process with intermediate products of reaction — hydroperoxides of ROOH hydrocarbons and free $R^{\cdot}$ hydrocarbons and $RO_2^{\cdot}$ peroxide radicals.

2. Ideas about the kinetic mechanism of action of retarders well-developed on this basis, made it possible to establish:

a) the possibility of successfully stabilizing power engineering oils with the help of antioxidants, not only in the fresh state but also after their oxidizing aging and use has already begun;

b) a high effectiveness of mixtures of antioxidants used for stabilization of power engineering oils during fundamental selection of components of these mixtures.

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INFLUENCE OF BASIC TYPES OF ADDITIVES ON OPERATING PROPERTIES AND OXIDATION OF OILS IN AN INTERNAL COMBUSTION ENGINE

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VNII NP*

To clarify the mechanism of action of antioxidant additives there is great value in a study of their influence on oxidation of oils in an engine. From a large number of compounds possessing antioxidant action, for investigation one additive each was selected of the phenol (barium para-tert-octylphenolate), amine (phenyl-α-naphthylamine), and phosphite (tributylphosphite) type.

Those changes were studied which are undergone by oils and the structural-chemical groups of hydrocarbons which compose them during use in an internal-combustion engine (IT9-2 and GAZ-51) without additives and with the above-mentioned additives.

The most deposit was given by naphthene-paraffin hydrocarbons, and the least by polycyclic aromatic hydrocarbons; monocyclic aromatic hydrocarbons occupy an intermediate position.

The amount of deposit in grooves, on rings, and piston of the engine is increased linearly in time.

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Barium para-tert-octylphenolate turned out to be the most effective additive of the ones investigated. The amount of deposit and varnish decreases most significantly during application of additives in naphthene-paraffin hydrocarbons. The response of oils to barium para-tert-octylphenolate is determined by the composition of oil, decreasing with increase of content of aromatic hydrocarbons, sulfurous compounds and resinous substances in oils. Upon addition of barium para-tert-octylphenol to industrial oil 50 (0.5% calculated on barium) the deposit of carbon in grooves, on rings, and piston of IT9-2 engine decreased from 0.39 to 0.13 g/hr, i.e., 3 times, or with evaluation by conventional method in points (after 10 hours of work of motor) from 6 to 1.9 (average of four determinations). The effectiveness of barium para-tert-octylphenol in oil AS-10.7 (NKZ from sulfurous oils) is lower: there was only a 40% decrease of deposit.

Crankcase oils affect magnitude of wear of cylinder and piston rings of internal-combustion engines, which is closely connected with viscosity of oils and their composition. For a quantitative evaluation of magnitude of wear it is possible to use data on wear of piston rings.

During application of a fraction of polycyclic aromatic hydrocarbons of industrial oil 50, having a 3.4 times larger viscosity than a naphthene-paraffin fraction of the same oil, 3.2 times wear was obtained. At the same time during application of aromatic hydrocarbons of oil AS-10.7, having after 10 hours of work in an IT9-2 engine almost the same viscosity (20.3 cs at 100°) as monocyclic aromatic hydrocarbons of industrial oil 50 (20.0 cs at 100°), wear was 4 times less.

As a result of the oxidation of oils in an engine are formed polar compounds, which, on one hand, decrease friction in boundary conditions and lower wear, and on the other increase corrosive wear. Introduction of additives or the presence in oil of sulfurous compounds which are polar surface active materials, decreases wear. The most effective antiwear additive turned out to be tributylphosphite;

some [illegible] worse was phenyl-α-naphthylamine. The comparatively high wear observed during use of barium para-tert-octylphenolate perhaps is explained by high the abrasive properties of the suspension of barium carbonate forming on the surface of the cylinder during the burning out of oil. This is confirmed by an experiment using as an additive a colloidal hydrate of barium oxide and an equimolecular mixture of barium para-tert-octylphenolate and para-tert-octylphenol which caused practically identical wear with an identical concentration of barium in oil.

In the presence of additives the viscosity of oil and hydrocarbons in the first 25-30 hours of work of the motor increases not as fast as without additives, then the action of additives ceases.

Upon the addition of additives the burning out of oil decreases in a comparatively insignificant degree.

Oxidizability of oils and separate groups of hydrocarbons repeatedly was investigated by different laboratory methods. Oxidation of oils in piston group of the motor occurs in conditions of contact with burning fuel-air mixture which is not reproduced during laboratory investigation of oxidizability of oils. Meanwhile burning of fuel essentially affects the mechanism and kinetics of oxidation of oil hydrocarbons.

We have experimentally shown that oxidation of hydrocarbons and oils in a motor passes through a stage of formation of hydrogen peroxides. An analytic method developed for this purpose made it possible to trace the dynamics of the accumulation of peroxide compounds in oils and individual structural-chemical groups of hydrocarbons separated from them. Data obtained during oxidation of industrial oil 50 and hydrocarbons separated from it showed that the largest quantity of peroxide compounds is stored in polycyclic aromatic hydrocarbons, and the least in naphthene-paraffin hydrocarbons. This is the result of different thermal stability hydrogen peroxides. In oils is stored a smaller amount of hydrogen peroxides than in pure hydrocarbons. This is explained by the fact that

resinous substances playing the role of inhibitors of oxidation, are stronger acceptors of the oxygen of the hydrogen peroxide radical than are hydrocarbons. Absolutely analogous is the role of sulfurous compounds. Accumulation of peroxide compounds passes through a maximum, advancing for pure hydrocarbons through 25-40 hours of work of the motor. Position of maximum depends on structure of hydrocarbons of oil and presence of inhibitors.



Fig. 1. Influence of additives on change of peroxide number (motor IT9-2).
a) naphthene-paraffin hydrocarbons of industrial oil 50; b) industrial oil 50; c) oil AS-10.7; 1) without additive; 2) with barium para-tert-octylphenolate; 3) with tributylphosphite; 4) with phenyl-a-naphthylamine.
KEY: (a) Peroxide number, milligrams O_2/100 g product; (b) Time, hours.

The dynamics of accumulation of peroxides in oils containing additives and in oils without additives are essentially distinguished. In Fig. 1 is shown the influence of additives on change of peroxide numbers of industrial oil 50, naphthene-paraffin hydrocarbons separated from it, and oil AS-10.7 during the work of motor IT9-2; the peroxide numbers, due to the action of additives, decrease by 2-3 times. Phenyl-a-naphthylamine is the most effective; effectiveness for barium para-tert-octylphenolate is lower; tributylphosphite occupies an intermediate position. The presence in oils of sulfurous compounds and resinous substances lowers effectiveness of the additives.

During the operation of a motor the action of additives decreases in time by the linear law. Data obtained, for instance, with naphthene-paraffin hydrocarbons, show that barium para-tert-octylphenolate abrades faster than others, and the

stablest is phenyl-α-naphthylamine. Tributylphosphite occupies an intermediate position. Consumption per hour of barium para-tert-octylphenolate in industrial oil 50 is around 1.4% or 0.5 mmole/l, and in oil AS-10.7 it is 1.05% or 0.38 mmole/l. The expenditure of phenyl-α-naphthylamine is significantly lower (for instance, in industrial oil it is 50 0.8% per hour or 0.18 mmole/l). Together with a decrease of effectiveness of additives under the influence of sulfurous compounds and resinous substances, the duration of the action of additives is increased.

During comparison of data obtained on motor IT9-2 with results of investigations carried out on motor GAZ-51 (in stand conditions) and on motor vehicle GAZ-51 (in conditions of use), it was shown that the magnitudes with respect to which are given the characteristics of changes of oils, are rather close for these motors and the regularities of the dynamics of their change are kept. Somewhat more rigid conditions in using oil in motor GAZ-51 and lower specific provision of oil to the oxidation surface (ratio of quantity of oil in crankcase to working surface of cylinders) explain the fact that curves of peroxidation for GAZ-51 motors lie lower than the curve for motor IT9-2. In crankcase oil of motor vehicle GAZ-51 is stored somewhat less peroxide compounds than during bench tests, since in actual working conditions frequent stops of motor vehicles are combined with alternate cooling and heating of oil, leading to a strengthening of conversion of peroxides into products of their further transformation.

As a result of the destruction of hydrogen peroxides there are formed oxy-compounds belonging to the class of alcohols or phenols, and carbonyl compounds containing the aldehyde and ketone groups.

During the operation of a motor in oils and aromatic hydrocarbons separated from them will be formed an almost identical quantity of free (not esterified) oxy-compounds, whereas in naphthene-paraffin hydrocarbons will be formed almost 2 times more of them (Fig. 2). According to the character of generated hydroxy-groups, polycyclic aromatic hydrocarbons very strongly differ from naphthene-paraffin

hydrocarbons: in the first for the share of tertiary alcohol groups around 16% is necessary, in naphthene-paraffin hydrocarbons they reach to 85%.

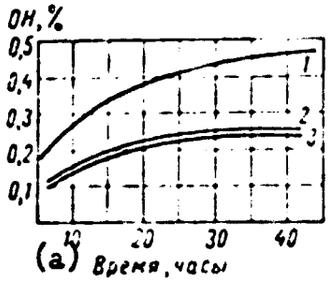


Fig. 2. Formation of oxy-compounds in oil AS-10.7 and of separated structural-chemical groups of hydrocarbons during operation of motor IT9-2.
1) naphthene-paraffin hydrocarbons; 2) aromatic hydrocarbons; 3) oil.
KEY: (a) Time, hours.

Additives lower content in oil of oxy-compounds by 20-40%, and in naphthene-paraffin hydrocarbons, having the highest content of them, by 60%. Phenyl-a-naphthylamine decreases the content of oxy-compounds in industrial oil 50 by 44%, and barium para-tert-octylphenolate by 24%; the effectiveness of barium para-tert-octylphenolate in oil AS-10.7 is the same (27%).

The formation of compounds containing aldehyde groups is very undesirable, since they present a potential source of neutral resins forming as a result of reactions of condensation, and carbonaceous acids forming as a result of further oxidation. For analytic determination of aldehydes in petroleum products containing other oxygen compounds, a special argentometric method has been developed. Use of it made it possible to study the dynamics of accumulation of aldehydes. It turned out that in the course of 50 hours of work of oils in a motor, the content of aldehydes in them is gradually increased, reaching almost 10% of the total quantity of carbonyl compounds; ... separate structural-chemical groups of hydrocarbons, not containing tarry ... stances, for the share of aldehydes around 15-20% is necessary.

A large distinction is observed between separate types of additives with respect to influence on formation of aldehydes. Phenyl-a-naphthylamine sharply lowers content of aldehydes; barium para-tert-octylphenolate, on the contrary, stabilizes aldehydes, promoting their accumulation. Therefore, in oils from this additive the content of aldehydes was almost 2 times higher than in oil without it.

Ketones are a basic form of carbonyl compounds, forming as a result of disintegration of hydrogen peroxides. For the share of ketones 80-90% of the total quantity of carbonyl compounds which form is necessary. In naphthene-paraffin hydrocarbons will be formed twice more ketones than in polycyclic aromatic hydrocarbons; monocyclic aromatic hydrocarbons occupy an intermediate position. The investigated additives lower the content of ketones in oils by 2-3 times. In Fig. 3 is shown the influence of additives on the accumulation of aldehydes and ketones in oil.

Carbonaceous acids are formed in oils as a result of further oxidizing transformation of aldehydes and ketones. The dynamics of accumulation of acids in oils and individual hydrocarbons have already been shown by a number researchers [1]. The results obtained by them, just as the data of other investigations, show that during work of a motor in oils will be formed less acids than in hydrocarbons of structural groups. Aromatic hydrocarbons are rather close to oils; among the latter polycyclic give less acids than monocyclic. A very large amount of acid products of oxidation will be formed when a motor works on naphthene-paraffin hydrocarbons; as soon as 1.5-3 hours of work of the motor the acidity is the same as oil has after 50 hours of work in a motor. Consequently, naphthene-paraffin hydrocarbons are a basic group of compounds yielding acids during oxidation of oils. The acids which form contain a significant quantity of low-molecular water-soluble acids. This indicates that they are products of oxidizing destruction of hydrocarbons. This process is the most energetic in polycyclic aromatic hydrocarbons; in them water-soluble acids constitute around 85% of the total quantity of acids. Monocyclic aromatic hydrocarbons yield acids containing around 30% water-soluble acids, and naphthene-paraffin hydrocarbons around 20%. The formation of acids in oil inhibits the presence in them not only of resinous substances, but also of sulfurous compounds.

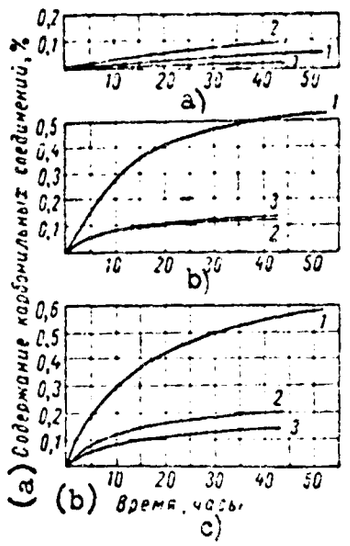


Fig. 3. Influence of additives on change of content of carbonyl compounds in industrial oil 50 during work of motor IT9-2.
a) content of carbonyl aldehyde groups; b) Content of carbonyl ketone groups; c) total content of carbonyl groups; 1) without additive; 2) with barium para-tert-octylphenolate; 3) with phenyl-α-naphthylamine.
KEY: (a) Content of carbonyl compounds, %; (b) Time, hours.

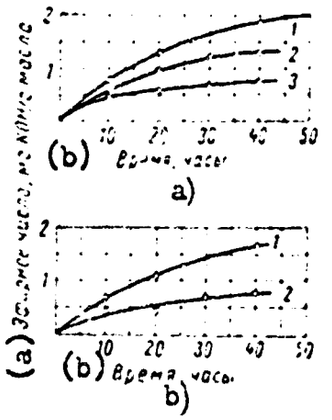


Fig. 4. Influence of additives on change of ester number of oils during work of motor IT9-2.
a) industrial oil 50; b) oil As-10.7; 1) without additives; 2) with barium para-tert-octylphenolate; 3) with phenyl-α-naphthylamine.
KEY: (a) Ester number, milligrams KOH/g oil; (b) Time, hours.

The acidity of oils most effectively drops under the influence of barium para-tert-octylphenolate (2-3 times) and phenyl-α-naphthylamine (almost 2 times). Tributylphosphite, although significantly lowering acidity, still has a significant quantity of free acids in it.

The basic form of oxygen compounds forming as a result of multistage oxidizing transformations, are esters. Among them the most important are esters of oxy-acids, represented by lactides, lactones, and polyesters (estolides). Oxy-acids serve as source of formation of oil-insoluble deposit on piston and rings (varnish, carbon deposits). The formation of esters is very strongly influenced by the structure of hydrocarbons. During oxidation of naphthene-paraffin hydrocarbons 2.5 times more esters will be formed than during oxidation of aromatic hydrocarbons

and 3-4 times more than corresponding oil. Polycyclic aromatic hydrocarbons yield approximately 20% less esters than monocyclic. Among esters the basic component turned out to be esters of oxy-acids. Complex esters of fatty acids are secondary components.

The accumulation of esters in oils under the influence of additives may be essentially decreased. In Fig. 4 are given data on change of ester numbers under the influence of additives. Phenyl-α-naphthylamine turned out to be the most effective additive in this case. Barium para-tert-octylphenolate lowers the content of esters in oils by 30-50%, while in sulfurous oil its action turned out to be more effective.

In not one of the experiments we conducted did we discover any period of induction during accumulation of products of oxidation in crankcase oil, i.e., to confirm the opinion about the fact that the action of additives leads to increase of period of induction. Meanwhile in all cases we observed an effect of inhibiting primary and secondary processes of oxidation. This is in accordance with the idea which we advanced that the process of oxidation is essentially influenced by the contact of the thin butyric film on the wall of cylinder with the burning fuel-air mixture. For confirmation of the opinion that the action of additives leads to an increase of the period of induction, it is necessary to investigate dynamics of accumulation of products of oxidation during the elementary period of oxidation.

On the basis of conducted research were composed so-called multicomponent additives possessing sufficiently high working properties (barium alkylphenolate with zinc dithiophosphate, barium alkylphenolate with additive tsiatim-339*, additive tsiatim-339 with DF-1 and others). Results of certain tests on motor IT9-3 according to method IDM-1-5 (VNII NP) of oils MK-22 (from Baku oils) and

*Ed. Note: tsiatim = Central Scientific Research Institute of Aviation Fuels and Lubricants. The additive is named for the institute.

DS-11 (from eastern sulfurous oils) with such multicomponent additives are given in the table.

Results of Tests of Oils MK-22 and DS-11 with Different Additives on Motor IT9-3 According to Method IDM-1-5 (VNII NP)

Oils with additive	Quantity of additive, %	Ash content of oil with additive, %	Color of deposit on piston, points	Amount of deposit, g				Corrosion of lead plate, g/m²	Motor index
				On piston	In 1-st groove and on 1-st ring	In 2-nd groove and on 2-nd ring	In 3, 4 and 5-th grooves, 3, 4 and 5-th rings		
MK-22	—	—	4	3.7	0.7	0.4	0.3	1.8	21.9
MK-22 with additive:									
tsiatim-339	3	0.26	2.5	1.6	0.4	0.2	0	3.7	10.5
DF-1	3.5	0.28	2.5	1.8	0.4	0.1	0	1.0	9.4
vnii np-360	3	0.45	4.0	2.5	0.5	0.3	0.3	1.5	17.7
vnii np-371	3	0.44	4.5	3.5	0.5	0.4	0.3	4.6	20.5
PMS$_{ya}$	10	1.70	1.5	1.0	0.4	0	0	0	6.5
tsiatim-339	3	0.42	1.5-2.0	0.8	0.2	0	0	1.2	4.3
DF-1	2								
PMS$_{ya}$	5	1.2	1.0	0.7	0.2	0.1	0	—	4.7
vnii np-360	2.5								
PMS$_{ya}$	5	1.35	1.0	0.5	0.1	0	0	3.5	2.9
vnii np-371	3								
DS-11	—	—	4.5	1.47	0.37	0.16	0.07	3.7	13.2
DS-11 with additive:									
tsiatim-339	3	—	2	1.21	0.33	0.16	0.01	2.9	9.0
tsiatim-339	3	—	1.0	0.99	0.23	0.10	0	1.2	5.8
AFB	2								
vnii np-371	6	—	3.0	1.51	0.36	0.20	0.01	4.1	11.6
vnii np-371	3	—	0.5	0.36	0.06	0.02	0	12.5	2.0
PMS$_{ya}$	3								
Santolube	19.6	3	0.5	0.10	0	0	0	0	0.9

As tests have shown, the composition of additives tsiatim-339 and DF-1 significantly increased the working properties of oil as compared to indices obtained in those cases, when each of these additives was applied independently.

Oil DS-11 with a two-component composition, composed from additives tsiatim-339 and AFB, also showed very high working properties. Further tests of this composition on tractor motors confirmed the obtained data.

Oil MK-22 with the proposed combination of additives tsiatim-339 and DF-1 was tested on a forced, thermally very stressed, special-duty motor, where positive results were obtained. Further research showed that addition of sulfonate type (PMS_{ya}) badly is combined with phosphorous-containing additives, but gives very good results in composition with additive vnii np-371.

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CHAPTER V

RESEARCH METHODS FOR ADDITIVE EFFECTIVENESS

COMPLEX OF METHODS TO APPRAISE THE EFFECT OF ADDITIVES ON THE WORKING PROPERTIES OF MOTOR OILS

K. K. Papok, A. F. Zarubin, B. S. Zuseva, V. P. Danilin, G. V. Zakharov, Ye. G. Kuznetsov, and A. G. Slavinskiy

Solving the most complicated problems of quality and application of oils and additives, the fastest creation of high-quality sorts of them and putting them into use, and also improvement of existing sorts of oils and additives -- all this first of all depends on methods which give possibility in short periods with small expenditures of investigated oils of reliably estimating their working properties.

In developing methods of appraising the quality of oils and additives very little is yet done. With the exception of several organizations (VNII NP, NAMI, NATI) [VNII NP: All-Union Scientific Research Institute on Processing Petroleum and Gas and Production of Artificial Liquid Fuel; NAMI: Scientific Research Automobile and Automotive Institute; NATI: State United Scientific Research Tractor Institute] almost no one is working in this field.

For full appraisal of working properties of oils and additives it is necessary to dispose the following three complexes of methods:

1) laboratory methods;

2) methods of bench tests on one-cylinder (with real cylinder) and on full-measured motors;

3) methods of field tests.

Laboratory Methods

A complex of laboratory methods have been developed which, in our opinion, can be applied for fast appraisal of working properties of oils and additives.

The complex of laboratory methods includes:

a) micro-methods, through which with expenditure of only 10 ml of oil we can determine its thermal properties and fractional composition;

b) methods of test on model installations, which give possibility with expenditure of 0.5 liter of oil to evaluate its washing and crankcase* properties;

c) methods of testing one-cylinder installations of the type IT-9, and especially primary motor test on IT9-5 according to method GSM-20 [GSM: Fuels and Lubricants], which give possibility with expenditure of 2.5 liters of oil to estimate its lacquer deposition and corrosion properties, and also coordination of oil and additive and test on IT9-3 to evaluate the scale forming ability of oil in combination with fuel.

Let us consider each of these methods in greater detail.

Micro-Methods

Among these are determining thermooxidizing stability and coefficient of lacquer deposition of oil (GOST 4953-49 and GOST 9352-60) [GOST: All-Union Government Standard], determining volatility of its working fraction and formation of lacquer (GOST 5737-53), and determining fractional composition by means of thin-layer evaporation of oil (GOST 8674-58); furthermore, among micro-methods are nonstandardized methods of determining the critical temperature of lacquer deposition and scale properties of oils based on using standard equipment.

*Here and later the author uses a new term, "crankcase properties," having in mind certain indices of the quality of processed oil characterizing the aging of oiling the crankcase system of lubrication. Since corrosion, sedimentation and volitility are not the only or sufficient criteria determining the oil's resistance to aging, the right to use this term in this case is discussed. (Ed. note).

The critical temperature of lacquer deposition shows at what temperature starts intense transformation of oil into lacquer deposit, i.e., determines the temperature limit at which it is still expedient to use the oil.

For the critical temperature of lacquer deposition we take the temperature at which the oil tested according to method of GOST 5737-53 will form 3% lacquer.

The method of determining the scale properties of oil serves to evaluate the high-temperature properties of oils and additives. Essentially it consists of the following.

Aluminum cups with 0.2 g suspension of oil each are placed in a lacquer depositer at 400° until the oil is transformed into a carbon deposit. Difference in weight of the cups before the experiment and after it expressed in percents of the oil suspension are taken as an index of scale properties of oil.

Using the offered micro-methods, with expenditure of 10 ml of oil at most it is possible to make a preliminary judgement on its following properties:

a) about antioxidant properties of oil, appearing in film at high temperatures, i.e., on effectiveness of the action of antioxidant (passive) additives, on inclination of oil to lacquer deposition (with what speed, what quantity and at what temperature is the oil turned into lacquer);

b) about the fractional composition of oil;

c) about the high-temperature properties of oil, i.e., on inclination of oil to f[illegible]

[illegible], 2 and 3 are given the changes of working properties of different oils under the effect of additives determined by above-mentioned methods.

Table 1. The Effect of Additives on the Working Properties of MS-20 and MK-22 Oils

Oils	Motor properties at 250°			Critical temperature, °C	Thermal stability at 260°, minutes	Lacquer deposit at 260°, %	Coefficient of lacquer deposition
	Volatility, %	Working fraction, %	Lacquer, %				
MS-20 (Grozny).....	59	32	9	240	23	40	2.0
MS-20 NKZ.....	44	54	2	255	31	43	1.4
MS-20 NKZ with additives:							
3% tsiatim-339.....	49	51	0	255	46	36	0.7
4.5% IP-22k.....	39	61	0	280	67	36	0.5
6% vnii np-360.....	35	65	0	280	93	34	0.4
MK-22.....	52	45	3	245	21	40	2.0
MK-22 with additives:							
3% aznii-tsiatim-1.....	45	55	0	255	27	26	1.0
3% tsiatim-339.....	39	61	0	260	35	26	0.7
4.5% IP-22k.....	36	64	0	275	74	32	0.4
6% vnii np-360.....	36	64	0	280	95	30	0.3
Mobileguard (v_{100} = 18.33 centistokes	44	56	0	290	155	24	0.15

Table 2. The Effect of Additives on Working Properties of Automobile Oil AS-9.5

Oil	Motor properties at 250°			Critical temperature, °C	Thermal stability at 250°, minutes	Lacquer deposit at 250°, %	Coefficient of lacquer deposition	Washing properties per PZV, points
	Volatility, %	Working fraction, %	Lacquer, %					
AS-9.5 NKZ.....	79	9	12	240	29	46	1.6	4.0
AS-9.5 NKZ with additives:								
3% tsiatim-339 and 1% aznii-tsiatim-1.....	69	31	0	255	37	23	0.6	—
3% tsiatim-339.....	69	31	0	250	43	22	0.5	—
4.5% IP-22k.....	68	32	0	255	57	18	0.3	0.5—1.0
6% vnii np-360 and 3.5% DP-1.....	65	35	0	270	101	12	0.1	—

Table 3. The Effect of Additives on Working Properties of DS-11 Oil

Oil	Motor properties at 250°			Critical temperature, °C	Thermal stability at 250°, minutes	Lacquer deposit at 250°, %	Coefficient of lacquer deposition	Washing properties per PZV, points
	Volatility, %	Working fraction, %	Lacquer, %					
DS-11	69	28	3	250	29	32	1.1	4.0--4.5
DS-11 with additives:								
3% aznii-tsiatim-1	12	24	4	245	29	28	1.0	—
3% aznii-tsiatim-339	67	33	0	260	55	22	0.4	1.0
4.5% IP-22k	63	37	0	260	70	20	0.2	0.5
6% vnii np-360	60	40	0	280	100	16	0.2	0.5
5% Gintset (German Democratic Republic)	68	32	0	275	74	20	0.3	0.5
10% M-120 (Hungary)	68	32	0	255	32	26	0.8	2.0
3% Bartiol (Czechoslovakia)	60	40	0	280	112	16	0.2	1.0
3% Bartiol alkaline (Czechoslovakia)	60	40	0	280	100	18	0.2	2.5
3% Zintiol (Czechoslovakia)	63	37	0	280	105	18	0.18	0.5—1.0
3% Zintiol 2p (Czechoslovakia)	64	36	0	280	100	20	0.2	2.0

Test Methods on Model Installations

As model installations for appraisal of working properties of oils both in pure form and also with additives it is suggested to use PZV and PZZ installations.

On PZV installation according to method of GOST 5726-53 one can estimate the washing properties of oils. On this installation their emulsifying ability can also be determined.

The emulsifying ability of oils is estimated according to method developed by A. B. Vipper, which consists of the following.

On the PZV installation under the conditions of GOST 5726-53 for 30 minutes test 250 ml of oil. Then mix the oil with water in a 3:1 ratio and in a special instrument for emulsification mix at 30 for 30 sec (mixer 1000 rpm). The formed

mixture is poured into a measuring test tube and centrifuged for 30 minutes at 1000 rpm. The quantity of unstratified emulsion in volume percents is taken as the index of emulsifying ability of oil.

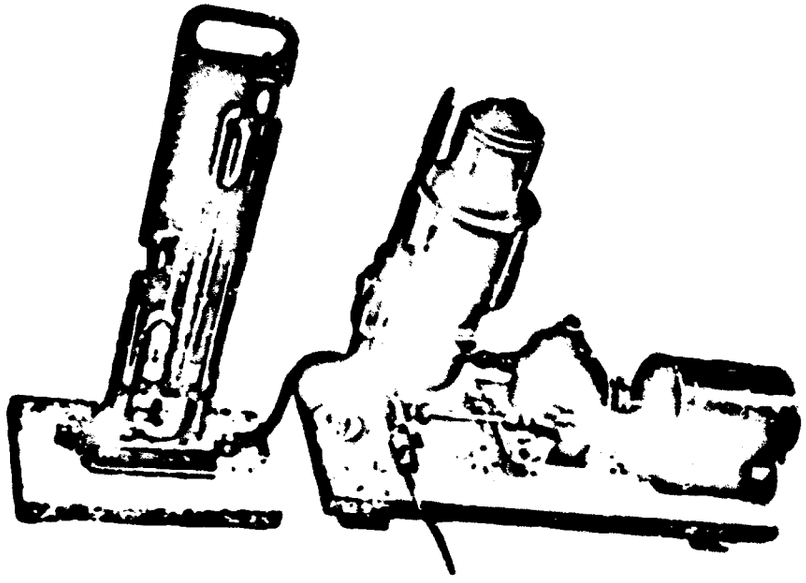


Fig. 1. General view of PZZ installation.

For appraisal of crankcase properties of oil installation PZZ, in which the basic conditions of work of oil in lubricating system of motor are simulated, is recommended.

The PZZ installation (Fig. 1) consists of expenditure tank, into which the test oil is poured, a BNK-12AK pump, put into motion by electric motor, a cassette with six lead and two copper plates. The walls of tank and the test oil are heated and kept at a constant temperature with the help of electric heater. Installation has a closed oil system, along which the oil circulates from the tank, through the cassette and again to the tank, where it is sprayed on its heated walls.

Tests are conducted under the following conditions:

Quantity of tested oil, ml	250
Duration of test, hours	2
Temperature of oil (before entrance into cassette), °C	150
Speed of circulation of oil, liter/hr	125
Quantity of air, proceeding in suction main line of oil system, liter/hr	50

After termination of test pour the oil from tank and system of installation. Estimate the results of test according to the following indices: corrosion properties, which are determined by change of weight in g/m^2 of all lead plates (taken totally) during the test; the quantity of products of contamination in volume percents, accumulated in the oil (sedimentation), which is determined by dilution of tested oil by isooctane with subsequent centrifuging of mixture; volatility of oil, determined by the difference of quantity of oil before and after the test.

Table 4. Crankcase Properties of Oils in Pure Form and with Additions on the PZZ Installation

Oil	Viscosity ν_{50}, centistokes		Acidity mg KOH/g		Crankcase properties		
	Before the test	After the test	Before the test	After the test	Corrosion, g/m^2	Deposit, %	Volatility, %
Baku	6.5	9.0	0.01	6.03	89	1.4	18
Tuymazinskiy	6.2	6.7	0.01	1.51	26	6.2	14
Anastasyevskiy deep purification	8.5	16.9	0.03	5.98	224	14.0	24
The same with additives:							
0.05% FCh-16	8.5	16.4	0.03	7.11	164	6.8	24
0.05% MSA	8.5	15.1	0.03	6.21	143	13.0	24
0.05% FOA-2	8.5	12.6	0.03	3.05	72	6.2	24
1.5% IP-22k	8.5	10.4	0.03	0.29	47	1.4	22
0.5% ionola	8.5	9.3	0.03	0.03	0.3	0.6	20
Tuymazinskiy transformer	8.6	10.8	0.02	3.89	26	6.8	18
Baku transformer	8.8	12.8	0.03	4.28	115	6.6	20
Industrial 50	46.8	66.2	0.12	1.34	130	4.0	14
The same with additives:							
3% tsiatim-339	46.8	55.5	0.00	0.28	5	Traces	14
6% vnii np-360	46.8	50.1	0.00	0.04	0.0	Traces	15
Lubricating oil AU-5 NKZ	22.8	27.8	0.03	1.33	87	2.0	16
The same with additives:							
3.5% DF-1	22.8	23.8	0.00	0.03	0.5	Traces	17
4% vnii np-361	22.8	23.6	0.00	0.02	0.0	Traces	18
DS-11 NKZ	74.6	80.9	0.01	0.23	38	Traces	10
Rimula-30	69.0	69.6	0.00	0.00	0.0	0	—

Besides determining these indices, a physical chemistry analysis of the processed oil is produced (determination of viscosity, acidity, and others).

Table 4 shows the change of crankcase properties of different oils under the effect of additives.

Test Methods on One-Cylinder Installations of Type IT-9

Test of oils and additives on one-cylinder installations of type IT-9 gives possibility of quickly obtaining the results with insignificant expenditures of test samples.

For this purpose it is recommended to use installation IT9-5 and IT9-3; the first — for appraisal of lacquer deposition and corrosion properties of oils, the second — for appraisal of scale forming properties of oils in combination with fuel.

Primary Motor Test of Oils on Installation IT9-5 According to Method of GSM-20

Primary motor test of oils is first checked on motor of results of laboratory physical chemistry research before transmission of sample for test on full-scale motor.

Earlier* we presented changes introduced in construction and equipment of installation IT9-5, due to which it is possible to use it for appraisal of lacquer deposition and corrosion properties of oils.

Tests according to the GSM-20 method are conducted under the following conditions.

Quantity of tested oil, kg	2
Duration of test, hours	5—20
Number of engine revolutions, rpm	1200
Temperature in combustion chamber, °C	500
Temperature of liquid coolant, °C	220
Temperature of oil in crankcase, °C	100
Speed of oil circulation system liter/hr	100
Discharging in crankcase, mm of water column	30

*Chemistry and technology of fuels and oils, No. 2, 1959.

The lacquer deposition property of oils is estimated by the degree of contamination of lateral surface of piston by lacquer deposit after the 5-20 hour test.

Degree of contamination of piston is determined with the help of special scale ruler or photometer and expressed in percents (from 0 to 100) of the area of lateral surface of piston covered by black lacquer. The degree of contamination of a piston completely covered by black lacquer, is taken as 100%, and of a clean piston as 0%.

The corrosion properties of oils are estimated by change of weight of lead plates placed in special cassette during the test and expressed in g/m^2.

The results of tests of oils with different additives on installation IT9-5 according to the GSM-20 method are given in Tables 5 and 6.

Table 5. Results of Test of Oils in Pure Form According to the GSM-20 Method

Oil	Viscosity, centistokes		Acidity, mg KOH/g	Coke, %	Formation of black lacquer after 5 hours, %	Efficiency, hours	Corrosion after 10 hours, g/m^2
	at 50°C	at 100°C					
MS-20 Grozny.....	136.9	20.07	0.0094	0.28	100	5	50
MK-22.....	155.7	22.7	0.0067	0.67	80	10	45
MT-16 Emba.....	--	16.7	0.15	0.50	100	5	60
MT-16 NKZ.....	119.7	17.33	0.0056	0.35	55	12	20
Diesel NKZ.....	—	—	—	—	65	8	70
Industrial 50.....	48.01	8.39	0.13	0.064	65	9	85
AS-9.5 NKZ.....	51.56	9.43	0.032	0.23	75	9	50
AS-5.....	--	7.2	--	--	100 (in 4 hours)	4	60
D-8 NKZ.....	36.6	7.79	0.33	0.05	85	7	18
D-11 NKZ.....	--	10.5	--	0.31	85	--	--

Table 6. Results of Test of Oils with Additives According to the GSM-20 Method

Oil	Formation of black lacquer, %		Corrosion, g/m^2
	After 5 hours	After 20 hours	
MT-16 NKZ	55	100 (after 12 hours)	20
The same with additives:			
4.5% IP-22	20	40	0
6% vnii np-360	30	50	0
2.5% tsiatim-339 and 1.0% aznii-tsiatim-1	35	100	6.0
MT-16 Pmba	100	—	60
The same with additives:			
3% aznii-4	100	—	0
3% aznii-tsiatim-1	35	100	1.0
3% tsiatim-339	35	70	18
DSp-11 Ufim	20	35	1.7
DS-8 NKZ	85	100 (after 7 hours)	18
The same with additives:			
0.5% Lubrizol 1060 and 1.7% lubrizol 612	25	40 (after 15 hours)	10
SAE-30HD	15	35 (after 15 hours)	0.2
Rimula-30	0	5	0

Determining the Scale Forming Ability of Oils According to the PZI Method

To evaluate the scale forming ability of diesel fuels, kerosene and lubricating oils the PZI method founded on application of one-cylinder installation IT9-3 is suggested.

Test under the following conditions.

Number of engine revolutions, rpm..... 900
Compression ratio..... 14
Temperature of liquid coolant, °C..... 100
Temperature of oil in crankcase, °C.....50--65
Temperature of water cooling the burner, °C..... 38
Lead angle of fuel injection, deg, (before v.m.t.) 13
Pressure of fuel injection, kg/cm^2..... 106
Quantity of injected fuel, ml/min..... 13

To evaluate the scale forming ability of one sample of oil conduct four five-minute tests.

Estimate the scale formation by the quantity of scale forming on special aluminum scalers, which are placed in the precombustion chamber of the motor during the test.

Since in the precombustion chamber of the motor of the IT9-3 installation the lubricating oil practically does not get, the scale forming on the scalers, will have purely fuel origin. Therefore, to evaluate the scale forming ability of oils test them mixed with fuel in relationship (in volume percents) of 100% fuel + 3% oil.

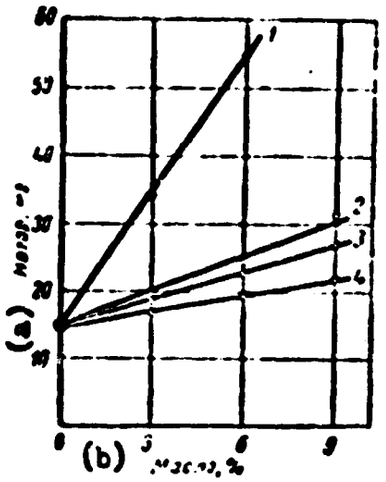


Fig. 2. Scale forming ability of TS-1 fuel with different oils added.
1) MK-22; 2) DS-11; 3) DS-8; 4) AKZ$_p$-6.
KEY: (a) Scale, milligram; (b) Oil, %.

As fuel use TS-1 or white alcohol.

The effect of different oils and additives on scale formation is shown in Figs. 2, 3 and 4.

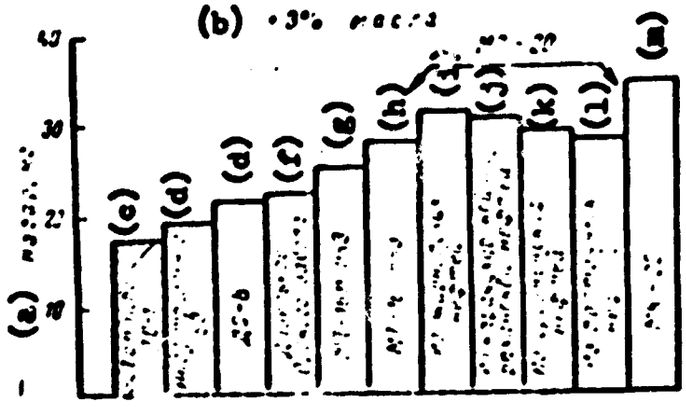


Fig. 3. The effect of oils on scale forming ability of TS-1 fuel.
KEY: (a) Scale, milligram; (b) Oil; (c) Fuel TS-1; (d) Industrial 50; (e) DS-8; (f) Diesel from Orsk factory; (g) MT-16p MKZ; (h) MT-16 MKZ; (i) From Zhirhovsk oils; (j) From Karachukhursk and Surakhansk oils; (k) From Grozny oils; (l) From eastern oils; (m) MK-22.

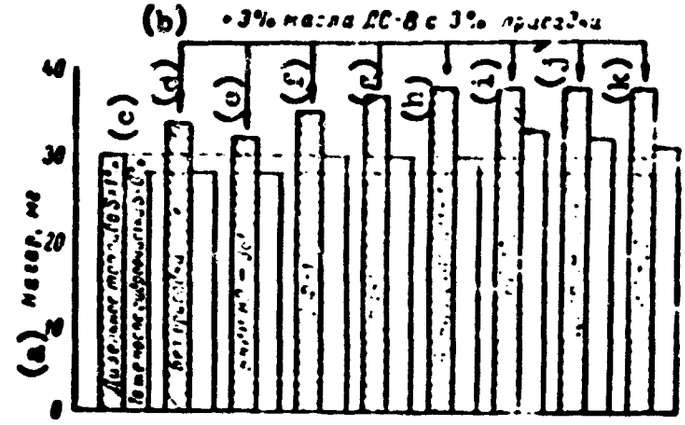


Fig. 4. Scale forming ability of fuels with DS-8 oil and different additives.
KEY: (a) Scale, milligram; (b) +3% DS-8 oil with 3% additive; (c) Diesel fuel S = 1% the same after water cleaning S = 0%; (d) Without additive; (e) VNII NP-361; (f) DF-1; (g) Naks; (h) Azniitsiatim-1; (i) NG-102; (j) Tsiatim-339; (k) IP-22.

Test of Oils on One-Cylinder Installation OD-9

One-cylinder installation OD-9 with cylinder of powerful full-scale diesel engine is well-known since it is widely used for preliminary tests of fuels and oils.

At present the following method is applied to evaluate the tendency of oils to contaminate pistons by lacquer deposit.

Duration of test, hours..... 10
Quantity of tested oil, kg..... 15
Number of engine revolutions, rpm.....1800
Angle of start of fuel feed, deg. (to v.m.t.).... 31
Temperature of liquid coolant (at output) °C..... 140
Temperature of oil (at the motor output) °C.....100-105
Speed of oil circulation, kg/hour.....430/450

Lacquer deposition on piston after test is estimated in points by the standard color scale in accordance with GOST 5726-53.

Furthermore, the weight of the deposit on piston and rings, and also quantity of lacquer deposit on special "witnesses" placed on piston is evaluated.

Evaluating the Working Properties of Oils with Additives by the First Complex of Methods

Each of the methods included in first complex can have independent value in solving these or other questions. For instance, to determine the antioxidant properties of oil it is sufficient to use only thermooxidizing stability.

Using all the methods of first complex on the whole gives possibility of reliably estimating the basic working properties of oil.

Below we give the results of check by first complex of methods of MT-16 oil both in pure form and with the well-known additives tsiatim-339, vnii np-360 and IP-22k (Table 7).

Table 7. Evaluating the Working Properties of Oils with Additives by the first complex of methods

Index	Oil MT-16 NKZ			
	Without additive	with additive		
		3% tsiatim-339	6% vnii np-360	4.5% IP-22k
Motor properties:				
Volatility, %.....	51	48	40	40
Working fraction, %.....	47	52	60	60
Lacquer, %.....	2	0	0	0
Antioxidant properties:				
Critical temperature, °C.....	225	265	270	270
Thermooxidizing stability at 260°C, minutes.....	34	39	62	71
Lacquer deposit at 260°, %.....	41	35	25	28
Coefficient of lacquer deposition	1.2	0.9	0.4	0.4
Washing properties per PZV points	3.0—3.5	—	0.5—1.0	0.5—1.0
Scale properties, %.....	6.0	6.8	7.9	5.8
Crankcase properties:				
Corrosion, g/m^2.....	19	1.6	1.6	1.1
Deposit, %.....	Absence	Traces	Absence	Traces
Volatility, %.....	12	10	12	10
Primary motor test according to GSM-20:				
Formation of black lacquer on piston, %:				
after 5 hours.....	55	35	30	20
after 20 hours.....	100	90	50	40
Corrosional properties after 10 hours, g/m^2.....	18	6	0	0

Comparison of results obtained by methods of first complex with results of test of these oils on one-cylinder installation OD-9 with full-scale cylinder and on full-scale motor (Table 8) shows good coordination between them.

Table 8. Results of Test of MT-16 Oil with Additives on Motors

Index	Oil MT-16 NKZ		
	Without additive	With additive	
		6% vnii np-360	4.5% IP-22k
Test on one-cylinder installation OD-9			
Appraisal of lateral surface of piston by PZV, points	4.5—5.0	1.5—2	2.0—2.5
Deposit on piston, g	2.7	2.7	2.9
Deposit on piston rings, g	0.47	0.15	0.13
Deposit on "witnesses", milligram	25	13	7
Test on full-scale motor (fuel S = 0.97%)			
Total quantity of scale on pistons, g	—	170.4	41.7
Piston rings:			
Coked	—	1	0
Dense	—	1	0
Scale on rings, g	—	0.277	0.134

Conclusions

1. It is recommended to preliminarily evaluate the working properties of oils and additives by the first complex of laboratory methods, including:

a) Micro-methods — to determine the thermal properties and fractional composition of oils (with expenditure of 10 ml of oil);

b) Test on PZV and PZZ model installations to determine the washing and crankcase properties of oils (at expenditure of 0.5 liters of oil);

c) Test on one-cylinder installations IT9-5 and IT9-3 to determine the lacquer deposition, scale forming and corrosion properties, and also coordination of oils and additives (at expenditure of 2.5 liters of oil).

2. To further improve the methods of evaluating the working properties of oil it is necessary to develop work in this direction in scientific research institutes and factory laboratories.

3. Scientific research institutes solving problems of quality and application of oils and additives must create:

a) A laboratory of Soviet methods of evaluating the working properties, ensuring timely mastering and use in research works of new methods of working properties;

b) A laboratory of foreign methods of evaluating the working properties, ensuring timely mastering of new foreign methods and comparison of foreign methods with Soviet.

4. It is necessary that the Committee of Standards, Measures and Measuring Instruments of the Council of Ministers of USSR in standardizing new methods ensures the issue of equipment and instruments (let this be even in minimum series) for introduction of standardized methods.

RADIOTRACER METHODS OF RESEARCH OF FUNCTIONAL PROPERTIES OF OILS WITH ADDITIVES

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VNII NP*

Radiotracer Method of Research of Dispersing Properties of Oils with Additives

Because of the high sensitivity of method of radioactive tracers the development of short-term laboratory methods of investigating the working properties of oils with additives became possible.

Works published in recent years [1-4] and dedicated to the study of the connection of dispersing action of additives with electronkinetic processes gave the possibility of obtaining new interesting data about the action of these additives.

The vnii np developed a radiotracer method of studying electrokinetic processes combined with mechanism of action of certain dispersing additives to motor oils. The peculiarity of this method is the use of counters of radioactive radiation simultaneously both as electrodes to create an electrical field and for registration of shift of labeled dispersed phase.

*The All-Union Scientific Research Institute on Processing Petroleum and Gas and Production of Artificial Liquid Fuel.

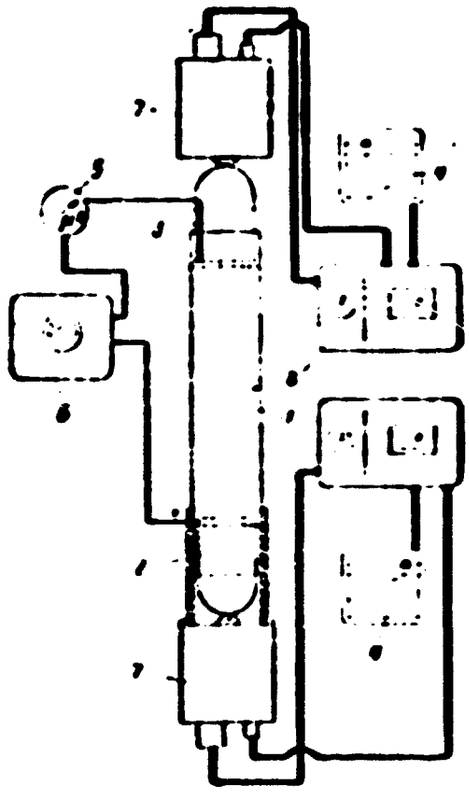


Fig. 1. Experimental installation for radiotracer research of electrokinetic processes and sedimentation in dispersed systems. 1) glass cylinder; 2, 3) beta-counters T-25-BFL; 4) electron potentiometer; 5) microammeter; 6) VSM; 7) BGS; 8) bamboo.

Soot, simulating the dispersed phase, — a product of oxidation of oil and combustion of fuel, — is labeled by radioactive isotope Tl^{204}. This isotope was selected because it has a sufficiently long half-life (3.5 years) and possesses only beta radiation with energy of 0.76 Mev. This last enables us with great effectiveness to record the appearance of marked particles in a given narrow zone. The soot is activated by Tl^{204} by wetting its suspension with a solution of thallium chloride (activity 1-2μ [μc]) with subsequent washing by distilled water and drying. The dried radioactive soot is introduced into 90 g investigated base oil to obtain a tracer dispersed system. In carrying out the experiment into the sample of oil with additive we introduced 1 cm^3 of the tracer dispersed system preliminarily treated by ultrasonics with frequency of 20 kilocycle for 1 hour. Optimum duration of treatment was selected experimentally. Diagram of experimental installation is shown in Fig. 1. Installation consists of a glass cylinder 38 mm in diameter, 120 mm in height with its bottom from brass foil 0.05 mm thick. To bottom from below was pressed the face of beta-counter 2. A second counter 3, on whose face was glued a similar brass foil, was immersed from above in the cylinder filled with investigated oil. The counters were connected to radiometric installations, whose readings were continuously recorded by electron potentiometers 4. To bottom

of cylinder and to foil on upper counter flowed potentials from high-voltage rectifier, which was thoroughly isolated from radiometric instrumentation. Upper beta-counter recorded the speed of deposition of marked soot on foil of counter under action of electric field, i.e., intensity of electrophoresis in oils with investigated additives. The lower beta-counter recorded the deposition of marked soot from oil both in conditions of action of electric field and in its absence. In the last case with the help of upper counter for control we recorded the change of average concentration of marked soot in oil.

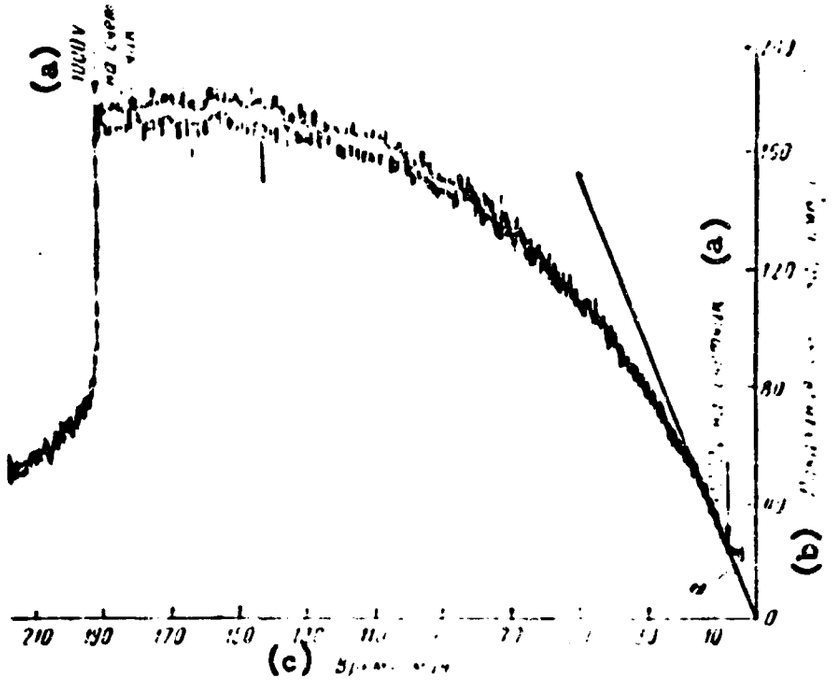


Fig. 2. Diagram of electrophoresis of marked soot in motor oil AS-5 from sulfur-bearing oil containing additive vnii np-354.
KEY: (a) On counter; (b) Counter reading, imp/s; (c) Time, minutes.

Figure 2 gives the diagram of electrophoresis of marked soot in motor oil AS-5 from sulfur-bearing oil containing the additive vnii np-354. The diagram was recorded from the readings of upper beta-counter when + 1000 v was supplied to its foil. From the diagram it is easily to determine tan α characterizing the speed of electrophoresis. Upon changing the sign of charge passed to the foil of counter, we observed a fast "departure" of marked soot from the foil, which testifies to

invariability of sign of charge of dispersed phase. Speed of sedimentation was determined by tangent of angle of inclination of the curve on a diagram, analogous to the one above described [5].

Radioisotope Methods of Research of Washing Properties of Oils with Additives

To evaluate lacquer deposition on details of motor a radiometric method has been developed based on measuring the quantity of lacquer film by the Co^{60} β-irradiation adsorbed in it [6]. On lateral surface of piston the sections (I-V) characteristic for lacquer deposition and not subject to abrasion were activated. Activation was produced by placing a solution of Co^{60} $(NC_3)2$ on selected sections with subsequent thermal diffusion annealing in a muffle furnace. The radiation on the piston was measured before and after testing the oil in a one-cylinder motor with the help of a measuring device fixing the corresponding labeled sections of the piston relative to the face of the beta-counter.

The quantity of lacquer film formed on surface of piston during the test was estimated with the help of a calibrated graph expressing change of radiation intensity in units of density of lacquer film (milligram/dm^2).

Figure 3 gives the results of evaluating the lacquer deposition ability of motor oils, expressed depending upon temperature conditions of their work in piston group of one-cylinder motor. From Fig. 3 it is clear that this method ensures differentiated appraisal of lacquer deposition ability of oils with or without additives.

The known laboratory methods useful for studying the mechanism of additive action can be significantly improved by using radioactive isotopes. The method of investigating the washing properties of oils with additives, based on oxidation of oil in film on a heated slanted steel plate [7], was improved by radiometric measurement of the quantity of deposit formed during the tests. Measurements

were conducted with the help of a Ca^{45} source scattering beta radiation which was recorded by an end-window Geiger counter as shown in Fig. 4. The calibrated graph enabled us to express the results of measurements in units of density of the deposit formed during the experiment (milligram/cm^2). The character of the deposit, in particular, its ability to serve as a binding agent for carbon particles, -- products of oxidation of oil and combustion of fuel -- was studied in the same conditions in which we estimated the quantity of deposit, with the help of soot labeled by Tl^{204}. The labeled soot was introduced in tested oil with additive and upon completion of experiment we radiometrically determined its quantity on surface of plate. For example in Table 1 are given the results of experiments on AS-5 oil from sulfur-bearing oil with different additives.

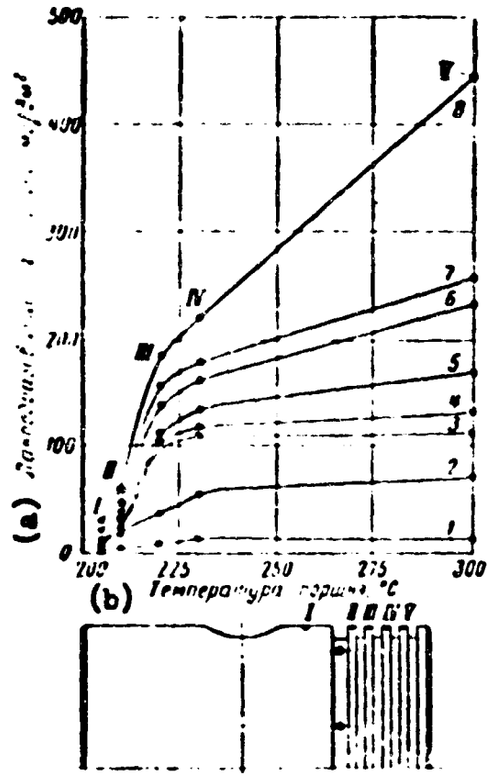


Fig. 3. Results of determining the lacquer deposition ability of different oils and additives on IT9-2 motor.
1) oil AS-9.5 with 5.5% PMS$_{ya}$;
2) the same with 4.5% IP-22k;
3) the same with 5% vnii np-360;
4) the same with 3% tsiatim-339:
5) MK-22 oil; 6) AS-9.5 oil; 7) MS-20 Grozny oil; 8) AS-5 oil.
KEY: (a) Lacquer deposition on piston, milligram/dm^2; (b) Temperature of piston, °C.

On the basis of determining the quantity and character of deposit it is possibile to more correctly differentiate the investigated additives.

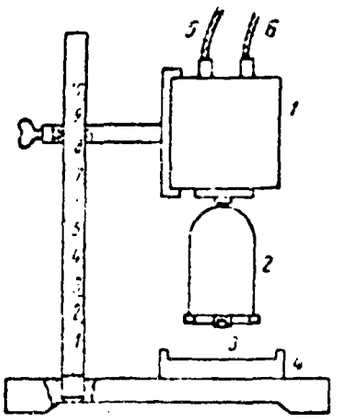


Fig. 4. Scheme to measure the quantity of deposit on surface of steel plate with the help of a Ca^{45} source.
1) BGS input block; 2) T-25-BFL counter; 3) Ca^{45}; 4) steel plate; 5) high tension line; 6) line to radiometric installation.

Table 1. Results of Radiometric Determination of Quantity and Character of Deposit by Laboratory Research of Washing Properties of Oils

Oil	Quantity of deposit on surface of plate, milligram/cm^2	Quantity of soot in deposit, (imp/min)/cm^2
AS-5 without additive.....	>1.0	188
The same with additives:		
5% vnii np-350.....	0.01	147
1.5% vnii np-354.....	0.01	140
5% vnii np-350 and 1.5% vnii np-354.	0.01	36
5.85% tsiatim-339.....	0.02	193
5.85% tsiatim-339 and 3% DF-1.....	<0.01	41
7.5% vnii np-370.....	0.01	27
6.6% vnii np-371.....	0.05	393
1.5% MASK-2 (ash content 33%).....	<0.01	95
3.1% MASK-2 (ash content 16%).....	<0.01	0

Note. All additives were introduced calculated on identical molar content of cations of neutralizing components in oil.

Radiotracer Methods of Evaluating the Chemical Activity of Antiburr Additives

The vnii vp has developed radiotracer methods of evaluating the chemical activity of antiburr additives to oils. They are based on the fact that the most effective antiburr additions have to be chemical compounds having the highest corrosion aggressiveness [7, 8]. The chemical activity of antiburr additives is evaluated by determining the kinetics of transition of radioactive steel (irradiated by neutrons of Fe^{59}) or copper (activated by introduction of tracer quantities of Ag^{110} into molten copper) in oil under the effect of the tested additives [9].

In Table 2 are given the results of radiometric determination of chemical activity of antiburr additives with respect to steel and copper.

Table 2. Results of Radiometric Determination of Chemical Activity of Antiburr Additives

Tested oil with additive	Iron in oil, milligram (200°)				Copper in oil, milligram (150°)			
	Time of test, hours							
	5	15	25	75	5	10	15	50
Orsk winter with additives: 3% dibenzuldisulfide and 7% chlorinated paraffin.....	0.008	0.014	0.018	0.180	4.81	15.6	18.2	—
The same with 12% 1-L.....	0.008	0.015	0.018	0.042	0.17	0.80	8.64	32.4

For identical character of comparative data the chemical activity of additives is determined with the help of radioactive steel at oil temperatures of 200° for 50-75 hours with small quantities of corroded metal, whereas with the help of radioactive copper the chemical activity can be estimated at a oil temperature of 150° in less than 5 hours with significantly larger quantities of metal passing over into the oil.

The obtained results fully agree with indications available in literature [10, 11].

The data of radiometric determinations of chemical activity of antiburr additives corresponded to the results of tests of these additives on four-ball apparatuses and in real mechanisms.

Because during application of oils with chemically active antiburr additives the chemical wear of friction surfaces may be heightened during their work at normal or even small loads, the VNII NP has developed a radiotracer method of evaluating the wear properties of oil with additives on a specially designed friction machine. The working friction details of the machine were activated by inserts of Co^{60}. The peculiarity of this machine is its use of small quantities of tested oils (to 1 cm^3) and measurement of radioactivity of all the oil. The machine is equipped with heating and can work at loads up to 80 kg/cm^2, up to 1000 rpm and oil temperatures up to 250°.

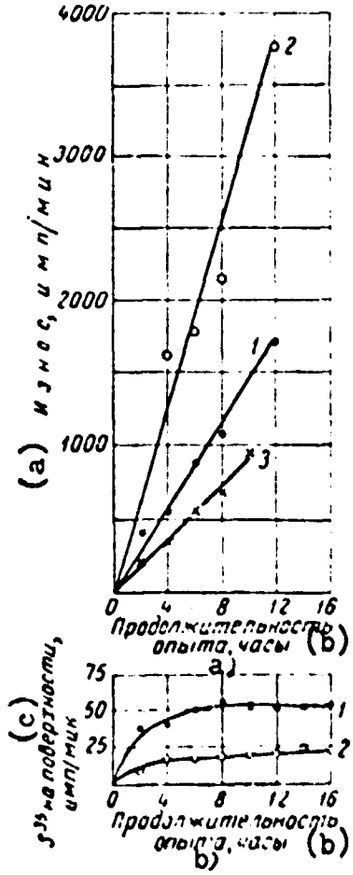


Fig. 5. Results of investigating wear properties of oils with chemically active additives on VNII NP friction machine.
a) wear of friction surfaces; b) kinetics of interaction of additives with friction surfaces according to measurement of beta radiation of S^{35} which labeled the dibenzyldisulfide.
1) MT-16 oil with 3% dibenzyldisulfide; 2) MT-16 oil with 3% dibenzyldisulfide and 7% chloroparaffin; 3) MT-16 oil.
KEY: (a) Wear, imp/min; (b) Duration of experiment, hours; (c) S^{35} on surface, imp/min.

In using nonradioactive friction details and additives marked by radioactive isotopes of basic components, it is possible to establish kinetics of interaction of additives with metal surfaces in conditions of friction.

In Fig. 5 are given the results of investigating oils with chemically active antiburr additives on the VNII NP friction machine.

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A LABORATORY STUDY OF THE ANTIOXIDATION EFFECTIVENESS OF MOTOR-OIL ADDITIVES

K. S. Ramaya, M. S. Borovaya and

R. Kh. Sil's

A large part of the papers dealing with the effect of additives which increase the stability of mineral oils with respect to oxidation pertain to turbine and transformer oils with the scope of these investigations being confined to relatively low temperatures — 100 - 140° C.

Recently, antioxidation additives to motor oils have also acquired broad application, but there is very little data pertaining to their effectiveness at the temperatures characteristic of the operating conditions of an engine. We are not always able to determine the effect of an additive on the extent of oxidation of an oil from this data, since at high temperatures the oxidation processes in the oil are extremely complicated and proceed in parallel with polymerization and condensation reactions between the products of the oxidation and also with reactions involving the cleavage and volatilization (loss) of these products.

The criterion often applied to determine the extent of oxidation

of motor oils is not the amount of oxygen entering into the reaction, but the amount of certain products which are formed as a result of the oxidation and which are of practical importance under operating conditions. Thus, for example, in the thermal-oxidation stability method (GOST 9352-60) the criterion for the rate of oxidation has been taken as the time necessary to obtain a "residue", consisting of 50% lacquer (a product of the oxidation polymerization and condensation), which is not soluble in light gasoline, and 50% soluble lacquer. The oxidation proceeds at a temperature of 250° under conditions of free diffusion of atmospheric oxygen (oxidizing agent) and free vaporization of volatile oxidation products as well as of the light fractions of the oil itself. According to the method developed by NAMI, (State All-Union "Order of The Labor Red Banner" Automobile and Automobile Engine Scientific Research Institute), oxidation is carried on for 50 hrs at 200° under conditions of free access of the oxidizing agent, atmospheric oxygen, but preventing the free vaporization of the oil and the products of its oxidation. The criteria for appraising the extent of oxidation are the increase in the oil viscosity and the amount of sediment (the oxidation products) not soluble in light gasoline. Therefore, the lacquer in the GOST 9352-60 method and the sediment in the NAMI method are in this sense identical concepts.

The criterion for the extent of oxidation of the oil proposed by the Azerbaydzhan Scientific Research Institute for Oil Refining is the amount of absorbed oxygen. The oxidation is carried out in a closed system at 175° with oxygen at atmospheric pressure. But the oil does not undergo any pronounced change, and the rate of oxidation is evaluated on the basis of the time necessary for the absorption of

0.8 ml of O_2 by 1 g of oil.

In this paper the authors have attempted to compare and interpret results obtained by these three methods in an effort to ascertain the antioxidation effectiveness of motor-oil additives.

The experiments using the ASRIOR method were carried out under a different regime: a temperature of 200° and an absorption of about 5 ml of oxygen by 1 g of oil.

Data from investigations of 6 oil samples are presented in Figs. 1 to 3: 1) DS-11 base oil (NKZ); 2) the same oil with 3% cyatim-339 additive; 3) the same with 3% cyatim-339 additive (alkaline) containing an excess of barium (BaO, $BaCO_3$); 4) the same with bartiol import additive (3%), which is barium dialkyldithiophosphate; 5) the same with bartiol additive (alkaline) containing an excess of barium; 6) the same with gintset additive, which is a mixture of zinc dialkyldithiophosphate and barium and calcium sulfonates.

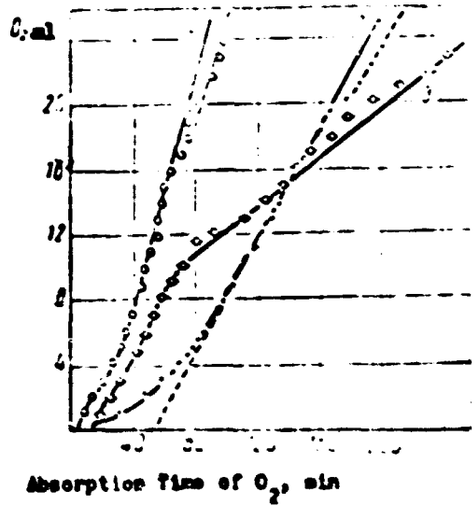


Fig. 1. Absorption of oxygen by oil at 200°. ASRIOR instrument, 5 ml of oil. 1) DS-11 (NKZ) without additive; 2) the same with 3% cyatim-339 additive; 3) the same with 3% cyatim-339 alkaline additive.

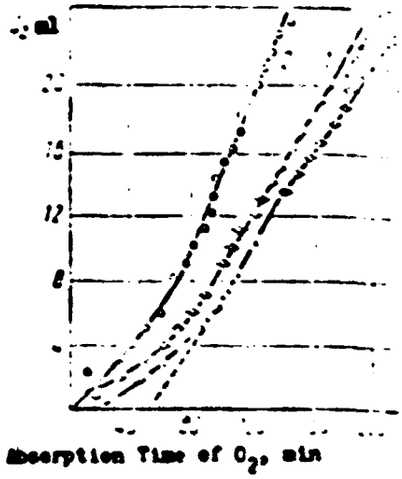


Fig. 2. Absorption of oxygen by oil at 200°. ASRIOR instrument, 5 ml of oil. 1) DS-11 (NKZ) without additive; 2) the same with 3% bartiol additive; 3) the same with 3% bartiol alkaline additive.

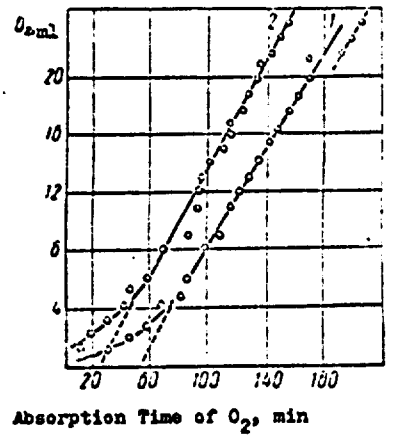


Fig. 3. Absorption of oxygen by oil at 200°. ASRIOR instrument, 5 ml of oil. 1) DS-11 (NKZ) without additive; 2) the same with 5% gintset additive.

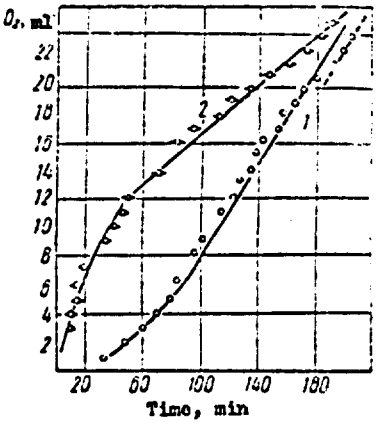


Fig. 4. Absorption of oxygen by oil at 200°. ASRIOR insrument, 5 g of oil. 1) DS-11 (NKZ) oil without additive; 2) SAE-30 oil (with alkaline sulfonate additive).

The results of experiments on the absorption of oxygen by 5 g of the first three samples in the ASRIOR instrument at 200° are plotted in Fig. 1. Similar data are presented for the fourth and fifth samples in Fig. 2 and for the sixth sample in Fig. 3. The curve for the base oil, the first sample, is also given in Figs. 2 and 3 for the purpose of graphic comparison.

The absorption curves do not indicate the presence of any real induction period characteristic of the oxidation of oil at lower temperatures. In the first period (60-70 min) the absorption proceeds at a variable rate, after which the curves straighten out. The absorption rate of the oxygen was calculated on the basis of the rectilinear portions of the curves. The values thus obtained give some idea of the rate of the oxidation reaction for more pronounced oxidation.

In the data presented in Figs. 1-3 it is noteworthy that the cyatim-339 (curve 2 in Fig. 1), bartiol (curve 2 in Fig. 2), and gintset

(curve 2 in Fig. 3) additives do not decrease, but rather increase the rate of absorption of the oxygen, in spite of the fact that the bartiol additive is barium dithiophosphate in pure form, while the gintset additive contains zinc dithiophosphate in its composition. On the other hand, in the presence of excess alkalinity the cyatim-339 and bartiol additives significantly decelerate the absorption of oxygen (curves 2 in Fig. 1 and 3 in Fig. 2). The effect of this alkalinity on the rate of oxygen absorption is also common to the other additives; this is illustrated in Fig. 4 for SAE-30 oil (curve 2 in Fig. 4).

In the table we have compared the results of investigations of the value of the thermal-oxidation stability in minutes obtained by the GOST 9352-60 method and the percentage of lacquer obtained during this time. These studies were conducted on 6 oil samples on the DK-2 instrument at 200° for a period of 50 hrs using the NAMI method. In the same place we have listed the values of the oxygen absorption rate (curves 1, 2, and 3) calculated in ml of O_2/min·g of oil·100.

TABLE 1

Results of Oxidation of DS-11 Oil with Additives in a DK-2 Instrument at 200° and by the Method of Thermal-Oxidation Stability at 250°.

Sample Number	Additive	Oxidation temperature of 200°				Oxidation temperature of 250°	
		DK-2			ASRIOR		
		Viscosity, cs (with sediment)	Viscosity, cs (without sediment)	Sediment, %	Oxidation rate, ml/min·g	TOS, min	Lacquer, %
	Without additive						
	Cyatim-339(3%)						
	Cyatim-339 alkaline (1.5%)						
	Bartiol (3%)						
	Bartiol alkaline (3%)						
	Gintset (5%)						

From the data listed in the table concerning the increase in viscosity during oxidation by the NAMI method, $\Delta\nu_{100}$ cs (with sediment), it follows that all 5 additives are oxidants at 200°. On the basis of this criterion excess alkalinity in the additive material lessens its oxidant effect If we judge on the basis of sedimentation (NAMI method), it follows that the cyatim-339, bartiol, and gintset additives are oxidants. Excess alkalinity in the cyatim-339 additive makes it an antioxidant, while alkalinity in the bartiol additive destroys its oxidant property. Therefore, the evaluation of the additives by the NAMI method and on the basis of oxygen absorption in the ASRIOR instrument at 200° is practically the same.

The results obtained with the thermal-oxidation stability method at 250° give a contradictory evaluation of these additives. All the additives tested were evaluated as antioxidants both on the basis of the formation time of a lacquer residue of prescribed composition (in minutes), and on the basis of the amount of lacquer obtained (in %). Excess alkalinity does not increase the antioxidant effectiveness of the additive, but, instead, decreases it.

Data concerning the magnitude of the increase in the viscosity $\Delta\nu_{100}$ cs (without sediment) are presented in the table. This value was obtained by determining the viscosity of the oxidized oil after the removal of the sediment and represents the increase in viscosity due to the accumulation of gums formed in the oil during its oxidation. With further oxidation these gums may be converted into more compact compounds and are separated out of the oil in the form of a sediment. It is noteworthy that the amount of gum increases with the alkalinity of the additive with a concomitant decrease in the sediment, which is apparent from samples 2-3 and 4-5. In the experiments at 250° an

The bartiol and gintset additives which contain the thiophosphate group behaved as oxidants in the experiments at 200° not only with respect to sedimentation, but also with respect to the oxygen absorption rate. This occurs as a result of the fact that the antioxidation effectiveness of thiophosphate additives, as that of many other antioxidants, decreases with an increase in temperature, and, when a certain temperature has been reached, they become oxidants. However, as is apparent from Fig. 5 (thermal-oxidation stability method), these same additives behaved as extremely effective antioxidants.

This apparent contradiction is explained by the fact that under conditions of free vaporization a number of products of the oxidation of the oil, which are capable of undergoing condensation and polymerization, are volatilized. These same products under conditions which hinder vaporization may be separated out in the form of a sediment which is not soluble in light gasoline. The presence of an additive which acts as an oxidant at a given temperature increases the formation of these volatile oxidation products.

All of these theories concerning the effectiveness of antioxidant additives, which have been put forth on the basis of the experimental data presented herein may serve as a working hypothesis for further investigations of oils with additives. Final and comprehensive data concerning the antioxidant and oxidant effects of motor-oil additives may be obtained only by methods based on absorption of oxygen at high temperatures. The development of such methods is a problem which is inseparable from the problem of developing antioxidant additives.

NEW METHOD OF EVALUATING THE EFFECTIVENESS OF ANTIBURR ADDITIVE ACTION IN OILS AND FUELS

K. I. Klimov, A. V. Vilenkin, and G. I. Kichkin

In the specification on lubricating oils as a rule parameters characterizing their antiwear properties are absent. In selection of oils even for gear transmissions a single working index of quality of oil -- viscosity is still used [1, 2].

In solving questions about fitness of oils for one or another aggregate and about advantages of one oil over others, we resort to prolonged, expensive, labor-consuming and badly reproduced tests in real mechanisms.

Tendency to reduce time and value of tests has lead to creation of large quantity of friction machines of different types and laboratory methods of comparative appraisal of oils quality [3-8]. Up to now universally recognized friction machines and methods of comparative appraisal of antiwear properties of oils are lacking. The very wide-spread is the opinion that testing oils on friction machines cannot give results of appraisal of oil similar to results obtained with using real aggregates [1, 2].

Not being of such opinion, the authors consider that its source was the huge number of works in which researchers tried to create methods of accelerated tests for wear without simulating the conditions of friction in laboratory instruments

along the basic parameters, those most essentially affecting the process of interaction of metallic surface, lubricant and environment.

First requirement which should be observed in testing oils is simulating the friction conditions in speed of relative slip of surfaces.

In spite of the fact that this requirement is well-known, it is not considered in testing oils on friction machines. Many mechanisms, e.g., automobile gear transmissions, in conditions of use work in a wide range of speed and loads; however, comparative appraisal of antiburr properties of oils on friction machines is produced at one slip speed, frequently very far from the real one. This non-correspondence is one of the most important causes of incorrect comparative appraisal of automobile transmission oils obtained on friction machines and the absence of correlation between results of testing oils on friction machine and in mechanisms. About the correctness of such conclusion testify, in particular, the data of tests of series of oils by the MIL-L-2105 method on power (high load -- low speed) and high-speed (high speed -- low load) conditions [10]. In many cases oil which works satisfactorily at low slip speeds turns out to be unfit for work at high speeds.

Inasmuch as the basic processes occurring during friction of surfaces in conditions of imperfect lubricants, such as formation and destruction of threshold oily films, chemical reactions in oily film and surface layer of metal, abstraction of heat from "hot points" and others, occur in time, in evaluating the antiwear properties of oil on friction machines large value belongs to conformity of time between repeated contacts in friction machine and in real conditions. In other words, simulating real friction conditions in periodicity of contact is the second important requirement in testing oils on friction machines.

The third requirement in testing oils on friction machines is conformity of temperature of friction pair and oil (in volume) in laboratory instrument -- real conditions of application of tested oil. This last requirement is especially

important for oils with additives whose mechanism of action leads to chemical interaction with metal. To evaluate the antiburr properties of oils the authors created the KV-1 friction machine which simulates the condition of work of a friction pair of a real mechanisms in slip speed (0.5-30 m/sec), temperature (to 200°) and periodicity of contact within wide limits.

A diagram of the machine is shown in Fig. 1. Its basis is a friction pair, one of whose elements is a spiral coil of wire 2 (diameter of 2 mm of 50KhFA steel per GOST 2052-53 or CVS GOST 1546-53) [GOST: All-Union Government Standard] secured on generator disk 3, and cylindrical roller 1 (from needle bearing, diameter 5 mm, length 50 mm), placed in clamp cartridge 10. In one turn of disk every point of wire contacts the surface of roller only once.

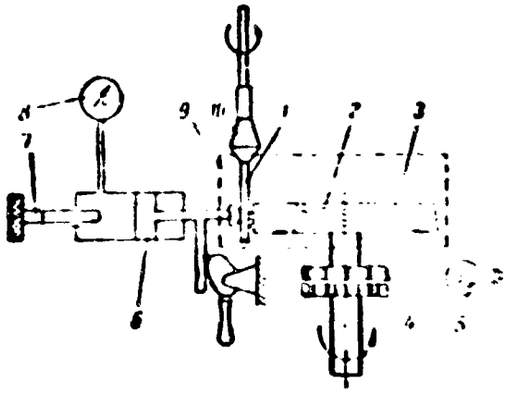


Fig. 1. Diagram KV-1 friction machine.
1) roller; 2) wire; 3) disk; 4) stroboscope; 5) small neon tube; 6, 7) loader; 8) manometer; 9) bath; 10) clamp cartridge.

The friction pair is immersed in metal bath 9, in which the tested oil is poured. The bath is equipped with electric heating with automatic controlled temperature. The load is set by a hydraulic loader 6 ± 7 and is fixed by manometer 8. Rotation speed of disk 3 is established and controlled with the help of stroboscope 4.

Materials of wire and roller can be changed in accordance with research problems. The roller can be put into rotation by special drive, in this sliding friction is combined with rolling.

In this work questions of the effect of the material of the friction pair and additional rotation of roller are not considered.

Method of comparative appraisal of antiwear properties of oils and liquids gives the following. On the basis of operating conditions of node which has as a

lubricant a tested oil product, we select a disk of corresponding diameter and step so that when changing the rotation speed of disk tc 3000 rpm a typical speed range of slip and periodicity of contact of friction surfaces is covered in this node. On selected disk reel the wire under constant tension, equal to 35 kilogram. Then disk with coil of wire secured on it is put in bath on drive shaft. Pour the tested oil in bath, turn on the drive and, revolving the disk with speed of 300-400 rpm (disk in this case plays role of mixer), turn on the heater. After arriving at the given temperature regime rate establish the needed rotation speed of disk and start to load the friction pair by special program: load is increased by steps (from 0.5 to 3 kg depending upon absolute value of load). At each load the friction continues for 10 sec, after which follows a 10-second pause with removal of load. Increase the load as long as a burr does not start. Then drop the load, stop the disk and replace the wire on it. Appearance of burr is easily fixed by hearing and is checked by visual inspection of place of roller contact during the pauses.

Depending upon research problems these tests are repeated under other conditions (rotation speed, temperature, material of wire and roller) obtaining in this a dependence of jamming load on the selected variable.

Reproducibility of experimental results on KV-1 stand is equal to $\pm 15\%$.

The described method was used for research of oil products sharply distinguished in antiburr properties. The stand turned out to be useful both to evaluate appraisal hypoid oils with high antiburr properties and also to research low-viscosity distillates.

From Fig. 2 it is clear that on the basis of test results we can clearly differentiate oil products according to the investigated index. It is important to note the high sensitivity of the instrument. At slip speed of 5 m/sec the jamming load obtained on spindle AU oils (curve 8) and MK-22 oil (curve 7), differ from each other by 5 times. At the same time in a test on four-ball machine they differ by only 2-2.5 times.

Sensitivity of instrument to action of different additives is illustrat -y curves 2, 5, 6 and 8. At slip speed of 12 m/sec the jamming load is increased upon introduction to spindle AU oil of 5% sulphurized sperm whale fat by 8 times, 5% of additive EZ-5 -- by 9 times, and 5% of additive lenii-1 m, by 33 times.

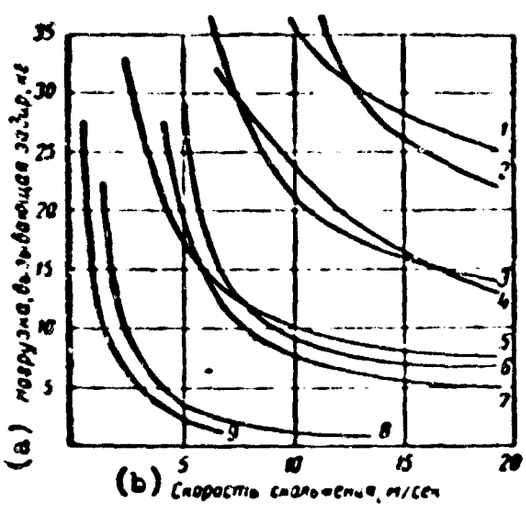


Fig. 2. Results of evaluating antiwear properties of oil products on KV-1 stand (disk 126 mm in diameter, step 4 mm, temperature 20°).
1) extract of purification of oils Novokuybysheyskiy oil refining factory with 5% of additive INZ-6/9; 2) spindle AU with 5% of additive lenii-1 m; 3) mixture of hypoid and AMG-10 oils (2:1); 4) sulphurized transmissional motor and tractor; 5) spindle AU and 5% EZ-5; 6) spindle AU and 5% sulphurized sperm whale fat; 7) MK-22 oil; 8) spindle AU; 9) propellant T-2.
KEY: (a) Burr causing load, kg; (b) Slip speed, r/sec.

Experience of working with the instrument showed its fitness for evaluating antiburr properties not only of oils, but also of propellants distinguished by comparatively low lubricating ability. Dependence of jamming load on slip speed obtained for T-2 fuel is shown in Fig. 2 (curve 9).

The instrument's area of application is limited by magnitude of jamming load for the tested oil products. For a jamming load below 1 kg the accuracy of measuring the applied load is sharply lowered, inasmuch as it becomes commensurable with frictional force in load system. For loads above 35-40 kg slip of friction pair is accompanied by noticeable crumpling of wire and distortion and test results connected to this.

Systematic research of the effect of geometric dimensions of instrument on results of evaluating antiburr properties of oils lead to the conclusion that the instrument's area of application may be expanded by corresponding change of step of wire coil fastened to it.

Increasing the step of wire creates softer test conditions and leads to increase of jamming load at that same (practically) slip speed.

As can be seen from Table 1, with 126 mm diameter of disk changing the step of wire coil by 4.8 times (from 2.5 to 12.0 mm) leads to increase of magnitude P_K of MK-22 oil by 2.5-2.9 times.

When the tested lubricating substances have small magnitude of jamming load, one should use disks with wire coil of large step and conversely, during comparative appraisal of products with large values of jamming load (above 35 kg) one should use disks with wire coil of small step.

Table 1. Influence of Step of Spiral Coil on Magnitude of Load (P_K) Causing a Burr (diam of disk 126 mm, MK-22 oil, t = 20°)

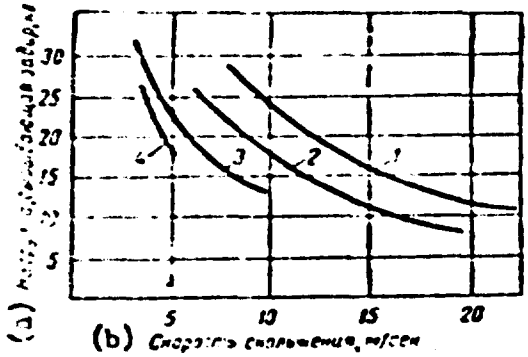
Step, mm	P_K (kg) at slip speed of m/sec			
	5	10	15	19
2.5	13.7	5.0	3.0	2.7
4	19.2	8.0	5.6	5.0
6	23.1	9.8	6.9	6.2
8	29.3	11.1	8.0	7.0
12	35.0	12.0	8.7	7.8

Above we noted the necessity in testing on friction machines of simulating real conditions of work in nodes of slip speed, periodicity of contact and temperature. Experiments on KV-1 stand completely confirm this conclusion.

The importance of testing oils not at one arbitrary slip speed, but in interval of speeds, covering in real friction nodes, is confirmed by the results of research shown in Fig. 2. Actually, if at slip speed of 5 m/sec spindle AU oil with 5% sulphurized sperm whale fat turned out to be significantly better than the same oil with 5% of additive F2-5 (P_K is 28.7 kg and 17.1 kg respectively), at slip speeds above 8 m/sec, conversely, the first oil is worse than the second.

This and other analogous cases, shown in Fig. 2, indicate the necessity of carrying out comparative appraisal of oils in interval of slip speeds characteristic for the real friction node.

Results of research explain the cause of non-correspondence of test results of oils on friction machines and results obtained in real conditions of use [10].



(b)

Fig. 3. The effect of disk diameter on magnitude of P_K (TAp-15 oil, step 4 mm, temperature 20°). 1) disk 1 210 mm in diameter; 2) disk 2 126 mm in diameter; 3) disk 3 65 mm in diameter; 4) disk 4 34 mm in diameter.
KEY: (a) Burr causing load, kg; (b) Slip speed, m/sec.

The necessity of considering of contact periodicity follows from analyzing the test results of TAp-15 oil (GOST 8412-57) shown in Fig. 3).

Curves 1-4 are obtained by using disks (spiral coil of wire) of different diameters. Step of wire coil for all disks was identical, equal to 4 mm.

The points of curves 1-4 with identical slip speeds correspond to different rotational speeds of disks. For instance, at slip speed of 9 m/sec the rotational speed of disks 1-4 is equal to 815 rpm, 1340 rpm and 2640 rpm. In other words, at equal slip speeds on various disks is observed unequal number of contacts of surfaces in a unit of time (different periodicity of contact). At slip speed 9 m/sec a change of contact periodicity by 3 times (from 14 to 44 contacts per second) lead to a change of magnitude of jamming load by 1.75 times (from 26.7 to 15.3 kg). Consequently, simulating friction conditions by contact periodicity has large value in evaluating antiburr properties of lubricating materials.

Research of antiburr properties of oils with additives in interval of temperatures from 20 to 100-150° on KV-1 stand showed that depending upon temperature of the oil in volume and the friction pair the effectiveness of additive action can essentially be changed. Actually, increasing the temperature of TAp-10 oil (GOST 8412-57) from 20 to 100° caused consecutive noticeable lowering of magnitude of load P_K (Table 2). When working on mixture of MK-8 oil with sulphurized steam engine cylinder oil and chlorinated biphenyl increasing the

temperature from 20 to 50° also lead to decrease of P_K, although small in magnitude. However, with further increase of temperature to 100° load P_K sharply increased, considerably exceeding its value at 20°.

Table 2. Effect of Oil Temperature on Magnitude of Load (P_K) Causing a Burr. (diameter of disk 126 mm, step 4 mm)

Oil	Temperature, °C	P_K at slip speed of m/sec	
		5	10
MK-8 NKZ with 8% sulphurized steam engine cylinder oil and 10% chlorinated biphenyl	20	12.9	5.9
	50	11.6	5.0
	100	18.0	7.2
TAp-10	20	24.0	15.4
	50	17.4	11.2
	100	10.6	3.0

Consequently, for correct characteristics of oils with additives their antiwear properties must be estimated at those temperatures at which they work in real friction nodes. Non-observance of this condition can lead to incorrect appraisal of antiburr properties of oils.

Work on comparative laboratory appraisal of antiburr properties of lubricating materials with additives on friction machines should start with a determination of conditions of work of the friction pair in real mechanisms: interval of operating temperatures, characteristic slip speed range and contact periodicity. Information on slip speed and contact periodicity are initial data for selection of disk diameter and interval of numbers of disk turns, in which it is necessary to estimate the jamming load, in a fixed range of change of operating temperature.

With such approach to determining the effectiveness of action of antiburr additives for every typical friction pair (hypoid transmission of automobile, gear box of automobile transmissions, pair of "cam — pusher of motor") one should estimate by an independent method.

Conclusions

1. To evaluate the antiburr properties of lubricating materials we have developed and offer a new in principle diagram of a friction machine with a pair of crossing cylinders and periodic contact of surfaces.

2. We have shown the necessity in comparative appraisal of antiburr properties of oils with additives on friction machines of modeling the test conditions by slip speed, contact periodicity and temperature in a wide interval of their changes.

We have developed a method of comparative appraisal of antiburr properties of lubricating materials under conditions simulating the real working conditions of oil.

3. We have investigated antiburr properties of certain oil products in pure form and with additives. We have shown that the offered instrument and method of appraisal possess high sensitivity, considerably exceeding the sensitivity of appraisal by other methods and instruments (e.g., on four-ball friction machine).

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THE EFFECT OF LUBRICATING MATERIALS AND THEIR ADDITIVES ON FORMATION OF PITTING

M. D. Bezborod'ko and G. S. Krivosheyn

Smallpox-like wear (pitting) is a characteristic form of wear of toothed wheels of heavily loaded reductors and roller bearings. In this insignificant losses of metal, calculated in grams, put details whose weight sometimes exceeds ten of kilograms out of order.

Up to now there is no single view on mechanism of pitting formation. The most probable hypothesis is that at high cyclical contact loads during rolling with slipping on friction surfaces fatigue cracks are formed. Subsequently due to wedging action of lubricating materials [1] on the friction surfaces these cracks are turned into pitting sores.

Appearance of prepitting cracks on surface of metal can be explained from positions of theory of dislocations [2]. The appearance of pitting on friction surfaces will be influenced by the magnitude of tangential stresses in contact, depending on load and coefficient of friction, frequency of change of load, and also presence in contact surfaces of adsorbed or chemically combined films. The majority of these factors depend on the applied lubricating materials. This dependence was fixed long ago [1, 3]; however, methods of evaluating antipitting properties of oils started to be developed only recently [4, 5]. Therefore,

lubricating materials and their additives intended for work in reductors till now continue to be evaluated only in their antiwear properties, without calculating their antipitting properties.

Antipitting properties of lubricating materials are most conveniently studied on four-ball friction machines adjusted for work in conditions of rolling. These machines [5, 8] lack the deficiencies inherent in gear and roller stands: great duration of tests [1], expensive working bodies [toothed wheels or disks] and absence of clear criterion for determination of appearance of pitting on tested surfaces.

In the friction nodes of four-ball machines intended for work in conditions of rolling the lower balls in cup are not secured but are freely rolled. In this on the upper ball a trace of friction will form in the form of a ring.

During the work of four-ball machine pitting appears on the internal edge of the trace of friction on the upper ball due to presence there of high cyclical contact loads and rolling friction with slipping. Time to formation of pitting is a convenient appraisal index of antipitting properties of oils [6, 7]. For its determination it is expedient to use methods of sound ranging [8]. The diffusion of results observed in process of experiments obeys the law of distribution, which, using methods of mathematical statistics, enables us to determine minimum quantity of experiments and to compare the arithmetic mean values of time obtained in different series of experiments.

The experiments were conducted on ShKh6 steel balls 12.7 mm in diameter with hardness of 56 and 62 R_c. Usually the upper ball was of less hard steel.

Before beginning the work the balls were washed in gasoline and dried; then we selected the friction node and filled its lubricating material so that the lower balls were completely covered by it.

The machine was put under load after the tested lubricating material achieved a given temperature. During experiment the friction node was supported at a

constant temperature. Majority of experiments were conducted at load of P = 390 kg, rotational speed of upper ball n = 1500 rpm and temperature of 20 and 80°. Cases of deflection from these conditions will be discussed.

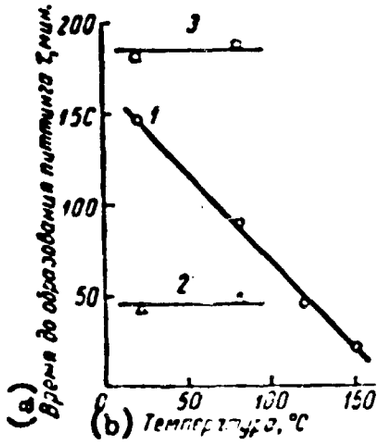


Fig. 1. The effect of temperature on the time of pitting formation.
1) MS-14 oil; 2) MT-16p oil; 3) lubricant tsiatim-208.
KEY: (a) Time to formation of pitting t, minutes; (b) Temperature, °C.

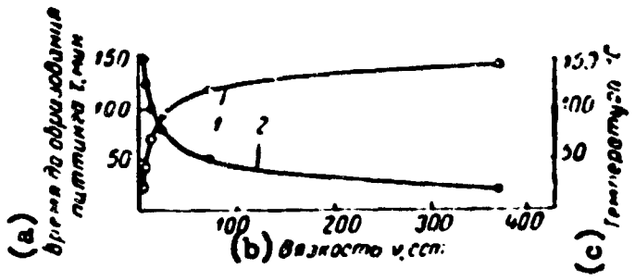


Fig. 2. The effect of viscosity on pitting formation.
1) dependence of time of pitting formation on viscosity MS-14; 2) viscosity-temperature characteristic of oil.
KEY: (a) Time to pitting formation t, min; (b) Viscosity in centistokes; (c) Temperature, °C.

The effect petroleum products on formation of pitting is caused by the differences in their composition and viscosity. Increasing the viscosity of petroleum oils of type MS-14 without additives leads to delay of appearance of pitting. This time τ can be estimated by the formula

$$\tau = A - Bt,$$

where A and B are constants determined from experiment and t the temperature of oil in °C.

For MS-14 oil (curve 1 in Fig. 1) A = 166 and B = 0.97. However, during application of oils containing additives, in interval of temperatures from 20 to 80° the time to formation of pitting was not changed (curves 2 and 3 for oil MT-16p and lubricant tsiatim-208).

Dependence of time to formation of pitting on viscosity for oils of type MS-14 is expressed by curve 1 in Fig. 2. This curve is a mirror image of viscosity-temperature characteristic of oil (curve 2). Therefore, the time of pitting

formation for similar oils can be determined by converted formula of Walter

$$\lg(111.3 - 1.9\tau) = \frac{A}{B} - \frac{\lg(\nu + 0.6)}{B},$$

where τ is the time of pitting formation in minutes;

ν is the viscosity in centistokes;

A and B are constants of the Walter equation.

Impairment of antipitting properties of petroleum oils as temperature increases is explained by two circumstances. First, as temperature increases the thickness of oil film separating the friction surfaces decreases. This, evidently, leads to an increase in the coefficient of friction and an increase of tangential stresses in material [9], promoting acceleration of appearance of prepitting cracks. Second, the less viscous oil more easily penetrates cracks and strengthens the formation of sores.

For oils containing antiwear additives the influence of viscosity may be not determining. Thus, during change of temperature of lubricant tsiatim-208 from 20 to 80° viscosity is changed from 3080 to 40 centistokes, i.e., decreases by 77 times, and time to formation of pitting remains constant. Apparently, as temperature increases the conditions for formation chemisorption films on friction surfaces are improved; that can ensure constancy of coefficient of friction (and correspondingly, the magnitude of tangential stresses), in spite of the decreased thickness of butyric film. This circumstance is cause of formation of pitting in one and the same time, in spite of different viscosity of oils. We must assume that formation of pitting can be slowed down by the fact that in presence of sulfur heightened wear of friction surfaces is usually observed in regimes before their jamming [9].

Influence of composition of lubricating materials on formation of pitting is well illustrated by following experiment. MT-16p oil and lubricant tsiatim-208 were heated to temperatures (73 and 80° respectively) at which they had equal viscosity (40 centistokes). However, antipitting properties of lubricating

materials determined in these conditions turned out to be different (tsiatim-208 - - 189 minutes; MT-16p — 43 minutes).

Consequently, antipitting properties of lubricating materials are affected both by their chemical composition, and by viscosity. Table 1 gives the antipitting properties of certain lubricating materials determined in different test conditions.

Table 1

Lubricating material	Test conditions			Average time to pitting τ, min
	Temperature, °C	Load		
		P, kg	per cycle, kg/cm²	
Transmission motor and tractor.	80	390	74,600	93
Sulphurized transmission motor and tractor.....	80	390	74,600	238
Experimental transmission with additive.....	80	390	74,600	87
SAE-30.....	80	390	74,600	85
DS-8 with additive vnii np-360.	80	390	74,600	100
Experimental transmission motor and tractor oil.....	80	390	74,600	71
Tsiatin-208.....	80	390	74,600	189
MT-16p.....	73	390	74,600	43
MS-14.....	80	390	74,600	89
Diesel fuel.....	20	390	74,600	13
Naphthene-paraffin fraction MS-14.....	20	300	68,400	41
Aromatic fraction MS-14.....	20	300	68,400	130
MS-14.....	20	300	68,400	89

We must assume that the antipitting properties of oils are greatly affected by chemical activity of products entering in composition of oil. The dominating role of aromatic fraction in oils without additives [7], and also retarded appearance of pitting of products of oxidation forming in process of work of oil testify to this. This fact was noted in carrying out of experiments with sample of synthetic oil. For this sample the time to formation of pitting was equal to 147 minutes. Adding to it an antioxidant additive decreased the time to formation of pitting by 4.5 times. On the basis of these results it is possible to assume that products of oxidation forming in oils during work of machines can

[illegible] the antipitting properties of initial oils. Positive influence of products of oxidation can apparently be explained by their high chemical activity and ability to form a chemisorption film on friction surfaces, which leads to change in conditions of friction. Joint introduction of anticorrosive and antioxidant additives did not change the time to formation of pitting. The absence of essential distinction between a sample containing only an antioxidant additive and a sample with antioxidant and anticorrosive additives testifies to insignificant effect of corrosion processes in neutral media on the appearance of pitting.

In contrast to the effect of antioxidant and anticorrosive additives, introducing oil products of sulfur-bearing substances led to improvement of antipitting properties of initial products. This was confirmed by results of experiments using Captax (mercaptobenzothiazole) and dibenzyldisulfide.

The Captax was introduced in diesel fuel in quantity up to 0.5% by weight. In this the antifriction properties of diesel fuels determined on four-ball friction machine by the one minute method at 20° and 600 rpm were significantly improved. At loads lower than loads of jamming the maxima of coefficients of friction dropped as the loads were increased as shown in Table 2.

Table 2.

Load, kg	Coefficient of friction	
	Diesel fuel	Diesel fuel and 0.5% Captax
50	0.12	0.11
60	0.12	0.11
65	0.42	0.42
75	0.40	0.42
100	0.41	0.31
125	0.43	0.23
150	0.40	0.14
175	0.42	0.14
200	0.41	0.14

At loads over 150 kg the coefficient of friction was not higher than 0.15, whereas at loads of close to jamming loads its value attained 0.4, i.e., was equal to coefficient of friction when diesel fuel was used without Captax. Apparently, due to lowering of friction the formation of pitting was significantly delayed. Thus, if when using diesel fuel (300 kg, 1500 rpm and 20°) pitting on ball was formed educated on the average after 30 minutes, then introduction Captax led to increase of time to 114 minutes.

The essential influence of Captax on improvement of antipitting properties of even those materials possessing poor lubricating properties such as diesel fuel shows the perspectives of using additives, strongly able to lower friction in conditions of high contact loads to improve the antipitting properties of oils.

The antipitting properties of oils with additives, just as their antiwear properties [9], depend on the concentration of the additives. Thus, introduction of 0.05 mole/liter of dibenzyldisulfide into napthene-paraffin fraction (NPF) oil MS-14 did not affect the antipitting properties of initial product. Increasing the concentration of dibenzyldisulfide to 0.15 mole/liter had an essential influence on improvement of antipitting properties of NPF. Average time to formation of pitting was increased from 41 to 69 minutes. However, it turned out that with increase of load to 390 kg, dibenzyldisulfide did not have an essential influence on improvement of antipitting properties of initial oil. We can assume that significant increase of loads can lead to destruction of the relatively soft sulfide layers of metal, forming during friction. Wide research using different additives can give the final answer to this question.

Molybdenum disulfide has an especially high effect in improvement of antipitting properties of oils. Adding specially pure MoS_2 (quantity of impurities in it was less than 0.20%) of high dispersiveness (95% particles had radii of particles less than 2 μ) in mineral oils in quantity about 1% led to increase of time to formation of pitting by 2-3 times. However in carrying out the experiment was

impossible to guarantee absence of precipitation of molybdenum disulfide from oil and continuous entering of preparation in contact zones of friction surfaces. Therefore, to clarify the effect of MoS_2 concentration in lubricating materials on their antipitting properties it is expedient to use semithick lubricants. A mixture consisting of 60% diesel fuel and 40% GOI-54 lubricant turned out to be expedient. Experiments were conducted at 20°, 390 kg and 1500 rpm. Molybdenum disulfide was introduced in quantity from 0.1 to 2.0% by weight. Small additions of MoS_2 to oil turned out to be (Fig. 3) absolutely ineffective. However, already at a concentration equal to 1% by weight, pitting was not revealed even after 5 hours of continuous work, whereas during work on initial mixture it appeared in 13-26 minutes.

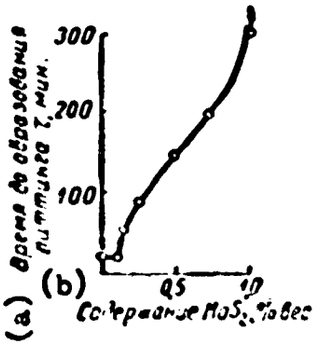


Fig. 3. Influence of concentration of MoS_2 on antipitting property of lubricant.
KEY: (a) Time to formation of pitting τ, minutes; (b) Content of MoS_2, % by weight.

Special experiments established that stopping the introduction of MoS_2 during friction in contact zone stopped the braking of formation of pitting [7].

The high pitting-stability of oil products containing MoS_2 can apparently be explained by the following. In conditions of high contact loads MoS_2 promotes significant lowering of friction of contacting surfaces. Due to this the contact tangential stresses decrease and formation of surface cracks from which subsequently pitting sores are developed is hampered.

The effectiveness of using MoS_2 was checked in reductors. During introduction of it in quantity of 1.5% by weight in mineral oil it was established that the working surface of toothed wheels of reductor with transmitting power up to 500 hp after 400 hours of work almost did not have pitting destructions. The toothed

wheels of a second reductor working in analogous conditions using an oil not containing MoS_2 had significant pitting destructions and, in accordance with their repair specifications they had to be replaced.

Using MoS_2 not only slowed down the development of pitting, but also promoted a significant lowering of wear of teeth by abrasion. Wear of teeth during application of oil with MoS_2 was in 2-2.5 times less than during application of oil not containing MoS_2.

The qualitative correlation of results obtained on laboratory installation and in using machines was determined on six samples of lubricating materials. Lubricating materials, in whose presence the time to formation of pitting was large, turned out to be best when using reductors with straight-toothed gears. However, for reductors with teeth of other types (in particular spiral) a similar correlation was not marked.

With the help of qualitative correlation we can determine the antipitting properties of lubricating materials in laboratory conditions on four-ball friction machine, which significantly accelerates these tests and lowers their expenditure.

Conclusions

1. Antipitting properties of lubricating materials can quickly and reliably be estimated on a four-ball friction machine adjusted for work in conditions of rolling.

2. Ability of lubricating materials to slow down the development of pitting depends on their viscosity and chemical composition.

3. Additives introduced in lubricating materials depending upon their composition and concentration can manifest braking action on development of pitting or accelerate it.

4. Determining the properties of lubricating materials and their additives enables us to more fully estimate their exploitational qualities.

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THE EFFECT OF OIL ADDITIVES ON CORROSIONAL WEAR OF BEARING ALLOYS

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NAMI*

For lubricants of motors with bearings of plumbous bronze oil with additives, containing an anticorrosive component are used. In certain oil additives this component is sulphurized oil — additive tsiatim-300 (naks), additive aznii-4, [tsiatim: Central Scientific Research Institute of Aviation Fuels and Oils; aznii: Azerbaijan Scientific Research Petroleum Institute named for V. V. Kuybyshev], and others. In alkylfenol additives the anticorrosive component may be the disulfide group introduced into the molecule of additive. The thiophosphoric group contained in multifunctional additives, has, besides other properties, anticorrosive ones.

Recently for bearings of automobile gasoline motors we have used lead alloy SOS6-4 [SOS: lead, tin, antimony] with high antifriction properties, into whose composition enters 88% lead, 6% tin and 6% antimony.

Such alloys are less stable in an corrosional-aggressive oil medium than stannous babbit, whose stability significantly exceeds that of plumbous bronzes. During creation of SOS6-6 alloy its corrosion in an oil medium was specially investigated and that composition which ensured normal work of bearings in running

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motors on oil without additive was selected. Therefore, the question about application of oils with special anticorrosive additives for motors with bearings of SOS6-6 alloy did not arise.

Multifunctional additives to motor oils contain other components besides the anticorrosive component. The washing component, in most cases a compound of metal with organic acids or phenols, usually is a catalyst to oil oxidation. It can appear that anticorrosive component of such additive is not in a state to counteract the corrosional aggressiveness of the oil strengthened by oxidation.

Addition tsiatim-330 (naks) containing cobalt naphthenate as a washing component belongs to this category of additives. For this reason oil with this additive is not used in motors with plumbous bronze.

The question of what effect the additive, in particular, tsiatim-330 (naks), has on corrosion wear of SOS6-6 alloys remains unclarified. Therefore, many autoworkshops do not use oil with additives in motors with bearings of SOS6-6 alloy. The MZMA instruction for the "Muscovite" automobile [MZMA: Moscow Factory of Small displacement Automobiles] contains a reservation prohibiting using oil with additive tsiatim-330 (naks).

This work is dedicated to clarification of the effect of oil additives on corrosion wear of SOS6-6 alloy.

Wear of SOS6-6 alloy was determined on installation IPS-NAMI and compared with wear of stannous alloys B-83.

The following additions were investigated: tsiatim-330 (naks), tsiatim-339 and DF-1.

The corrosional aggressiveness of oils with these additives with respect to lead was determined in a DK-2 instrument at 140° (GOST 8245-56) [GOST: All-Union Government Standard] for 25 hours. We found how much the corrosional wear of lead during work without friction corresponds to the corrosional wear of lead alloy SOS6-6.

Research of Lead Corrosion in a DK-2 Instrument

During the test on the DK-2 instrument the weight of SOS6-6 alloy plates did not decrease.

Results of test of lead plates in industrial 50 and DS-8 oils without additive and with 3% naks and the washing component of naks -- cobalt naphthenate (1.34%) are shown in Fig. 1.

Results of test of oils with addition DF-1 are not shown on the graph since oil with this additive practically did not corrode lead after 25 hours.

Curves 1 and 2 show that additive naks, added to industrial 50 oil in first 5-6 hours of the test almost completely prevents corrosion, but subsequently sharply strengthens it. The additive cobalt naphthenate in first moment of test strengthens corrosion -- curve 3.

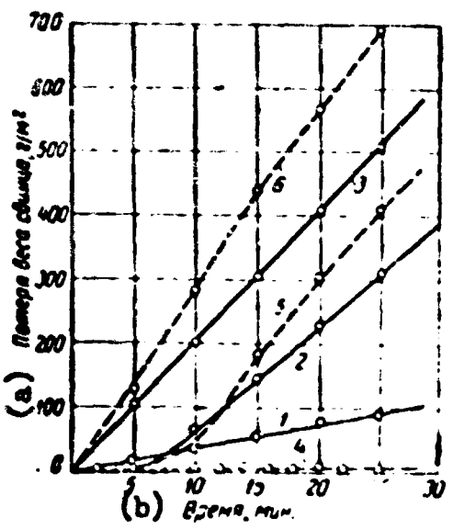


Fig. 1. Effect of additive naks and cobalt naphthenate on corrosion of lead in industrial 50 and DS-8 oils determined on a DK-2 instrument at 140°.
1) industrial 50 oil; 2) with additive naks; 3) with cobalt naphthenate; 4) oil DS-8; 5) with additive naks; 6) with cobalt naphthenate.
Key: (a) Weight loss of lead, g/m^2; (b) Time, min.

Since addition naks consists of cobalt naphthenate and sulphurized oil, the difference in corrosion of lead in samples of oil with these additives should be a result of the protective property of film, which the sulphurized oil creates on surface of lead. In the first hours of test, obviously, the film completely prevents penetration of aggressive acids to surface of metal; subsequently the film is destroyed, but not completely, which is confirmed by data of speed of corrosion. The higher anticorrosive effectiveness of additive tsiatim-339 as compared to additive naks

is explained not only by the large effectiveness of protective film, but also by the fact that this additive can to a known degree neutralize the acids forming during oxidation of oil.

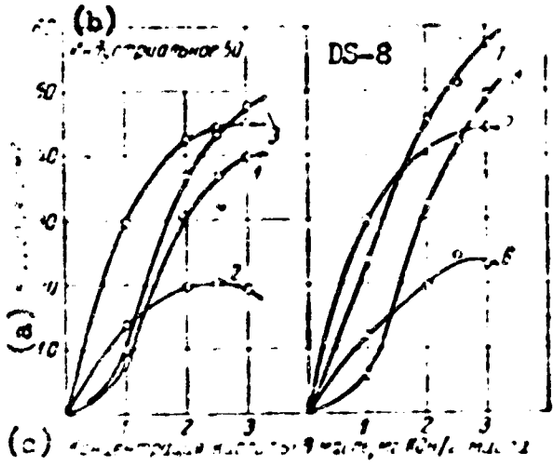


Fig. 2. Influence of oleic acid on lead corrosion in industrial 50 and DS-8 oils with additives, determined on DK-2 instrument at 140°. Time of test, 30 minutes.
1) industrial 50 oil without additive; 2) with additive naks; 3) with additive tsiatim-339; 4) with additive DF-1; 5) DS-8 oil without additive; 6) with additive naks; 7) with additive tsiatim-339; 8) with additive DF-1. KEY: (a) Corrosion, g/m^2; (b) Industrial 50; (c) Concentration of acid in oil, mgKOH/g of oil.

To clarify the particular anti-corrosive properties of additives, including the effectiveness of the protective film created by the additives, we set up special experiments on a DK-2 instrument. To the tested samples of oil were added various quantities of oleic acid. The experiments were conducted for 30 minutes, which precluded noticeable oxidation of oil and formation of additional quantity of acids, i.e., the method of determining the real corrodibility of oils was used.

The data in Fig. 2 show that the anti-corrosive properties of additive naks is sufficiently high. True, up to a concentration of oleic acid in oil equal to 1 mgKOH the corrosion of lead in industrial 50 oil with additive naks is greater than in the same oil with additives tsiatim-339 and DF-1, but during further increase of acid concentration the additive in this sample of industrial 50 oil corrodes less than additives in the other two samples of oils.

Consequently, the protective film created by naks on surface of lead is more effective than the films created by additives tsiatim-339 and DF-1. Furthermore, the film under action of increased concentration of acid in oil not only is not destroyed, but is even strengthened somewhat.

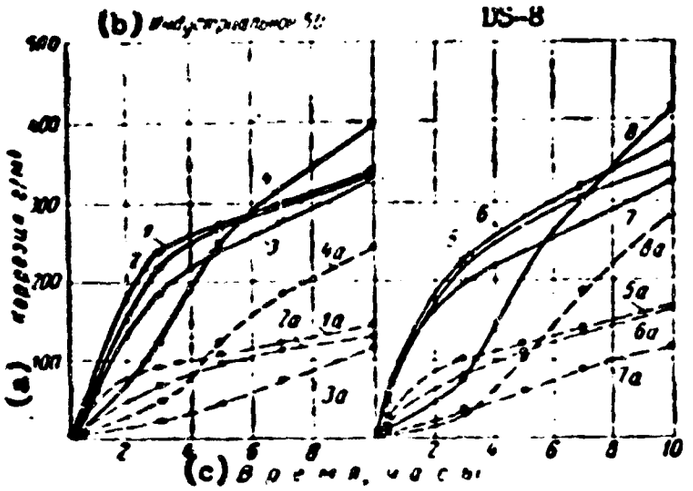


Fig. 3. The effect of oleic acid on corrosion of lead in industrial 50 and DS-8 oils with additives determined on DK-2 instrument (temperature 140°).
At acid concentration in oil corresponding to 3 mgKOH/g of oil:
1) industrial 50 without additive; 2) the same with 3% tsiatim-339; 3) the same with 3.5% DF-1; 4) the same with 3% naks; 5) DS-8 without additive; 6) the same with tsiatim-339; 7) the same with DF-1; 8) the same with naks. 1a-8a corresponding curves at acid concentration in oil corresponding to 1 mgKOH/g of oil.
KEY: (a) Corrosion, g/m^2; (b) Industrial 50; (c) Time, hours.

Continuation of test of these samples of oils with additives and added oleic acid added to them (up to 10 hours) shows a fundamental difference in behavior of films created by naks and the other two additives. As can be seen from Fig. 3, with increase of acid concentration the effectiveness of the film created by tsiatim-339 and DF-1 decreases. Thus, e.g., at an acid concentration equal to 1 mgKOH/g of oil, after 4-hour tests the film created by DF-1, decreases the corrosion in industrial 50 and DS-8 oils from 60-55 g/m^2 to 30 g/m^2. The film created by tsiatim-339 is even more effective. The film created by naks acts differently: thus, in industrial 50 oil after 4-hour tests as acid concentration increases 1 to 3 mgKOH/g of oil the protective effect of film is increased from 20 to 50 g/m^2, and in DS-8 oil, from 50 to 110 g/m^2. However, independent of acid concentration the film created by naks after 5-7 hour test loses its effectiveness;

corrosion in this oil sharply increases and starts to significantly exceed the corrosion in oil without additive. The research conducted on the DK-2 established that cobalt naphthenate in naks accelerates the corrosion of lead. The anti-corrosive component of additive can create a protective film chemically stabler in medium of organic acid than films created by tsiatim-339 and DF-1. However this film in an oxidizing oil medium is destroyed significantly faster.

Research of Corrosional Wear on IPS-NAMI Installation

To evaluate the dependence of wear of bearing alloys on quality of oil we used the IPS-NAMI installation, whose diagram is shown in Fig. 4. The friction pair of the installation is steel cylinder 1, put on vertical revolving shaft 2, and the two blocks 3 pressed to it with the help of load mechanisms. Diametrical location of blocks unloads the shaft. The blocks on "dovetail" are inserted in mountings 4. Mountings are united with load mechanism by ball and socket joint 5, making them self-adjusting. The load mechanism consists of pushers 6 and levers 7 and 8. Arms of levers are in such relationship that pressure of load 9 is increased tenfold.

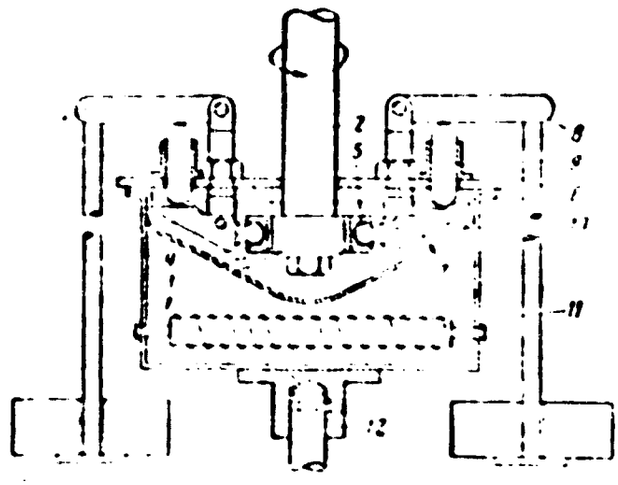


Fig. 4. Diagram of IPS-NAMI installation.

The friction pair is placed in bath 10 and during work is dipped in oil. The required temperature of oil is supported with the help of heating element 11, located under bath, and LATR [LATR: Laboratory Automatic Transformer].

The blocks are changed when the bath is lowered; to replace them lifting mechanism 12 will be used.

The corrosional aggressivness of oil, or corrosional stability of bearing alloy, are estimated by the decrease of weight of blocks.

For comparative appraisal of the effect of different additives on wear of bearing alloys the following method was used.

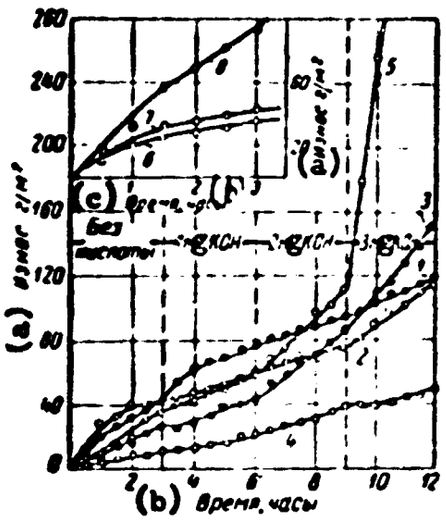


Fig. 5. Dependence of speed of wear of SOS6-6 alloy on acid concentration in oil, determined on IPS-NAMI installation.
1) industrial 50 oil without additive; 2) oil with tsiatim-339; 3) oil with naks; 4) oil with DF-1; 5) oil with cobalt naphthenate; 6) oil without additive; 7) oil with oleic acid (3 mg KOH/g of oil); 8) the same with naks.
KEY: (a) Wear, g/m^2; (b) Time, hours; (c) Without acids.

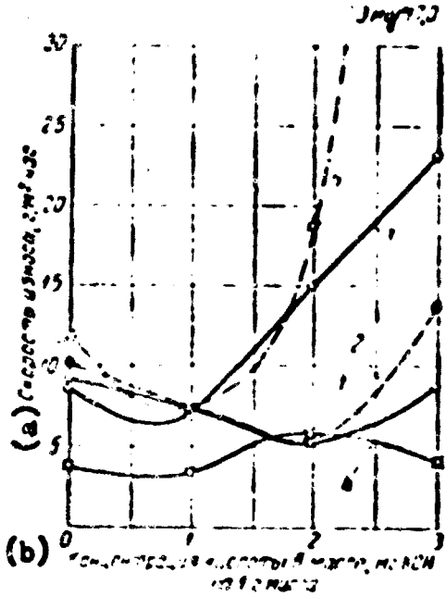


Fig. 6. Dependence of speed of wear of SOS6-6 alloy on acid concentration in oil with various additives determined on installation IPS-NAMI.
1) industrial 50 oil without additive; 2) oil with tsiatim-339; 3) oil with naks; 4) oil with DF-1; 5) oil with cobalt naphthenate.
KEY: (a) Loss rate, g/m^2 hr; (b) Acid concentration in oil, mgKOH/g of oil.

Into a washed and dried bath pour 250 ml of tested oil. Insert the preliminarily processed blocks, thoroughly washed in gasoline, dried and weighed, in mountings. Together with the mountings put them on spherical pins. Lift the bath and turn on the heating. After the oil temperature attains the required experimental index (in these experiments 140°), turn on the drive of installation and load. The specific pressure on the blocks is equal to 20 kg/cm^2. The wear of tested bearing alloy is determined by weighing the blocks every 0.5 hour of test. After 3 hours of work to the tested oil add oleic acid in such quantity so that its concentration corresponds to 1.0 mgKOH/g of oil. Then after 3 hours of tests the acid concentration is again increased to 2.5 or 3.0 mgKOH/g of oil. Thus, the test continues

12-15 hours.

The obtained data on wear of five samples of oils are given in graphs of Fig. 5. For all acid concentrations the curves for industrial 50 oil with tsiatim-339 (curve 2) and for oil with additive DF-1 (curve 4) lie lower than curve 1 for industrial 50 oil without additive. Meanwhile at acid concentration of 2 mgKOH/g of oil and above the curves for samples of oil with naks and cobalt naphthenate steeply rise and intersect curve 1 for oil with additive. In this the curve for sample of oil with naks lies lower than curve for oil with cobalt naphthenate, indicating that even in these conditions the protective film acts, although insufficiently effectively.

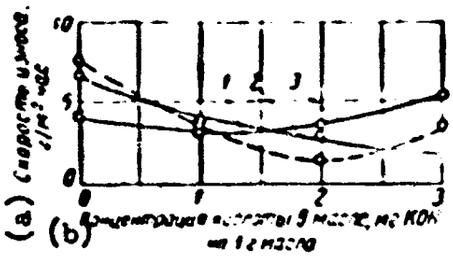


Fig. 7. Dependence of speed of wear of babbit B-83 on acid concentration in oils with various additives, determined on IPS-NAMI installation. 1) oil without additive; 2) industrial 50 oil with additive tsiatim-339; 3) oil with additive naks.
KEY: (a) Speed of wear, g/m^2 hour; (b) Acid concentration in oil, mgKOH/g of oil.

The speed of wear in g/m^2 hr for every concentration of acid in oil, calculated by slope of line segment of curve for this concentration, is graphically depicted in Fig. 6. Figure 7 gives similar data, obtained for babbit B-83. The results shown in these figures, and also additional materials on change of speed of wear of SOS6-6 alloy during test of DS-8 oil from sulfur-bearing oils and on speed of wear of lead are given in the table. In the same place are given the magnitude of change of speed of lead corrosion, determined on DK-2 instrument. From these data it is clear that as acid concentration increases to mgKOH/g of oil speed of wear of SOS6-6 alloy and babbit B-83 drops sharply. Speed of wear of lead is increased more than 2 times.

Influence of Oleic Acid in Oils with Additives on Speed of Wear of Bearing Alloys

Instrument	Oil	Additive	Plates	Speed of wear, g/m^2 hour			
				Without acid	Concentration of acid in oil, mgKOH/g of oil		
					1	2	3
IPS-NAMI	Industrial 50	—	SOS 6-6	9.0	7.5	5.2	8.7
		Tsiatim-339	SOS 6-6	10.3	7.5	5.3	13.7
		Naks	SOS 6-6	8.3	6.7	15.0	23.2
		DP-1	SOS 6-6	3.5	3.2	5.5	4.2
		Cobalt naphthenate	SOS 6-6	11.7	7.3	18.7	117.0
		—	Babbit	6.5	3.8	2.9	1.8
		Tsiatim-339	Babbit	7.5	3.5	1.4	3.5
		Naks	Babbit	4.0	3.2	3.6	5.5
		—	Lead	160.0	400.0	—	—
		Tsiatim-339	Lead	55.0	210.0	240.0	400.0
		Naks	Babbit	4.5	3.5	0.9	1.5
		Naks	SOS 6-6	9.2	6.0	6.0	18.5
DK-2 NAMI	Industrial 5C	—	Lead	4.0	—	—	—
		Naks	Lead	16.4	—	—	—
		Cobalt naphthenate	Lead	20.4	—	—	—
		Tsiatim-339	Lead	10.0	—	—	—
	DS-8	Naks	Lead	20.8	—	—	—

NOTE: Speed of corrosion of lead in DK-2 instrument is calculated between 20 and 25 hours of test.

Decrease of wear of alloys B-83 and SOS 6-6 for small concentrations of oleic acid is in full consent with conventional views on influence of organic acids on wear of metals.

With further increase of acid concentration in oil with additives naks and cobalt naphthenate, the speed of wear of SOS 6-6 alloy is sharply increased, and speed of wear of babbit (alloy B-83) remains very low. In comparing the data on change of speed of wear of lead and SOS 6-6 alloy (during test on oil with additive tsiatim-339) it is clear that lead wears out in a corrosive medium 30-40 times more

than SOS 6-6 alloy, and 100-130 times more than babbit. However, as one may see from given experimental material, the speed of corrosional wear of SOS 6-6 alloy with small concentrations of acid in oil is small, and, more importantly, in these limits it is increased as with acid concentration increases.

For all tested samples of oil with the exception of oils with additives naks and cobalt naphthenate the absolute value of wear of alloys SOS 6-6 and B-83 is approximately equal and does not exceed 10 g/m^2 hour.

The acid concentration is increased every 3 hour of the test; consequently, a concentration equal to 3 mgKOH/g of oil is attained after only 9 or 12 hours of test. Therefore, the question can arise: is not the observed increase of speed of wear with this concentration (see Fig. 6 and table) a result of destruction of protective film, as on lead plates (see Figs. 2 and 3). However, the data given in upper part of Fig 5, obtained during tests of samples of oils to which acid was added in beginning of experiment, show that protective film in conditions of friction acts differently. Curve 7, characterizing the effect of oleic acid, although it lies somewhat higher than curve 6, showing corrosional aggressiveness of clean oil, has a slope identical to it; this indicates that oleic acid does not increase the speed of wear of SOS 6-6 alloy. Curve 8, pertaining to additive naks, has a significantly larger slope, which indicates a higher speed of wear. If curves 6 and 7 show a speed of wear equal to 8 g/m^2 hour, curve 8 shows a speed of wear equal to 23 g/m^2 hour. These magnitudes coincide with magnitudes given in table. That is, the protective film created by additive naks is stable in aggressive acid medium in absence of friction; in conditions of friction it starts to be destroyed in the actual beginning of experiment, and corrosional wear increases intensely. Furthermore, in the presence of cobalt naphthenate in oil separately or in composition of additive naks the "lubricating" or "polishing" action of oleic acid on surface of SOS 6-6 alloy plate disappears. Consequently, the data shown in Figs. 6 and 7 and in Table 1 show that the dependence of speed of corrosional wear of

alloys SOS 6-6 and B-83 on acid concentration and effectiveness of protective films created by additives on surface of these alloys in conditions of friction.

Organic acids, forming in oil during work of motor, can be corrosionally more aggressive than oleic acid. These acids are formed not only due to oxidation of oil, but also as a result of incomplete combustion of fuel. However, one may assume that the general regularities, about which this article is concerned, are also just for conditions of work of motor.

In the table, in the column with the data on change of speed of wear of alloys SOS 6-6 and babbit, obtained on IPS-NAMI installation, are given the magnitudes of change of speed of lead corrosion. These magnitudes were calculated on the basis of curves of lead corrosion on DK-2 instrument between 20 and 25 hours of test (Fig. 1), i.e., after practically full destruction of protective film. It is easy to see their similarity with the data on speed of wear of alloy SOS 6-6. This similarity enables us to judge about corrosional aggressiveness of oil with additives with respect to this oil to alloy SOS 6-6 (or about corrosional wear of alloy SOS 6-6) based on the data of test of lead corrosion in DK-2 instrument.

This research was conducted at acid concentrations approaching high values in order to clarify character of behavior of oil with various additives in wide limits of acidity. In conditions of work of motor acid numbers on the order of 3 mgKOH hardly occur (in this the acids usually are more corrosively aggressive). Therefore, on the basis of conducted research one may assume that additives containing sulphurized oil as anticorrosive component are not useful for application in motors with plumbous alloy SOS 6-6 bearings. From the given data also it is clear that additives of type DF-1, in which the anticorrosive component is the thiophosphoric group, ensure the best protection to plumbous alloy bearings.

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METHOD OF APPRAISAL OF WORKING PROPERTIES OF INHIBITED INSULATING OILS

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VTI

The existing laboratory methods of evaluating the stability of insulating oils do not completely reproduce their working regimes, (the effects of hard insulating and constructive materials, electrical field and so forth are not counted), and, therefore, they can give results differing from those obtained in practice.

Moreover, oil acceptable in one country is frequently rejected as unfit in another country.

Especially unreliably laboratory methods (too optimistically) evaluate the inclination to aging of inhibited insulating oils.

The possibility of using the results of field tests to evaluate oil quality is very limited, inasmuch as such tests continue many years (for good and inhibited oils 10-15 years and more).

These causes made it necessary to create a method which would most closely approach the working conditions of oils in use.

The essence of this method, developed by the authors with the participation of Moscow Transformer Factory, consists in testing the oil for aging (for 750 hours) in a real small power transformer, idling at double the maximum electric field

strength. To decrease the test period the process of oil aging was strengthened by using special attachments ensuring oil heating to +95°, its saturation by oxygen and circulation of oil in the zone of the field.

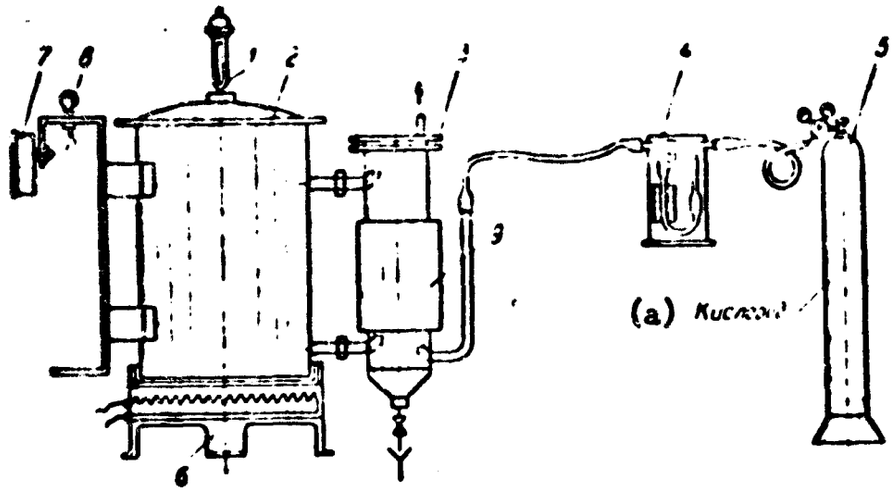


Fig. 1. Diagram of equipment applied for testing oils by the stand method.
1) contact thermometer; 2) transformer tank; 3) additional tank; 4) rheometer; 5) bottle; 6) electric stove; 7) relay; 8) signal lamp; 9) electric heater of tank.
KEY: (a) Oxygen.

The basic diagram of equipment used in testing by this method is shown in Fig. 1, and a general view of the transformer with outlying tank is shown in Fig. 2. The last one is united with the main tank of transformer by two branch pipes to guarantee oil circulation.

There are three sources of preheating: transformer, electric heater on spare tank and electric stove under the bottom of transformer; these ensure sufficient mixing of oil due to thermal convection.

The oil is saturated with oxygen by supplying it in the spare tank at speed 25 ml/min. This very insignificant quantity of oxygen is fully sufficient for necessary acceleration of aging process.

The quality of oil is determined during its work according to the change of complex of indices: inclination to form low-molecular water-scluble acids at the start of aging (after 100 hours), total acidity, quantity of deposit, tangent of

dielectric-loss angle ($tg\delta$), characteristics of the state of hard insulation (durability of surgical tape and paper to breaking and so forth), corrosional aggressiveness with respect to copper, and others [2].

With this new method we conducted a number of tests: Soviet goods and experimental oils obtained from new raw material and by improved technology (selective purification, hydrogenation, sulfonation), and imported oils.

With this method we also estimated the effect on stability of oils of land purification and degree of their washing after neutralization, etc., and ability of additives (inhibitors, deactivators, and others) to slow down the aging of oils.

Table 1 gives the results of test of certain investigated oils.

Uninhibited Soviet oils in process of tests significantly lower the mechanical durability of hard insulation -- surgical tape and cable paper. English oil will form 2-4 times less water-soluble and high-molecular acids.

In contrast to Baku oils of 1959 and Emba crude (1957-1959) English uninhibited oil in process of aging changes little externally (color, transparency) and does not evoke color change in insulation of transformer or formation of deposit on windings or in magnetic circuit.

The new method gives a more objective and diverse appraisal of working properties of inhibited insulating oils than other known Soviet and foreign methods.

Table 2 gives the results of test on stand and per GOST 981-55 of the ability of additive Ionol to inhibit the aging Baku and sulfur-bearing eastern (basically Tuymazinsk) oils.

Let us note that in studying the oxidation of oil in laboratory conditions by the method of GOST 981-55 or other methods (including MEK) additive Ionol, added in concentrations of 0.2% and higher, independent of origin of oils to which it is added from Baku, Emba or eastern sulfur-bearing oils, almost completely prevented the oxidation of oils, i.e., formation of deposit, low-molecular or high-molecular acids.

Table 1. Results of Testing Oils on Transformer Stand by the New Method

Origin and characteristics of oils	Physico-chemical indices			tgδ, % at		Results of tests on transformer stand									
						after 100 hours	After 750 hours								
	Kinematic Viscosity at 50°C	d_4^{20}	n_D^{20}	20°C	70°C	Content of water-soluble acids, alkalis, total acidity mgKOH/g	Total acidity mgKOH/g	Deposit, %	tgδ, % at 20°C	tgδ, % at 70°C	Durability to breaking, % of initial: surgical tape	Durability to breaking, % of initial: cable paper	Weight loss of copper plate, g/m²	Appearance: Surgical tape and paper	Appearance: Copper plate
Baku commercial, 1959	8.4	0.8816	1.4870	0.25	—	[illegible]18	0.14	0.030	0.38	—	—	—	+0.4	—	Pure
Baku commercial oil MK-8, 1959	8.5	0.8844	1.4880	0.21	1.0	[illegible]027	0.15	0.020	0.30	4.40	19.4	42.5	−0.5	Black, covered by deposit	Pure
Constantine from Emba oils, commercial, 1954	8.5	0.8752	1.4880	—	—	0.025	0.13	0.009	0.30	—	—	—	+0.1	—	Covered by black deposit
Novo-Ufimsk from sulfur-bearing oils, purified by phenol (sulfur 0.4%), with 0.3% Ionol per VTU-30-59, commercial, 1950	9.9	0.8601	1.4752	0.01	0.2?	0.024	0.13	Traces	0.07	1.40	36.5	53.5	−3.8	Light, without deposit	Covered greenish-steel deposit
From Anastas'insk oil, purified by sulfuric acid by usual technology, without additives, experimental	8.9	0.9008	1.5005	0.01	0.11	0.016	0.19	0.015	0.51	5.70	66.0	60.0	+0.4	Dark, with light spots, without deposit	Slightly darkened
From Emba oils, purified by gasiform SO_3, with depressor and 0.02% Ionol, experimental	6.1	0.8498	1.4660	0.03	0.24	0.005	0.05	None	0.02	0.14	95.0	13.5	−1.2	Absolutely pure	Darkened and covered with deposits
English, uninhibited, commercial	8.8	0.8794	1.4831	<0.01	0.06	0.011	0.07	0.003	0.04	0.88	70.2	72.5	+0.2	The same	Pure

Table 2. Test of Transformer Oils with Additives

No of the test	Origin and characteristics of oils	Oxidizability per GOST 981-55: Yield of low-molecular acids at start of aging, mgKOH/g: Sole-volatile	Sole-volatile	Convol-atile	General stability: Acidity, mgKOH/g	Deposit, %	After 100 hours: Yield of water-soluble acids, mgKOH/g	Test on stand: After 750 hours: Yield of water-soluble acids, mgKOH/g	Total acidity, mgKOH/g	Deposit, %	Durability on burst, % of initial: Surgical tape	Paper	tgδ, % at: 20°C	70°C	Weight loss of copper plate g/m²	Appearance: Surgical tape and paper	Copper plate
8	From Baku oils, commercial, 1955	0.004	0.004	0.20	0.03	0.023	44	0.13	0.015	—	—	0.20	0.20	—	—	—
8	The same with 0.2% Ionol	0.006	0.003	0.03	None	0.019	55	0.13	0.011	—	—	—	—	—	—	—
2	The same purified by 5% H_2SO_4, neutralised, washed by tap water, with 0.015% additive VTI-1	0.001	0.001	0.07	0.02	0.017	66	0.08	0.005	—	—	0.20	2.00	—	—	—
8	From eastern sulfur-bearing oils (sulfur 1%), lot 1, 1957	0.008	0.005	0.40	0.04	0.018	70	0.20	0.050	—	—	2.38	17.0	-2.9	—	Deposit weak, violet color
	The same with 0.3% Ionol	0.002	0.001	0.03	None	0.014	70	0.13	0.008	—	—	1.05	11.0	-2.9	—	—
11	The same with 0.7% Ionol	—	—	0.02	None	0.019	70	0.20	0.015	1.0	0.0	1.01	11.56	-5.3	Black, fragile	Deposit of brown color
9	From eastern sulfur-bearing oils (sulfur 0.4%), lot II, 1958	0.055	0.020	0.62	0.07	0.025	36	0.19	0.024	44.5	41.8	0.38	5.81	-2.1	Tape dark covered by deposit	Dark-gray spots
9	The same with 0.3% Ionol	0.004	0.003	0.05	None	0.024	36	0.13	Traces	63.5	53.5	0.07	1.46	-4.0	Pure	Deposit of greenish-steel color
11	The same with 0.5% Ionol	0.002	0.001	0.03	None	0.017	72	0.11	Traces	51.5	76.0	0.15	1.80	—	Pure	The same
13	From eastern sulfur-bearing oils, commercial, 1959 with 0.2% Topanol-O	Traces	Traces	0.00	None	0.00	[illegible]	0.06	Traces	76.0	71.5	0.18	1.20	-3.9	Pure	The same

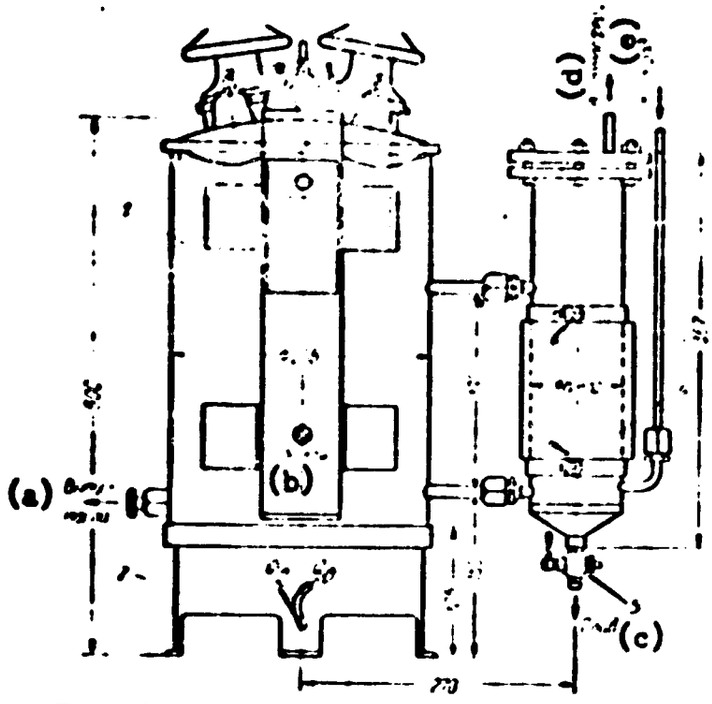


Fig. 2. General view of transformer.
1) transformer tank; 2) electric stove;
3) spare tank; 4) electric heater of tank;
5) cock.
KEY: (a) Oil output; (b) Earth; (c) Drain;
(d) To the atmosphere; (e) Oxygen.

In a test on stand additive Ionol turned out to be less effective, although the direction of its action determined by laboratory means was maintained.

According to laboratory data adding 0.3% Ionol (1957, lot I) to oil from sulfur-bearing eastern oils of phenol purification containing 1% sulfur makes the oil to very stable (deposit and acids practically will not be formed).

Bench tests of the same oil not only with 0.3, but also with 0.7% Ionol showed that although it decreases the content of deposit (true, not to such a degree as in laboratory appraisal), the additive but little affects the yield of acids, including low-molecular, does not prevent the ability of oil to destroy hard insulation, does not sufficiently lower the $tg\delta$, and even increases the corrosivity of oil with respect to copper.

The factory measures undertaken to improve oil quality by increasing phenol purification (1958, lot II) and improving production technology — narrowing the fractional composition (production of the end of 1959, commercial lot) gave positive results.

1958 oil containing 0.4% sulfur with 0.3% Ionol according to bench tests significantly exceeded the quality of 1957 oil with 0.7% Ionol. During the test it did not form a deposit and, as compared to the latter, to a lesser degree destroyed the hard insulation and increased $tg\delta$. As a result of these improvements it became possible to introduce this oil into production.

If oil from eastern sulfur-bearing oils of 1957 with 0.3% Ionol should be considered unsatisfactory, and 1958 with 0.3% Ionol — satisfactory, then oil at the end of 1959 with 0.2% Ionol, supplied under the brand Topanol-O, is good, although it has certain deficiencies.

These data show that laboratory methods give insufficiently objective appraisal of quality of inhibited oils and testify to decisive value of quality of the base product in production of inhibited oils.

It is necessary to indicate that determining the inclination to form low-molecular acids at the start of aging per GOST 981-55 coincides, as a rule, with behavior of oils on stand. The advantages of the stand method of evaluating oil are based mainly on the conditions of aging of oil in stand method being closer to the working conditions than in other methods.

More convincing proof of the advantage of this method would be coincidence of results of test on stand and in use.

However, full conformity between the data of these tests should not be expected at least because during use of one and the same oil in several transformers diverse results are obtained (Table 3)*. This is explained by distinction in conditions of use of transformers and their state (a difference of contamination) before tests.

Therefore, the results of field tests are estimated on the basis of average data of several tests.

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*The field tests of oils are conducted under the leadership of A. A. Luzhetskiy.

Since the offered method was developed relatively recently (1957), and period of service of good oil is more than 10 years, conformity between results of testing oils by new method and their behavior in use is confirmed on the basis of the following.

1. More than 15 years ago S. E. Kreyn [3] based on field tests proved that deeper purification of oil from Baku oils and adding to it 0.01-0.015% of additive VTI-1 increases the period of service of oil 2-3 times. Many years of experience of industrial use has confirmed the expediency of using this method.

Results of bench test (see Table 3) also confirmed the increase of period of service of such oil (judging by lowering the content of water-soluble acids by 1.4 times, total acidity by 2 times and deposit by 3 times).

Table 3. Results of 20-Month Field Tests of Transformer Oil of Phenol Purification from Tuymazinsk Oil (Sulfur ≈ 1%) Without Additive and with 0.3% Ionol

Power of transformer, kilovolt ampere	Acid number, mgKOH/g	Content of water-soluble acids, mgKOH/g	Presence of additive
100	0.017	0.006	No
180	0.025	0.012	No
50	0.059	0.03[illegible]	No
50	0.080	0.034	No
Mean value: 0.181: 4 = 0.43; 0.078: 4 = 0.020			No
180	0.049	0.018	Yes
180	0.023	0.011	Yes
320	0.025	0.016	Yes
100	0.028	0.012	Yes
50	0.0[illegible]	0.026	Yes
50	0.048	0.012	Yes
50	0.037	0.014	Yes
Mean value	0.272: 7 = 0.039	0.109: 7 = 0.0155	Yes

Table 4. Results of Tests

Results of 120-hour bench tests				Results of 20-month field tests (mean value)			
Content of water-soluble acids, mgKOH/g		Total acidity, mgKOH/g		Content of water-soluble acids, mgKOH/g		Total acidity, mgKOH/g	
Without additive	With additive	Without additive	With additive	Without additive	With additive	Without additive	With additive
0.021	0.015	0.053	0.042	0.020	0.015	0.043	0.039

2. In 1957 from commercial Tuymazinsk oil was obtained lot I of experimental transformer oil of phenol purification, containing about 1% sulfur, and tested in pure form and with additive Ionol (0.3%).

Laboratory tests of stability of this oil showed that without the additive it barely corresponds to requirements of specifications of GOST 982-56, and adding the additive makes it completely answer the requirements of this standard.

Adding the additive lowered the formation of deposit during the bench test of this oil, but had little effect on lowering the yield of low-molecular and high-molecular acids.

Results of 20-month field tests confirmed the results of initial stage of aging of oils, obtained on bench tests (see Table 3). This is illustrated by data (Table 4).

Consequently, all available data on exploitation of oils confirm the results of bench tests by the offered method.

Results of bench tests of transformer oils by this method are main criteria used to solve practical questions of introduction of new sorts of transformer oils, obtained by new technology from new raw material or with application of additives which is realized in practice.

Conclusions

1. A new bench method of appraisal of working properties of transformer oils has been developed.

2. As a result of numerous tests of large number of developmental types of oils by this method the following oils were introduced or were recommended for introduction:

a) oil of phenol purification from eastern oils (sulfur $\leq 0.6\%$) with 0.2% additive Topanol-O (VTU NP-30-59);

b) oil hydropurified from eastern oils (sulfur $\leq 0.2\%$) without additives; (VTU NP-75-60);

c) oil of acid-alkaline purification from Anastas'insk oil with additives;

d) oil from Emba oils, purified by gasiform SO_3 with 0.2% additive Ionol.

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CALCULATING THE NECESSARY CONCENTRATIONS OF NEUTRALIZING ADDITIVES IN MOTOR OILS

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VNII NP*

The increase of specific indices of motors, growth of requirements for working reliability and period of service, and also wide application of sulfur-bearing diesel fuels recently lead to using oils with heightened additive content. The tendency to increase the additive concentration is observed even now. However, high concentration of ash additives in oil entails a row of undesirable consequences (increase of abrasive wear of details, growth of scale formation in combustion chambers, and decrease of effectiveness of oil filters). Application of oil with unnecessarily high additive concentration, furthermore, increases its cost. Therefore, the foundation for selecting of additive concentrations in motor oils is an urgent problem.

This article expounds a method of calculating the necessary concentrations of neutralizing additives in oil depending upon sulfur content in fuel. In other words, the offered method enables us to determine how much the additive concentration should be increased when shifting to fuel with a large sulfur content.

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In first stage of work we fixed the basic possibility of full neutralization of harmful action of sulfur contained in fuel on wear and scale formation in high speed four-cycle diesel engine by increasing the additive concentration in the oil. With this goal we conducted series of motor tests. The tests were conducted by the 100-hour method, which we have successfully applied for the last 4 years. By successive trials on one motor using standard tests we attained fully satisfactory accuracy and reproducibility of experiments in all appraisal indices. Thus, we managed to avoid a number of known deficiencies of prolonged tests and at the same time ensure experimental conditions, sufficiently close to conditions of application of oil (full-scale motor of real construction, normal period of oil replacement and thermal engine operating conditions, etc.). All experiments were conducted with diesel oil DS-11 from eastern sulfur-bearing oils.

We investigated the effect of concentration of additives tsiatim-339 and vnii np-360 on scale formation and wear.

Additive tsiatim-339 was tested in concentrations from zero to 10% during work of D-35 motor on fuel with sulfur content of 1%. Effectiveness of this additive at identical concentration in oil is lower than that of additive vnii np-360. Apparently, increasing the concentration of additive tsiatim-339 within practically expedient limits cannot completely neutralize the effect of sulfur on wear of piston rings with its content in fuel near 1% and more. In reference to two-cycle diesel engine YaAZ-204 this was convincingly shown in preceding work [1]. Therefore, more specifically we investigated the effect of concentration of additive vnii np-360 on motor properties of oil. On the D-38 motor we obtained a dependence of scale formation and wear during change of additive concentration from 2 to 15% when working on fuels with sulfur content from 0.2 to 1.5%. These dependences are depicted in Fig. 1, from which it is clear that a corresponding increase of additive vnii np-360 concentration even when working on

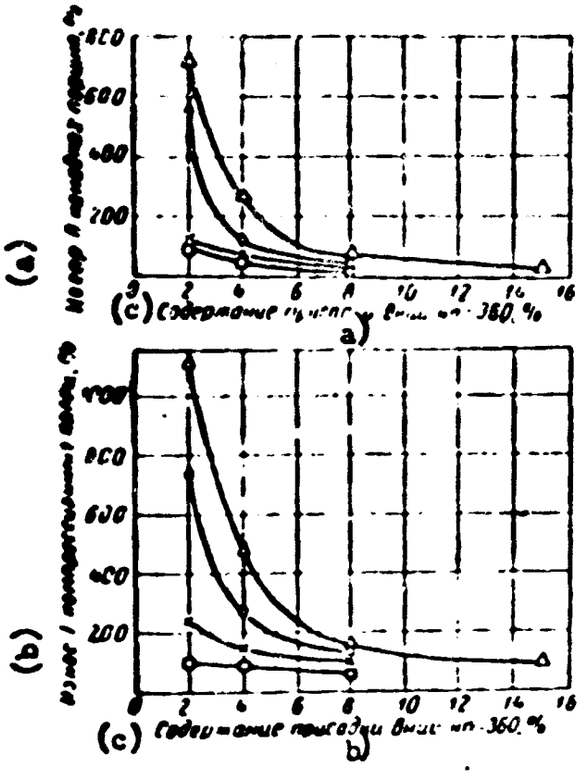


Fig. 1. Dependence of scale formation and wear on concentration of additive vnii np-360 in oil.
a) scale formation in piston grooves;
b) wear in compression rings.
Δ - fuel with sulfur content 1.5%;
○ - fuel with sulfur content 1.0%;
× - fuel with sulfur content 0.6%;
□ - fuel with sulfur content 0.2%.
KEY: (a) Scale formation in piston grooves, %; (b) Wear in compression rings, %; (c) Concentration of additive vnii np-360, %.

fuel containing 1.5% S, the level of scale formation and wear obtained in tests of low-sulfur fuel may be attained Consequently, harmful effect of sulfur contained in fuel on wear and scale formation in four-cycle diesel engine without pressure feed may be practically completely neutralized by adding a sufficient quantity of effective additiv to the oil. When using oils with high additive content (when working on fuels with sulfur content more than 1%) we observed a somewhat heightened wear of oil rings, most sensitive to abrasives in oil and comparatively little subject to corrosional wear. We observed this phenomenon during tests of high-ash oils for heavy conditions of work [2].

During experiments on the D-38 motor we observed expenditure of the additive. It is known that during work of oil in motor the additive is continuously expended in the neutralization reaction and its concentration in the oil is lowered. For observation of movement of this process earlier we applied a method in which the metal revealed in filtrate of benzene solution of the oil working in motor of oil was considered the active part of the additive [1]. However, at heightened additive concentrations this method turned out to be unsatisfactory, since the products of additive operation being strongly dispersed by the active addition remaining in oil pass through the filter. This can be seen graphically in Fig. 2a and b, on which the dotted line shows curves of change of active barium content in

oil during the time of work of motor. Decrease of barium concentration after 100 hours with a 8% additive content in oil was the same, as for a 2% additive content. This fact shows that at high additive concentrations the quantity of active barium is evidently oversized. At large additive concentration it should abrade in large quantity (until all the acids formed in the oil will be neutralized). On the same Fig. 2 there are solid curves of change of active barium content in oil determined by method*, based on determining the time of effective neutralization by investigated oil of vapors of aggressive acid passed to friction surfaces of radioactive details of laboratory installation RUM-1 [3]. The time of effective neutralization was converted into the active barium concentration from a calibrated graph drawn from the results of testing oils with known additive concentrations. By this method the active part of additive is determined directly from its functional action (neutralization).

Comparing the data obtained by both methods shows that at low additive concentration the results of determination are rather close and at great coordination of additive (during work on fuel with 1.5% sulfur content) they practically coincide. If, however, the concentration of additive is high, then the difference is very great. Our available data show that error of method of filtration is greater the higher the concentration of additive in oil. This explains the above-indicated possible cause of increased results of determining the active additive content in oil by method of filtration.

The data obtained by method of determining the time of effective neutralization of oils about coordination of additive vnii np-360 during work of motor on fuels with different sulfur contents show that sulfur content in fuel is the main factor affecting the speed of additive wearing out. At insufficient initial concentration of additive in oil it completely abrades after a certain time (Fig. 2a) and the motor actually works in oil containing no additive. When the active additive

*Developed jointly with Yu. S. Zaslavskiy and G. I. Shor.

concentration was lowered to zero, already in first half of oil replacement period we observed high wear of piston rings, intense scale formation and coking and significant decrease of their mobility.

Consequently, the initial additive concentration should be such that to the moment of oil replacement there is still a certain reserve of active additive in it.

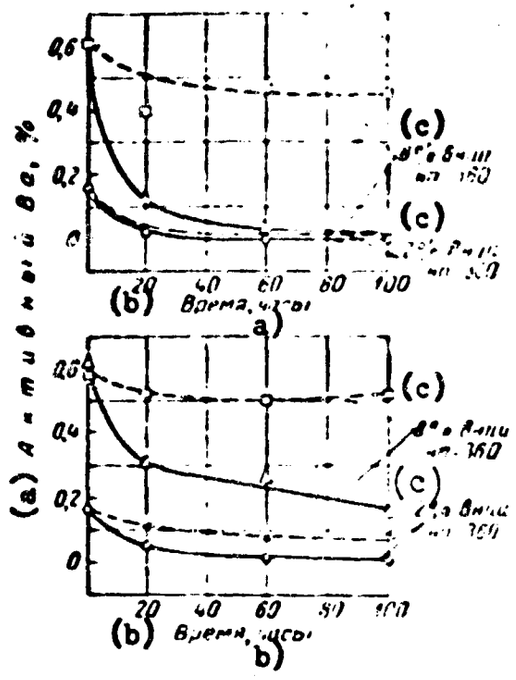


Fig. 2. Change of content of active neutralizing component of additive over time of work of oil in motor.
- - - method of filtration;
——— method of determining neutralizing ability. a) sulfur content in fuel 1.5%; b) sulfur content in fuel 0.2%.
Δ- fuel with sulfur content 1.5%;
○- fuel with sulfur content 1.0%;
× - fuel with sulfur content 0.6%;
□- fuel with sulfur content 0.2%.
KEY: (a) Active Ba, %; (b) Time, hours; (c) vnii np-360.

Of all the sulfur burned in the motor cylinder with fuel only an insignificant part of it reacts with the oil and corrodes details of cylinder piston group. A large part of products of sulfur combustion pass from cylinder with exhaust gases. Only that part of the products of sulfur combustion which together with the exhaust gas breaks through the piston rings or touches the oil film remaining on wall of cylinder above piston during movement downwards in expansion stroke interacts with the oil. This film will be formed by oil preliminarily subjected to the effect of breaking gases in zone of piston rings. The content of active additive in this part of oil is probably small in comparison with its content in the oil in the crankcase. Maximum content of barium in scale gathered in fourth and fifth grooves of piston indicates that the oil proceeding to the groove of first ring and in upper belt of cylinder loses part of additive while passing through the zone of the rings located below.

If the elementary composition of fuel and coefficient of air surplus, characteristic for working conditions of this motor are known, the sulfur content can be determined in the combustion products.

At a coefficient of air surplus larger than one the number of moles of combustion products is determined by the expression

$$M = \frac{g_C}{12} + \frac{g_H}{2} + \frac{g_S}{32} + (\alpha - 0{,}21) L_0. \qquad (1)$$

where g_C, g_H and g_S are weight shares of carbon, hydrogen and sulfur in the fuel; α is the coefficient of air surplus; L_0 is the theoretically necessary quantity of air in a mole/kg of fuel.

Knowing the sulfur content in fuel and volume of a mole of gas, one can determine the sulfur content ir a unit volume of gas:

$$S_v = \frac{S'}{24.4\,M},$$

where S_v is the sulfur content in 1 m^3 of gas; S' is the quantity of sulfur in 1 kg of fuel; M is the number of moles of combustion products; 24.4 is the volume of a mole of gas at normal technical conditions.

However, the crankcase gases will have a smaller content of sulfur than products of combustion, since gases break-through into the crankcase during the compression stroke when air is in the cylinder of motor. The share of gases, breaking through during the compression and expansion stroke can be determined either by measuring the break-through of gases during idling and under load, assuming that during idling the break-through of gases in both strokes is equal, or by analysis of crankcase gases for CO_2.

Having measured the break-through of gases in a unit of time and knowing the specific content of sulfur in them, one can determine weight quantity of sulfur passing into the crankcase during the time equal to the oil replacement period:

$$G_s = \beta b_e T S_v. \qquad (2)$$

where G_S is the quantity of sulfur in g; β is the coefficient, calculating the dilution of combustion products by air due to its break-through during the

compression stroke; b_0 is the break-through of gases in m^3/hour; T is the period of oil replacement in hours; S_y is the specific content of sulfur in combustion products in g/m^3.

If the magnitude of coefficient of air surplus is unknown, the sulfur content in the combustion products may be calculated by the average expenditure of fuel and coefficient of filling.

In order to clarify what part of the products of sulfur combustion, getting into the crankcase emerge from it in the atmosphere, we measured its content in the crankcase gases. For that, a definite volume of gas was passed through an absorber filled with a soda solution and the quantity of absorbed sulfur was determined by titrating with hydrochloric acid. It was established that in the presence of neutralizing additive in oil the gases outgoing from crankcase practically do not contain sulfur (Fig. 3). Consequently, it is necessary to calculate the additive concentration for the whole quantity of sulfur, determined by equation (2).

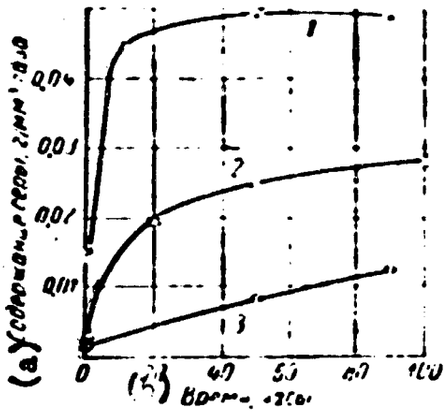


Fig. 3. Change of sulfur content in crankcase gases over time of work of oil in motor.
1) 1.14% vnii np-354; 2) 2.86% vnii np-350 and 1.11% vnii np-353; 3) 2.86% vnii np np-350.
KEY: (a) Content of sulfur, g/mm^3 of gas; (b) Time, hours.

During work on oil without neutralizing additive the sulfur content in crankcase gases in the first several hours of work attained the biggest value and remained almost constant. Sulfur content gradually attained the same value in crankcase gases during full wearing out of addition. However, this maximum content was 5-6 times lower than that determined by calculating the sulfur content in crankcase gases. From this it follows that in the absence of neutralizing additive in oil 80-85% of the products of sulfur combustion

passing through zone of piston rings into the crankcase remain in this zone, reacting with oil and corroding the metal surfaces of details. If there is a sufficient reserve of alkalinity in the oil, all the products of sulfur combustion are completely neutralized and crankcase gases practically do not contain them. As the additive concentration decreases the sulfur content in crankcase gases constantly increases. This index is so sensitive to change of active additive concentration that by it we can indirectly estimate this concentration.

From source material [4-6] the reaction of neutralizing the acid products of combustion by the additive occurs only in zone of piston rings, where at high temperature and significant pressure in the presence of increasing SO_3 dew point vapors are condensed and acid formed. In the motor crankcase this reaction does not occur.

To check this position we conducted special experiments, in which through a heated retort in which oil was supported in state of fog, for a prolonged time the products of combustion of sulfur-bearing fuels sucked directly from burner into the retort were passed. The gases passed through the retort were then passed through an absorber filled with a soda solution. The experiments were conducted with significant change of duration of experiment and quantity of burned sulfur. All the sulfur burned with fuel was revealed in absorber. Wearing out of additive, in oil did not occur.

These experiments once again proved that under conditions observed in a motor crankcase a reaction between neutralizing additive and acid products of combustion does not occur or occurs at a very low speed.

Having established the quantity of sulfur forming due to neutralization of acid one can determine the quantity of additive sufficient for full neutralization of these acids. During the period of oil replacement into the motor we introduced the quantity of metal entering in composition of additive determined by the

following expression:

$$G_M = C_0[V_k + g_M(T - t)]. \qquad (3)$$

where G_M is the quantity of metal in g; C_0 is the initial content in oil of metal of addition in g/g oil; V_k is the capacity of lubricant system of motor in g; g_M is the consumption per hour of oil (added) in g/hour; T is the period of oil replacement in hours; t is the time of work without adding fresh oil before its replacement in hours.

However, all the metal of neutralizing component of additive introduced with oil into motor can not always be expended on the neutralizing reaction. The presence of effect of suppressing the neutralizing ability of barium alkylfenolate during its sulfurization or mixing with zinc dialkyldithiophosphate fixed by laboratory methods was confirmed in our experiments on motor [7]. At an equal content of barium in oil pure barium alkylfenolate (vnii np-350) ensures more than double the lowering of wear of piston rings in comparison with additive vnii np-360; however, the latter noticeably yields in anti-scale properties.

The effect of suppressing the neutralizing action is considered as introducing a special coefficient, whose magnitude may be determined by testing the oil with investigated additive on installation RUM-1. A coefficient equal to one means that all the metal contained in the oil can be expended on reaction of neutralization, i.e., the effect of suppressing the neutralizing ability is lacking. In the presence of effect of suppression this coefficient will be less than one, and its magnitude is determined by ratio of time of effective neutralization of corrosional wear of the investigated additive to the time of effective neutralization of a compound having a coefficient equal to one (e.g., barium alkylfenolate). The magnitude of coefficient of suppression of neutralizing action is determined during equal content of metal of neutralizing component in oil (counted in moles per unit of weight of oil).

Proceeding from stoichiometrical relationship of reactants and introducing the coefficient of suppression of neutralizing action, it is possible on the basis of equations (2) and (3) to write the following equality:

$$\frac{C_s}{32} = \frac{C_M K_n}{m},$$

where 32 is the atomic weight of sulfur;

m is the atomic weight of metal;

K_n is the coefficient of suppression of neutralizing action.

This equality holds true for bivalent metals. If in composition of additive enters a metal with a different valence, it is necessary to introduce into the equality the corresponding coefficient K_{val}. Then in final form the calculating formula for determining initial content of metal of additive in oil after replacement take C_S and C_M from equations (2) and (3) in the following form:

$$C_0 = \frac{m\beta b_0 T S_0}{32 K_n K_{val} [V_k + \varepsilon_M (T-t)]}.$$

The determined by this formula initial content of metal of additive in oil is theoretically necessary for full neutralization of all products of combustion of sulfur which passes the zone of piston rings. The real content of metal of additive in oil may be more or less than theoretically necessary. In our experiments, as calculating by this formula shows, due to variation of sulfur content in fuel in wide limits and concentration of additive in oil, we could observe wear and scale formation at insufficient and excess content of additive in oil. The calculation is performed according to the following initial data:

L_0 = 0.495 moles/kg of fuel;

b_0 = 0.4 — 0.55 m^3/hour (limits of change during the tests are shown);

β = 0.7 (measured);

K_n = 0.5 (defined by time of neutralization);

T = 100 hours;

t = 10 hours (duration of stage of test);

V_k = 11500 g; ε_M = 150 g/hour.

Figure 4 gives the dependence of wear of first compression piston rings of D-38 motor as a function of the ratio of real content of metal of additive in oil $c_д$ to the theoretically necessary $c_т$. Up to a ratio equal to one (stoichiometrical), we observed a sharp lowering of wear. Further increase of additive concentration over that theoretically necessary leads only to a very small lowering of wear. This is explained by a certain incompleteness of reaction (part of additive is lost in active state due to waste of oil) and expenditure of additive for neutralizing other acids (besides sulfuric and sulfurous) forming during fuel combustion and oil oxidation. Since before replacement of oil there should remain a certain reserve of active additive in it and neutralization of oil acids forming in oil and getting into it is desirable, the additive concentration in oil should be somewhat higher than that theoretically necessary. However, in every case the additive concentration should be set taking into account economic considerations and requirements for exploitational reliability of motors.

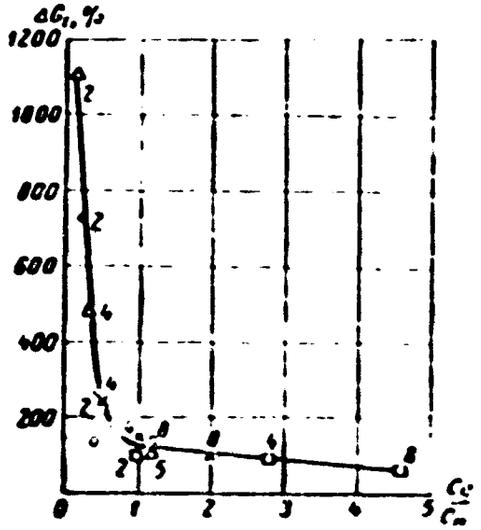


Fig. 4. Dependence of wear of first compression rings on ratio of real content of metal of additive in oil to that theoretically necessary.
DS-11 oil with addition vnii np-360.
Figures for points indicate additive content in oil in percents.
Δ - fuel with sulfur content 1.5%;
○ - fuel with sulfur content 1.0%;
▲ - fuel with sulfur content 0.6%;
□ - fuel with sulfur content 0.2%.

In the tentative calculation, when certain necessary magnitudes cannot be exactly determined experimentally, it is possible to use following average magnitudes typical for high speed transport diesel engines.

1. Magnitude of break-through of gases during good technical state of motor depending upon number of compression rings, operating conditions, geometry of cylinders etc. is from 0.2 to 1.0% of the motor's expenditure of air.

2. The value of the coefficient β depends on operating conditions of motor and a number of constructive factors. It oscillates from 0.5 to 0.8.

3. The expenditure of oil during normal technical state of motor is from 1.5 to 5 g/liter, s.-ch. The remaining magnitudes, necessary during calculation, except for the coefficient of suppression of neutralizing action are always known. This coefficient is needed only for calculating the concentrations of new additives. For calculating the necessary concentration of an earlier applied additive during change of sulfur content in utilized fuel the coefficient, calculating suppression, cannot be introduced, since magnitude of coefficient does not depend on additive concentration.

As a result of this work we revealed the character of the dependence of wear and scale formation in four-cycle diesel engine on concentration of additive vnii np-360 in oil. We have shown the exceptionally large exploitational value of correct selection of additive concentration when using high-sulfur fuels.

We developed a method of preliminary calculation of necessary concentrations of neutralizing additives by content of sulfur in applied fuel and a number of constructive and exploitational parameters of motor. The necessary concentrations of additive vnii np-360 during work of D-38 motor on fuels with different sulfur contents obtained by calculation closely coincide with results of experiments.

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METHOD OF DETERMINING REQUIREMENTS FOR QUALITY OF LUBRICATING OILS FOR TRACTOR MOTORS

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NATI*

The improvement of tractor motors towards increasing the liter capacity increases the thermal and mechanical stress on details. Because of this the requirement for quality of lubricating oils is substantially increased.

As numerous investigations have shown, the type of oil cannot be selected only by the physico-chemical indices. Recently motor methods of evaluating the quality of oils on special, chiefly one-cylinder motors have gained wide acceptance.

However, up to now in the Soviet Union we have not yet standardized the motor method of testing lubricating oils. Therefore, Soviet motor oils are classified not by results of their tests on motors, but depending upon the method of purification, additive, etc. This excessively increases and complicates oil nomenclature and hinders the consumers being correctly oriented in selecting the necessary sort of oil for motors of different types and working conditions.

One should classify crankcase oils mainly depending upon results of motor tests on special one-cylinder installations; in this the indices quality of oils are expediently estimated in total, in numerical values -- points.

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To evaluate the quality of diesel oils NATI has created a one-cylinder universal installation UIM-3-NATI based on tractor diesel engine D-54 and develop a method of accelerated tests of these oils [1].

Test results of a number of samples of Soviet and foreign oils (and additive) showed the high sensitivity of the installation UIM-3-NATI in determining their inclination to evoke sedimentation and coking of piston rings. The best samples of oils obtained an appraisal of 5-8 points, the worst, 38-39 points.

These tests enabled us to group oil in four groups by the degree of their fitness, estimated in a point system, for their use in variously rigorous working conditions of tractor motors.

Group	Oil
1-st	with appraisal up to 10 points
2-nd	with appraisal from 10 to 20 points
3-rd	with appraisal from 20 to 30 points
4-th	with appraisal from 30 to 40 points

Depending upon the regime indices of specific types of motors that group of oils should be selected which can ensure prolonged and reliable exploitation of the motor. However, selection of oils is complicated by absence of theoretically founded criteria for determining the requirements for quality of lubricating oils for motors of different construction.

According to the proposal of the American Petroleum Institute (API) the conditions of application of motor oils in motors of different types were divided into five groups: ML, MM, MS, DG and DS [2]. Thus, e.g., condition ML is considered typical for carburetor gasoline motors working in easy conditions, when the oil does not have to answer heightened requirements; condition DS is for diese engines working in moderate conditions, etc.

It is necessary to note that although this system originates from correct prerequisites, it cannot exactly orient machine builders and users in selecting and applying oils for different constructions and working conditions of motors due to the absence, as was already noted above, of basic criteria characterizing the work regime of motors.

To classify motors by their design features and working conditions it is necessary to develop a system which would enable us with the help of simple indices and quantitative measurements to establish rigidity of working conditions of oil in a motor.

Among the indices of the working properties of motor oils of important value are indices, characterizing the reliability of work of motors, which is determined by duration of their exploitation before mandatory repair (with disassembling of motor) caused by abundant formation of deposits on details of the cylinder-piston group and coking of piston rings.

Let us consider the basic factors causing contamination of motor by deposits and try to express the obtained dependences with the help of simple numerical coefficients.

Numerous investigations have shown that the rate of carbon deposition in diesel engines decisively depends on temperature of details of cylinder-piston group of motor, quality of fuel, composition and fullness of combustion of working mixture, servicing capacity of lubrication system, periodicity of oil replacement and technical state of the motor.

Let us consider the effect of each factor separately.

The temperature rate of the cylinder is mainly a function of the basic parameters of the motor — cylinder diameter and stroke and quantity of heat brought in per unit of time.

In the theory of internal-combustion engines we use the term, "thermal stress of cylinder," q, estimated by the quantity of heat Q in kilocalories passing through 1 m^2 of cylinder walls surface F into the liquid coolant during 1 hour, i.e.

$$q \quad \frac{Q}{F} \text{ kcal/m}^2 \text{ hr.}$$

To calculate the magnitude q professor I. A. Ponomarev [3] and professor V. A. Vanshеydt [4] offer different, but complicated mathematical relationships,

difficulty yielding exact calculation without special, very bulky experimental research. Furthermore, the formulas of these authors anticipate determining the thermal stress of cylinder during nominal operating conditions of motor, whereas the majority of motors depending upon executed work are exploited at partial loads.

The temperature regime of work of cylinder-piston group details can be determined by the quantity of combustible fuel per unit of working surface of cylinder, i.e.,

$$q = \frac{G_T}{Fi}.$$

where G_T is the average exploitational consumption per hour of fuel in kg/hr; $F = F_1 + F_2 + F_3 D^2 (1/2 + S/D)$ is the total working surface of bottom of piston, head of cylinder and mirror of cylinder in m^2; i is the number of cylinders.

Consequently,

$$q = \frac{G_T}{\pi D^2 \left(\frac{1}{2} + \frac{S}{D}\right) i} \text{ kg/hr m}^2.$$

This formula is simple, since it does not include complicated coefficients; it is sufficiently accurate for determining the temperature of regime of work of oil in motor cylinder and in the first approximation it enables us to determine the thermal stress of motors at any load.

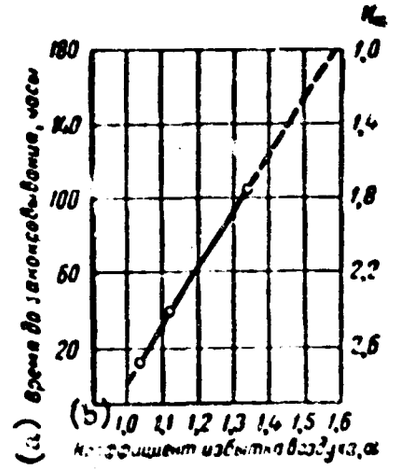


Fig. 1. Value of coefficient K_α depending upon coefficient of air surplus.
KEY: (a) Time before coking, hour; (b) Coefficient of air surplus, α.

Among the most important factors affecting the rate of oil aging depending on design features of diesel engines, are the magnitude of the coefficient of air surplus and the specific volume of oil in the motor crankcase.

Numerous observations have shown that as the coefficient of air surplus decreases, and, consequently, as combustion of diesel fuel is impaired,

the quantity of products of incomplete combustion increases and motor detail and nodes are more intense soiled by carbon deposits.

Figure 1 shows the dependence of duration of work of diesel engines before coking of piston rings on the coefficient of air surplus [5]. On the basis of this dependence the corresponding coefficients K_α, whose value of which can be used in determining the requirements for quality of oil for motors, are fixed.

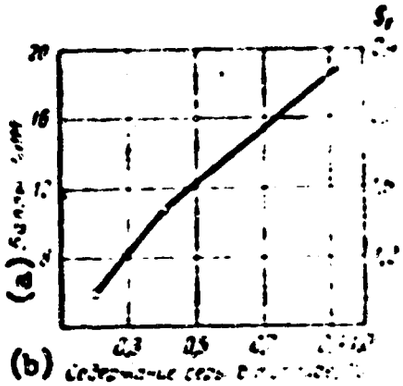
The rate of oil oxidation depends also on the specific servicing volume of oil N_e/G_M, hp/kg, i.e., the magnitude of motor power per kg of oil in the crankcase. Naturally, the less the quantity of circulated oil in system at the same motor power, the more frequently the same portion of oil will enter the zone of high temperatures and the more intensely it will be oxidized.

The amount of fuel, in particular its sulfur content, is one of the most important exploitational factors determining scale and lacquer deposition in a motor. The effect of sulfur contained in diesel fuel on deposits in motor and on wear of its details is sufficiently clearly revealed in works, conducted at NATI, NAMI, VNII NP, VIM [NAMI: Scientific Research Automotive and Automobile Institute; VNII NP: The All-Union Scientific Research Institute on Processing Petroleum and Production of Artificial Liquid Fuel; VIM: The All-Union Scientific Research Institute on Mechanizing Agriculture.]

Experiments carried out on installation UIM-3-NATI and agreeing with the data of field tests revealed degree of contamination of details of cylinder-piston group when using diesel fuel with different sulfur contents (Fig. 2).

On the basis of the obtained data we determined the corresponding index S_T, whose value is selected depending upon quality of fuel.

Up to now the basic data on selecting optimum periodicity of oil replacement for motors of different constructions are not yet sufficient.



(b)

Fig. 2. Value of coefficient S_T depending upon sulfur content in fuel.
KEY: (a) Points UIM; (b) Sulfur content in fuel, %.

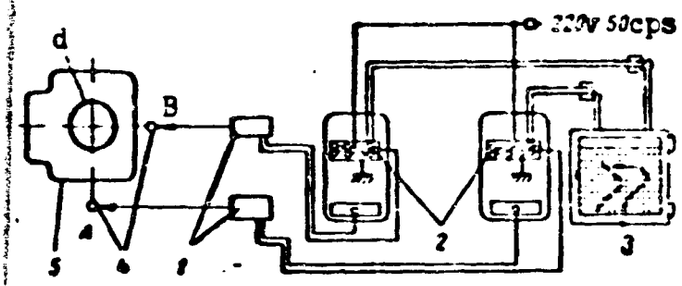


Fig. 3. Diagram of a complex of measuring instruments.
1) input blocks T4; 2) computing-indicating instruments T3; 3) electron potentiometer EPP-09; 4) geiger counters (A and B); 5) cylinder of motor UIM-3-NATI; 6) radioactive ring.

Wide field tests on DT-54 tractors conducted by VIM during 1956-1957 with different periodicity of oil replacement showed that as the working time of motors before oil replacement is increased the rate of deposit formation regularly increases.

To check the obtained VIM data, and also to exclude accidental factors frequently encountered in conditions of exploitation, on installation UIM-3-NATI we conducted experiments to elicit the inclination of oils to coke piston rings at different periods of oil replacement.

The start of ring coking was determined with the help of radioactive tracer fixed in the zone of the lock in the form of hidden "witness" from radioactive cobalt-60 [6]. Two geiger counters (Fig. 3), fixed on generators of motor cylinder, and connected separately to two radiometric instruments of type Tiss recorded the position of the ring lock during work of motor. For automatic recording the indicating instrument of each radiometer was connected in parallel to a self-recording electron potentiometer EPP-09. The start of ring coking is automatically recorded on tape by parallel vertical lines.

We tested fresh oil per VTU 363-51 with additive aznii-4 and the same oil, working in D-54 motors in exploitational conditions without replacement for different periods — from 120 to 1200 hours.

Results of tests (Fig. 4) showed that as the service period of oil increased the time the motor worked before piston ring coking was regularly reduced.

Consequently, the test results give a basis for establishing the corresponding coefficients П, which can be used in determining rigidity of working conditions of a motor depending upon periods of oil replacement.

The effect of the motor's technical state on the rate of oil aging can be examined with respect to wear of details of the cylinder-piston group. As wear of the friction pair increases the amount of gases entering the crankcase proportionally increases, in consequence of which the temperature of piston is increased and the process of thermal transformation of oil is accelerated. Furthermore, the products of incomplete combustion and sulfur oxides breaking through into the crankcase contaminate the piston, ring and motor in general on the way.

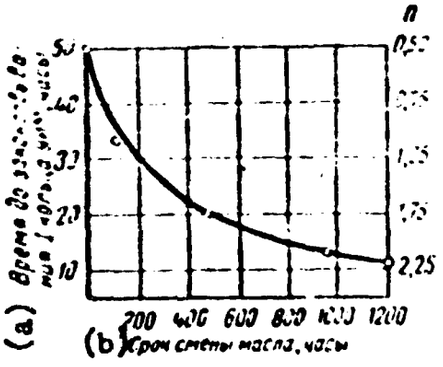


Fig. 4. Value of coefficient П depending upon period of oil replacement.
KEY: (a) Time before coking of the I ring on UIM, hours; (b) Period of oil replacement, hours.

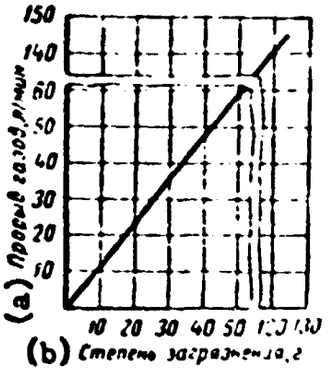


Fig. 5. The effect of the amount of gases entering the crankcase on degree of contamination of motor.
KEY: (a) Break-through of gases, liter/min; (b) Degree of contamination, g.

Investigations [7, 8] have shown that as the amount of gases breaking through into the crankcase increases, the contamination of motor by deposits proportionally increases (Fig. 5). Consequently, the index of technical state of motor T can serve as a ratio of the amount of gases breaking through into the

crankcase in a worn out motor V_r' to initial magnitude for a new motor $V_n(T = V_c' : V_1)$.

Having thus determined the degree of the effect of basic constructive and exploitational factors on the rate of oil aging, we can write the dependence with whose help we can in the first approximation establish the requirement for quality of lubricating oils for motor and tractor diesel engines of different types in specific conditions of their exploitation.

This dependence may be represented in the following form:

$$A = \frac{G_T}{Fi} S_T \Pi K_a T \frac{N_e}{G_M},$$

where A is the index of rigidity of working conditions of motor;

G_T is the average exploitational expenditure of fuel in kg/hour;

F is the total working surface of the piston bottom, cylinder and head and walls in m^2;

i is the number of cylinders;

S_T is the coefficient calculating the sulfur content in fuel;

Π is the coefficient calculating the periodicity of oil replacement;

K_a is the coefficient calculating the composition of the working mixture;

T is the coefficient calculating the degree of worn out nature of motor;

N_e is the effective capacity of motor in hp;

G_M is the servicing capacity of oil in crankcase in kilograms.

As an example we will give the specific working conditions of the most widespread tractor motors: KDM-46, D-54 and D-38, for a 2000-hour tests on Dp-11 oil.

By calculating we established (see table) that KDM-46 motors worked in heavier conditions when their A index was equal to 180; the A indices for D-54 and D-38 motors corresponding to 40 and 70 units were less.

Brand of motor	D, m	S, m	i	G_T, kg/hr	G_m, kg	N_e, hp	Sulfur Content in fuel %	Sulfur Content in fuel S_T	Period of oil replacement hrs	Period of oil replacement Π	Coefficient of air surplus α	Coefficient of air surplus K_α	A	Quantity of ring coking on the average for four tractors
KDM-46	0.145	0.205	4	14.25	27	68	1.0	2.3	120	1.1	1.6	1	180	5.5
D-54	0.125	0.152	4	9.4	23	46	1.0	2.3	120	1.1	>1.6	1	140	1.0
D-38	0.105	0.130	4	6.25	16	29	1.0	2.3	100	1.0	>1.6	1	110	0.25
D-54	0.125	0.152	4	11	23	54	1.0	2.3	240	1.37	>1.6	1	240	—
	0.125	0.152	4	8	23	40	0.2	1.0	120	1.1	>1.6	1	45	—

The test results confirmed the justice of the offered formula; on the average from four tractors of every brand the biggest number coked piston rings turned out to be in KDM-46 motors, then in D-54 and only one ring in one of four D-38 motors.

Consequently, there is a direct dependence between index A and results of prolonged field tests of oil on tractor diesel engines of different types.

While D-38 motors require D-11 oil with additive tsiatim-339, KDM-46 motors require oil of higher quality than Dp-11.

We must also consider that for motors of one and the same type depending upon conditions of exploitation (its load, quality of fuel, periodicity of oil replacement) will be required different in quality oil; thus, e.g., index A for a D-54 motor working in light conditions is equal to 45 (see table), when in heavy conditions this index increases 5 times.

Therefore the required sort of oil is expedient to select not only depending upon design features of motor, but also mainly on the real conditions of exploitation.

Considering that index A for tractor motors varies from 50 to 400 units, the authors suggest that the rigidity of working conditions, just as types of oils, be divided into the following four groups.

Group	A
1st	300-400
2nd	200-300
3rd	100-200
4th	100

For the first group of motors oil of the 1st type may be used, for the second group, the 2nd type, etc.

Conclusions

1. Reliable and prolonged work of tractor motors is ensured by rational selection of lubricating oils in reference to design features and conditions of exploitation of motors.

2. Crankcase oils are expediently classified mainly by the results of their tests on special motor installations; in this the basic exploitational properties of oils are desirably estimated in total — in points.

3. The conducted research fixed the dependence for approximate determination of requirements for quality of lubricating oils for motors of different types in different conditions of their exploitation.

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CHAPTER VI

TEST OF OILS WITH ADDITIVES ON MOTORS AND MECHANISMS AND EXPERIMENT IN THEIR USE

TESTS OF OILS FROM SULFUROUS CRUDES WITH DIFFERENT ADDITIVES

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VNII NP*

At present introduction has started of a new assortment of motor oils [1]. This assortment is based on classification of oils, anticipating division of them into groups not by type of carbuetion (for carburetor motors and diesel engines), but by strength of motor and rigidity of operating conditions.

Oils of various groups (series) for normal, heavy and specially heavy conditions of work of series I, II, III, etc., are prepared by means of the use of mainly distillate and residual oils of selective purification from eastern sulfur-bearing crudes and additives added to the oils in various combinations and concentrations.

Research of physical chemistry and performance properties of oils from eastern sulfur-bearing crudes [2-4] and, more than that, the five-year experiment of their use in internal-combustion engines and other mechanisms have revealed a number of positive properties of these oils, especially during use of them as a base. Correctly selected depth of purification and group chemical composition of oils in combination with new highly effective additives [5, 6, 7] can ensure production of motor oils of any class, including series II and III, i.e., for specially heavy conditions of motor operation.

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Practical resolution of this problem lagged behind mainly from an absence of production of effective additives.

In this work the authors have tried to generalize results of tests of a number of native additives, to compare them with certain foreign additives, and to reveal the possibility of obtaining oils of series I, II and III with the help of these additives.

For this, we investigated certain foreign additives of the firms "Anglomol" and "Monsanto" and also certain samples of foreign oils of premium type and series I, II and III.

1. Laboratory Characteristic of Imported and Native Oils with Additives

In Table 1 are given results of laboratory appraisal of imported and native oils with additives.

Imported low ash content oil ESSO-20W/30 "Premium" type is characterized by insufficiently good washing properties, low thermal stability, high sedimentation, and significant increase of viscosity during oxidation in DK-2 instrument.

Native oils of approximately this class with the same or larger ash content possess somewhat better washing properties, larger thermal stability, deposit formation and smaller increase of viscosity after oxidation.

Imported oils of series I with phosphorus-containing additives, Shell-X-100 and Castrol-30, possess best washing properties and thermal stability (especially Castrol), however, during oxidation in DK-2 instrument they turn out to be insufficiently stable. Characteristic peculiarity of Shell-X-100 is high initial acidity (1.6 milligram KOH), when all other oils have alkali reaction.

Native oils of this group with phosphorus-containing additive (vnii np-360, AP-22) possess approximately the same properties as imported oils.

High-ash imported oils of series II and III are characterized by a large reserve of alkalinity, good washing properties, and high thermal stability. These oils during oxidation in DK-2 instrument give small increase of viscosity in the absence of deposit.

Table 1. Laboratory Appraisal of Imported and Native Oils with Additives

Oil	Ash content, %	PZV, points	Oxidation in DK-2		Thermal stability, minutes
			Deposit, %	Δv_{100}, cs	
Premium (series 0)					
ESSO-20W/30	0.27	2.0	9	Thickens	32
AS-9.5 + tsiatim-339	0.27	1.5	8	22	45
AS-9.5 + tsiatim-339 + AFB	0.52	1.0	8	22	45
AS-9.5 + Vnii np-370	0.48	2.0	8	23	29
AS-9.5 + Vnii np-371	0.66	1.5	8	23	31
Series I					
Castrol-30	1.0	1.0	10	Thickens	36
Shell-X-100	0.6	1.0	10	Thickens	57
DC-11 + Vnii np-360	0.86	0.5	6	15	58
DC-11 + IP-22	0.46	0.5	6	—	60
DC-11 + PMS_{ya}	1.7	0	0	12	29
DC-11 + SB-3	0.8	0	12	25	27
DC-11 + NG-102	1.4	0	10	Thickens	28
Series II					
Rimula-30	2.2	0	0	7	43
SAE-30 (KNR)*	1.7	0	0	7	43
DC-11 + Vnii np-362	2.0	0	0	12	29
DC-11 + PMS_{ya} + Vnii np-353	1.8	0	Traces	12	29
Series III					
Mobilgrad-593	3.0	0	0	—	>80
DC-11 + Santolube-311	2.8	0	0	5	>80

*By label of the firm "Shell," 1956, the oil pertains to series III.

All native additives obtained on base of multiash sulfonates, have good washing properties at low thermal stability. Sulfonates of type PMS do not give deposit during oxidation in DK-2 instrument, however, as compared to foreign sulfonate additives they give more significant increase of viscosity.

We have, as yet, no such sulfonate additive, oil with which would sustain all laboratory tests with positive results during comparison with imported oils of series II and III.

Oil of series I can be obtained on a base of phosphorus-containing additives of type vnii np-360 (VNII NP, All Union Scientific Research Institute for Oil and Gas Refining and the Production of Synthetic Liquid Fuels) and IP-22.

2. Results of Motor Tests

Comparative tests of imported and native oils and additives were conducted in motors GAZ-51, D-35, and YaAZ-204, as the most wide-spread in the national economy, for which are required motor oils of good quality.

Tests of additives were conducted with oils from sulfur-bearing crudes during use of gasoline A-72 as fuel in motor GAZ-51 and diesel fuel with content of sulfur 1% in diesel engines D-35 and YaAZ-204. Testing lasted 100 and 140 hours.

In Table 2 are given results of comparative tests of native and foreign oils with additives in accordance with classification taken above. As standard oils and additives we tested imported samples: in motor GAZ-51 — ESSO-20W/30 and additive anglomol-612, by foreign classification belonging to premium oils; on diesel engines D-35 and YaAZ-204 — oil castrol-30 and 20, shell-X-100 and additive anglomol-917 as samples of oils of series I, and also oil shell-rimula-30 and addition santolube-311 — as samples of series II and III, respectively.

Native oils with additives tsiatim-339 (TSIATIM, Central Scientific Research Institute of Aviation Fuels and Oils), vnii np-370, vnii np-371 in concentration 3-3.5% (premium oil for carburetor motors) ensure practically the same condition of parts of the piston group of motor GAZ-51 as imported oil ESSO-20W/30. Additive anglomol-612 gives somewhat better results than the shown native additives.

Native oils with phosphorus-containing or sulfonate additives in concentrations 3.5-5.5%, conditionally belonging to oils of series I, ensured a state of the piston group of motor GAZ-51 approximately similar to the state which is ensured by an imported oil of this class — shell-X-100.

This group of oil with native additives in concentration 6-8% during test on diesel engines D-35 and YaAZ-204 showed certain advantage in antiwear properties and close results in scale-depositing and mobility of rings as compared to Castrol. On the whole this group of oils needs a certain improvement in washing properties, especially for application in diesel engine YaAZ-204. Improvement may be attained by means of compounding phosphorus-containing additives with formaldehyde and sulfonate additives.

Such recommendation may be referred to oils of first group (premium), which were compared with oils of series I (DS-11 + anglomol-917 and shell-X-100) on motors D-35 and YaAZ-204 accordingly (Table 2).

Oils of series II and II, as yet, we have not managed to obtain. This was shown by laboratory tests (Table 1) and, to a certain degree, was confirmed by motor tests (Table 2). Apparently, oil of series II and III can be obtained by high concentrations (10-12%) of mixtures of sulfonate additives with phosphorus-containing components, sulfonate with phenolate with obligatory addition of anti-oxidants. Tests of additive vnii np-362, presenting a mixture of sulfonate of calcium with phenolate of barium and dithiophosphate of zinc, on motor D-35, as compared to oil of series II (rimula-30), confirms such a possibility (Table 2).

One should consider that motor D-35 is not useful enough for classification and comparison of such oils.

Comparison of results of tests of oil with additive santolube-311 (oil of series III) with oil with native additives prepared on a base of multiash sulfonates showed insufficient motor qualities of the latter (Table 2). High-ash sulfonate additives possess good washing properties, but do not have necessary antioxidant

Table 2. Results of Tests of Motor Oils with Additives

Additive	Motor GAZ-51			[illegible]					Motor YaAZ-204				
	Mobility of rings %	Quantity of scale on piston with rings, %	Surface of piston covered by varnish, %	Wear of cases, %	Wear of rings, %	Mobility of rings %	Quantity of scale on piston with rings, %	Surface of piston covered by varnish, %	Wear o. cases, %	Wear of rings, %	Mobility of rings %	Quantity of scale on piston with rings, %	Surface of piston covered by varnish, %
	Shell-X-100 (series I)			Castrol-30 (series I)					Castrol-20 (series I)				
Standard	100	100	0	100	100	98	100	0	100	100	94	100	10
Vnii np-360	100	120	--	100	78	94	210	0	73	115	98	90	10
IP-22	—	—	—	100	88	94	230	0	—	—	—	—	—
SB-3	100	70	0	100	75	94	107	0	120	110	98	100	10
MG-102	100	115	0	100	70	94	100	0	80	--	95	105	5
IMS_{ya}	100	93	0	100	70	98	100	0	60	100	95	65	5
	ESSO-20W/30 (premium, series 0)			DS-11 + anglomol-917 (series I)					Shell-X-100 (series I)				
Standard	75	100	30	100	100	96	100	0	--	100	92	100	0
Tsiatim-339	85	120	55	145	123	82	123	55	--	114	90	120	30
Vnii np-371	90	125	55	—	57	85	100	15	--	42	100	83	30
Vnii np-370	100	94	68	—	—	—	—	—	--	—	--	—	—
Tsiatim-339-AFB	—	—	—	100	43	93	146	15	--	—	—	—	—
Anglomol-612	100	93	40	—	—	--	--	—	--	--	—	--	--
				Shell-rimula-30 (series II)					DS-[illegible] + santolube-311 (series III)				
Standard	—	—	—	100	100	100	100	0	--	100	99	100	0
Vnii np-362	—	—	—	100	100	100	83	0	--	70	95	114	0
IMS_{ya} + Vnii np-353	—	—	—	—	—	—	—	—	—	200	96	90	0

qualities protecting piston rings from scorching. It is necessary to conduct work on selection to additives of corresponding components, improving antiwear and antioxidant properties.

It is necessary also to note that during test of oils with high content of additives there were revealed heightened deposits of additive in combustion chambers of motors and on heads of pistons. Without removal of this phenomenon it is impossible to expect positive results.

The above considered preliminary appraisal and classification of oils with additives was needed in its check by means of prolonged bench tests and, if possible, operational tests.

Prolonged 600-hour bench tests of oils of series O and I on motor GAZ-51 confirmed the high motor qualities of these oils, especially series I with additives vnii np-360 and SB-3. During small wear and scale-deposit they ensured good mobility of rings (Table 3).

Table 3. Results of Prolonged Tests (Motor GAZ-51-600 Hours)

Index	Oil			
	Industrial 50	AS-9.5 + tsiatim-339	AS-6 + vnii np-360	AS-9.5 + SB-3
Wear of cylinders, mk.....	31	9	11	4
Wear of rings, g.....	0.74	0.35	0.28	0.30
Mobility of rings, points.....	26	0	0	0
Scale on piston and rings, g..	15.8	6.3	6.2	0.68
Varnish, points by PZV.....	4.5	2.5	2.2	0

It is possible to consider that existing mass automobile motors can be fully maintained by these oils.

Tests of oils in motors YaAZ-204 and 2D100 revealed the advantage of new additives with respect to washing properties (Tables 4 and 5). However, during tests on motor YaAZ-204 it was established that additives BFK, PMS and vnii np-360,

improving performance qualities of oils, do not ensure results corresponding to the results of motor operation on low-sulfur fuel and oil with additive tsiatim-339. This indicates that it is necessary to improve oil for this group of motors.

During use of oil with 8% additive vnii np-360 in motors 2D100 satisfactory results were obtained.

Operational tests on diesel locomotives TE-3 confirmed data of bench tests, and oil with this additive was taken into supply. Satisfactory results were obtained during test of this oil on new forced diesel locomotive motor 10D100.

In further tests it is possible to expect positive results from additive BFK under improved conditions of its washing properties. This additive showed not bad antiwear qualities, but caused significant varnish formation on pistons. Improvement of washing properties of additive BFK gives the possibility of recommending it for oils of series I.

Tests of additives of sulfonate type both in pure form and in mixture with antioxidant components, as yet, still have not given positive results, with the exception of tests in motor M-503. In motors 2D100 additive PMS_{ya} with addition of vnii np-354 ensured cleanness of parts, mobility of rings, but caused increase in wear of cases and rings due to heightened deposit of abrasive character on headpiston.

Unsatisfactory results of tests of all above-indicated additives were obtained in motor 40D, working both on sulfur-bearing and on low-sulfur fuels and oils DS-11 and DS-14.

In Tables 6 and 7 are given results of operational and prolonged bench tests of oils of series I in contemporary tractor diesel engines. As standards were used imported oil of series I Castrol-20 and oil applied at present with additive tsiatim-339 (series O by new classification).

Table 4. Operational Qualities of DS-8 Oil with Additives (Fuel S-1%, Motor YaAZ-204, Duration of Tests 550 Hours)

Index	Oil				
	Standard Industrial 50 + 3% tsiatim-339 (fuel S = 0.2%)	Series 0		Series I	
		3% tsiatim-339	5% BFK	5% vnii np-360	10% PMS_{ya}
Wear of cases, %.....	100	150	90	140	130
Wear of rings, %.....	100	200	200	150	155
Mobility of rings, %.....	100	92	100	94	75
Quantity of scale on piston with rings, %.....	100	165	155	120	115
Surface of piston, covered by varnish, %.....	60	85	50	35	10

Table 5. Operational Qualities of DS-11 Oil with Additives (Fuel S = 1%, Motor 2D100, Duration of Tests 600 Hours)

Index	Oil			
	Standard D-11 with aznii-7* (fuel S = 0.2%)	Series 0	Series I	Series II
		6% BFK	8% vnii np-360	8% PMS_{ya} + 2% vnii np-354
Wear of cases, %.....	100	107	90	115
Wear of rings, %.....	100	50	50	70
Quantity of burned rings, piece.....	0	3	1	2
Quantity of tight rings, piece.....	0	2	0	0
Quantity of scale on piston, %	100	145	140	90
Surface of piston, covered by varnish, %.....	100	70	50	30

*Additive is designated by number and name of institute, Azerbaydzhan Scientific Research Institute. Editors note.

These tests convincingly showed that oil with additive vnii np-360 and oil close to it in quality with additive II-22 fully ensure production of native oils of series I and that these oils satisfy requirements of both existing tractor motors and requirements of automobile motors. For long-term machines it is necessary

to create oil of series II and III, for which, however, necessary additives are still not selected.

Table 6. Operational Tests of DS-8 Oil with Additives (VIM* Data)
(Fuel S = 0.6%, Motor D-54)

Index	Oil		
	Standard DS-8 + 3% tsiatim-339 1% azniitsiatim-1 (series 0)	DS-8 + 6% vnii np-360 (series I)	Standard Castrol-20 (series I)
Wear of cases, mk	95	82	122
Wear of rings (increase of gap), mm	1.45	0.6	1.12
Mobility of rings	Part of rings tight	All rings move freely	
Quantity of deposit on pistons with rings, g	19.7	3.9	0.5

*Abbreviation for All-Union Scientific Research Institute of Rural Mechanization. Editors note.

Table 7. Operational Qualities of DS-11 Oil with Additives
(Fuel S = 1%, Duration of Tests of Motors: SMD -- 800 hours, KDM-46-- 2000 hours)

Index	Motor SMD		Motor KDM-46
	Standard 3% tsiatim-339 + 2% AFB (series 0)	6% vnii np-360 (series I)	6% vnii np-360 (series I)
Wear of cases, mk	30	17	5
Wear of rings (increase of gap), mm	0.20	0.20	0.30
Quantity of tight rings, piece	5	3	0
Varnish, points by PZV	4	2.5	0

Conclusions

1. Laboratory research and motor tests of oils with additives showed that available native additives ensure obtaining of motor oils of a new assortment corresponding to foreign oils of premium type and series I for heavy conditions of

work of motor. These oils are useful also for application in motors of old type.

For oils of series II and III, necessary for new, promising motors, development and application of corresponding additives are required.

2. Certain native additives useful for obtaining oils of series O and I, in quality, are near to quality of corresponding imported additives, however, it is necessary to conduct work on establishment of optimum combinations of these additives and [illegible]tion of their concentrations in oils.

It is necessary to continue work on improvement of additives for oils of series I, since for existing motors, such as diesel engines of the Kolomenskiy factory, SHGG, and other oils of good quality are required.

In particular, work is necessary on decreasing content or changing character of metalorganic compounds in additives for the purpose of decreasing deposit in combustion chambers, causing heightened wear, and also on improvement of anti-oxidant properties of additives.

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METHODS AND RESULTS OF TESTS OF OILS WITH ADDITIVES ON DIESEL ENGINES OF KOLOMENSKIY FACTORY

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Structural and Operational Peculiarities of Diesel Engines of the Kolomenskiy Factory

In accordance with contemporary requirements the main power units (diesel engines) of vessels and diesel locomotives have to possess great unit capacity (2000, 4000 hp and above), small specific gravity (6-3 kg/hp and lower), great motor period of service (15-20 thousand hours), great reliability in work (pistons without groove have to work 3000-4000 hour), high economy (expenditure of fuel should constitute 155—170 g/eff hp hr). Forcing index, corresponding to specific piston capacity (product of average effective pressure P_e by average speed of piston C_m, referred to number of cycles 0.75r, for such diesel engines reaches 60-65. Basic characteristics of diesel engines of the Kolomenskiy factory are presented in the table.

Motors, to which are presented such various, contradictory requirements (large aggregate capacity — small specific gravity, small specific gravity — great motor period of service), cannot be designed without use of materials possessing high durability, anti-wear, and anticorrosive properties.

Basic Characteristics of Diesel Engines of Kolomenskiy Factory

Brand	Capacity, N_e, hp	Number of turns in a minute n, rpm	Number of cylinders i	Cycles τ	Diameter of piston, mm	Stroke D, mm	Average effective pressure P_e, kg/cm^2	Average speed of piston C_m, m/sec	Forcing index $\frac{P_e C_m}{0.75}$, kg/dm^2	Specific gravity, kg/hp
9DM	1100	600	8	4	300	380	7.7	7.6	19.6	—
40D	2500	780	12	2	230	300	9.73	7.8	50.6	3.8
21D45	3000	750	16	2	230	300	8.9	7.5	44.5	4.3
2D100	2000	850	10	2	207	2X254	6.3	7.2	30.2	7.8
A	—	—	—	4	—	—	—	—	47.5	6
2A	—	—	—	4	—	—	—	—	47.5	5
B	—	—	—	2	—	—	—	—	62	2.5
B	—	—	—	4	—	—	—	—	62	2.5

N_e $\frac{N_e}{iF_n}$ $\frac{P_e C_m}{0.75}$ is specific piston capacity (forcing index).

High qualities must also be possessed by fuels and lubricants. However, up to now, the problem of maintaining diesel engines of the Kolomenskiy Factory by high-quality oils cannot be considered completely solved.

It is possible to consider it indisputable that the still insufficient reliability of work of our motors and their short periods of service are the result of unsatisfactory quality of fuels and lubricants, and also additives applied, which should improve performance properties of oils. Wide use of fuels and lubricants produced from crudes of eastern fields requires application of more effective additives than in the case of the use of oils and fuels from low-sulfur crudes.

Methods of Tests of Oils with Additives

Correct and fast appraisal of operational properties of oils with additives in reference to diesel engines of the Kolomenskiy factory, due to their specific peculiarities, may be obtained only when applying corresponding methods of tests.

As experience has shown, data obtained on other types of motors or on one-cylinder sections of motors, as a rule, are not reproduced by our diesel engines

This is explained, as already indicated, by the specific peculiarities of diesel engines, and also the small reserve of quality of existing fuels, oils an additives to them and the insufficient assortment of lubricating oils. The non-correspondence of assortment of lubricating oils to requirements of contemporary motors, along with other causes, may be explained by the absence of classificati of oils, considering intensity of process and operational condition of motors, and also absence of reliable methods of tests on one-cylinder sections of motors reflecting condition of work of oil in definite types of motors. Due to these causes selection is hampered of oils and additives satisfying operational requir ments of diesel engines.

In confirmation, it is possible to present an example with motor 2D-100. A is known, at present the problem, for that motor, of using fuel and oil from sulfur-bearing crudes can be considered, to some degree, solved. However, the attempt to extend the obtained data to a more forced motor (D45) showed that not one of the available experimental additives, as yet, could ensure satisfactory work of this motor on fuel with sulfur content up to 1%. Consequently, qualifie and correct appraisal of properties of tested oils with additives and the develo ment of corresponding requirements for them can be done only on the basis of res ts of tests conducted on concrete types of motors.

However, such a position, when every machine-building factory must conduct work on selection and tests of fuels and lubricants by individual methods, canno be considered correct. Obviously, it is extremely necessary to generalize all such works in some organizations (for instance, VNII NP), which have to be equi with the latest models of motors. There have to be developed methods of tests which correctly reflect operating condition of oil in motors, including high-for diesel engines, in the first place methods for short-term elimination tests.

This is all the more necessary, because the labor-consuming nature of work on selection of oils and additives complels us to conduct simultaneously development work with the motor so that by the moment of termination of the latter it is possible to determine requirement for quality of lubricating oil and optimum variant of oil to check in the process of factory and interdepartmental tests of motor.

At the Kolomenskiy factory tests of oils and additives are conducted both on one-cylinder sections and on full-size diesel engines.

Separate properties of oils and additives (antioxidant, washing, anti-scale), as a rule, are estimated on results of short-term 100-hour tests.

Conditions of tests are calculated so that a motor in 100 hours works on full load 60-65% of the time. During the 100 hours additions and replacements of oil are not made.

Before beginning of every test, the motor is washed by tested oil without additive (temperature of oil 60-70°). Depending upon arrangement of stand equipment and capacity of oil system, duration of washing varies from 3 to 6 hours where in some cases washing is conducted by pumping hot oil through the motor (motor turns during this), in other cases -- by means of operating in small turns and load.

Duration of washing usually is established by experimental means; for instance, during application of additives containing barium, by change in content of barium. It has been established that after 3-6 hours of washing, concentration of barium in washing oil is stabilized and constitutes nearly 10% of the concentration of barium in tested oil.

As appraisal indices are used quantity and character of scale and varnish deposit on motor parts, mobility of piston rings, and change in physical chemistry properties of oil.

Quantity of scale deposit is estimated by weight; degree of varnish deposit -- by area covered and with the help of a thickness gauge.

Final appraisal of quality of oil is conducted by means of prolonged (600-1000-hours) tests on full-size, developed motors. As comparison with actual operating conditions are applied more rigid operating conditions. Along with antioxidant and washing properties there are estimated also antiwear properties and duration of service period of oil, effectiveness of work of filtration units, and others.

Antiwear properties of oil are estimated by means of micrometric area of motor parts and also by accumulation of metallic particles in working oil, determined by spectral analysis.

Results of Tests of Oils with Additives

Diesel engines newly released and created at the Kolomenskiy factory, as experience shows, can reliably work only when using oils with additives possessing good antioxidant, washing, and other properties.

The Kolomenskiy factory tested, on motors of various types with different base oils, a large series of additives of both industrial production and development types.

All these tests can be broken down into three groups:

1) tests on oils and fuels from low-sulfur crudes;

2) tests on oils and fuels from sulfur-bearing crudes;

3) tests on low-sulfur fuel and oil from sulfur-bearing crudes.

The tests conducted showed that good additives (aznii-tsiatim-1, tsiatim-339) improve basically the washing properties of oils. With increase in forcing of diesel engines the effect of application of these additives decreases.

Thus, on diesel engine 40D during work even on low-sulfur fuel and oil, additive tsiatim-339 does not ensure reliable cleanness of piston group. During

prolonged work, on internal cooled surfaces of pistons is left a significant quantity of deposit (Fig. 1), which leads to overheating and burnt places on the bottoms of pistons.

During work of diesel engine D-42 (D-43) on low-sulfur fuel and oil, there occurs intense oxidation of oil, which is characterized by increase in viscosity of oil, contamination of oil filters (Fig. 2), condensers, and other parts, and insufficient cleanness of the piston group.

In 1959 on motor 40D was conducted a large series of experiments on fuel and oils prepared from sulfur-bearing crudes. A number of development types of additives were checked.

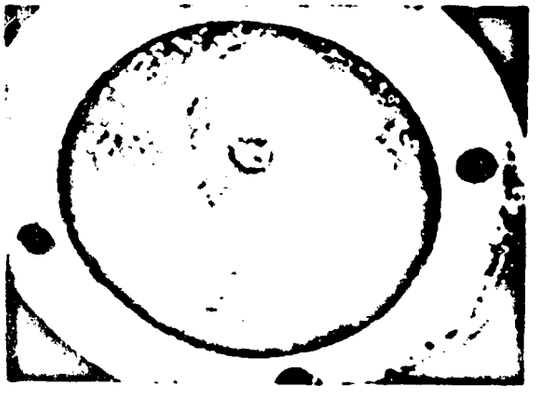


Fig. 1. Oil cavity of piston of 40D motor after 700 hours of work on MK-20 oil (30%) + D = 11 (70%) with 3% additive tsiatim-339 (weight of scale 8.35 g).

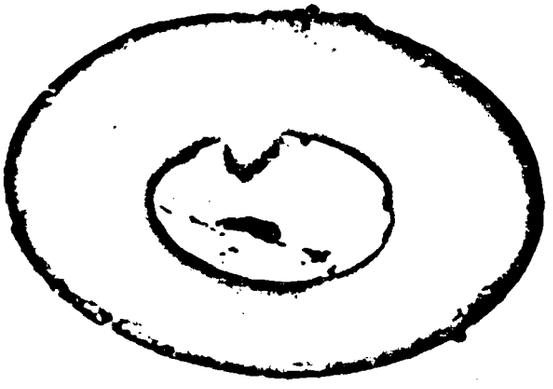


Fig. 2. Section of oil filter of 1D42 motor after 150 hours of work.

Tests were conducted for the purpose of determining possibility of using sulfur-bearing fuel (with sulfur content up to 1%) in high-forced diesel engines.

It is necessary to pay attention to one of the most characteristic indices by which was conducted appraisal of results of tests -- state of piston rings. Tests were conducted on motors 2D100, 40D, 42D0 and D-42.

In the process of tests were checked additives: tsiatim-339, vnii np-360, MNI-22K, vnii np-371, PMS_{ya}, MG-102Y, and also additive to fuel vnii np-111 and ammonia.

Not one of the checked additives failed to ensure efficiency of rings, equivalent to that which was observed in low-sulfur fuel and oils. It was established that scorching of piston rings is the result of increased scale and varnish deposit. During work on sulfur-bearing fuel and oil, thickness of scale on rings is increased for some additives 3 times and more. Burning of rings subsequently led to burrs of pistons and cylinder bushings, i.e., put the diesel engine out of commission.

During test of sulfur-bearing fuel and oil on diesel engine 40D there was established also a sharp reduction in service period of exhaust valves. Already after 100 hours of work on sulfur-bearing fuel on operating edges of valves appeared pits 1 mm in diameter, after 553 hours were revealed burnt places on several valves (Fig. 3). During work on low-sulfur fuel and oil similar phenomena were not observed.

By analyzing results of tests of sulfur-bearing fuel on a 40D motor and also results of numerous tests of such fuel on a 2D100 diesel engine-generator, the conclusion can be made that available additives to oils and fuels during use of sulfur-bearing fuels with sulfur content near 1% on high-forced diesel engines do not completely satisfy operational requirements.

Although on diesel engine-generator 2D100 this problem, as already was noted above, to some degree is solved with the use of additive vnii np-360, during an attempt to use sulfur-bearing fuel on a 40D motor with high forcing (forcing index is 30 for diesel engine 2D100, 50 for diesel engine 40D) it turned out that the most effective additives do not possess necessary properties allowing the use of sulfur-bearing fuel for this diesel engine.

On the basis of the given data it is expedient before setting up production of highly effective additives, to use high-forced diesel engines and newly created ones on diesel fuel with sulfur content of not more than 0.2%, diesel locomotive engines on diesel fuel with sulfur content not more than 0.6%, and high-forced

diesel locomotive engines on fuel with sulfur content not more than 0.2%.

On the basis of recommendations of scientific-technical conferences on questions of use of fuels and lubricants, the Kolomenskiy factory conducted a number of tests for the purpose of determining the possibility of using oils produced from sulfur-bearing crudes in high-forced diesel engines during their operation on low-sulfur fuels. Such tests were conducted on motors 40D and D-42.

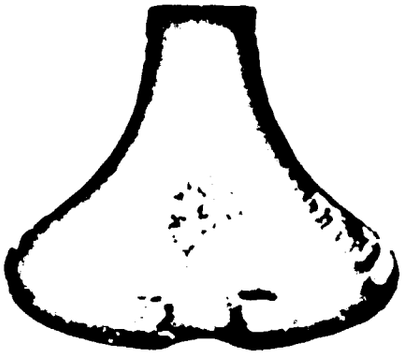


Fig. 3. Burnt place on exhaust valve of a 40D motor.

It was established that high-forced motors 40D and D-42 during work on low-sulfur fuel and during use of oils from sulfur-bearing crudes can work satisfactorily. However, it is necessary to note that quality of additives, even in this case, requires improvement.

Requirements for Oils and Additives

For further development of diesel construction, increase in period of service and operational reliability of diesel engines, wider and effective works are necessary in the region of creation and test of additives to oils. It is necessary to examine and to improve also the organization of these works.

For increase in effectiveness of tests conducted by factories and reduction of their quantity and duration, it is necessary to accelerate introduction into action of a new classification of oils and to ensure industrial manufacture of oils in accordance with this classification.

Oils with additives of series II and III* have to ensure the reliable work of contemporary high-forced diesel engines: first of all the reliable work of the

*See report of N. G. Puchkov, M. S. Borovaya, A. A. Deryabin and G. P. Belyanchikov "Tests of oils from sulfur-bearing oils with different additives." (Editors note).

piston group (without jamming of piston rings during small scale and varnish deposit, ensuring normal heat conduction of parts heated to 600° and continuously washed by oil having a temperature below 120°) and bearings from lead alloys.

Oils with additives must have high anticxidant properties allowing them to work 500 hours and more without replacement. Oils with additives must reliably work during water content in them up to 0.5%. Assortment of oils should be more varied in viscosity-temperature properties. Diesel oils must be produced with viscosity of 8, 10, 14, 16, 20 cs at 100°.

Oil with additives must be stable during storage; additives must not fall from oil during application of centrifugal filters.

Oils with additives have to possess good anti-wear properties ensuring reliable work of motor during assigned period of service (to 20,000 hours) and reliable work of piston group without groove of pistons for 4000 hours.

For the purpose of rational expenditure of oil and correct operation of motors it is necessary to establish sorting indices for working oils and their limiting numerical values.

TESTS OF ADDITIVES TO OIL ON A 2D100 MOTOR OF A DIESEL LOCOMOTIVE WHILE OPERATING ON SULFUR-BEARING FUEL

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Named after V. A. Malyshev

In the factory named after V. A. Malyshev, in the period of development and starting production of diesel engine 2D100 was faced the problem of ensuring work of motor on advanced oils and fuels. For solution of this problem, in the factory since 1956 have been conducted tests of the 2D100 motor on sulfur-bearing fuel and oil from sulfur-bearing crudes with different additives. Design features of diesel locomotive motors and the specific character of operating conditions (large mechanical and thermal strength, long duration of work on idling) essentially distinguish them from diesel engines of other types. These peculiarities demanded from the factory serious attention to selection and tests of high-quality additives to fuels and oils, possessing good performance properties, because behavior of fuels and oils in diesel locomotive motors had been weakly studied. During tests of fuels, oils and additives for the 2D100 motor, the factory was helped by the institutes VNII NP and INKhP* of the Academy of Sciences of the Azerbaydzhan SSR (formerly AzNII).

*Additive is designated by number and name of institute, Institute of Petrochemical Processes.

In accordance with the plan of work approved by the commission for tests of fuels, oils, and lubricants, the factory conducted tests of the following fuels, oils, and additives.

a) Fuel of All-Union Government Standard 305-42 with content of sulfur 1.2%;

Fuel of GOST 305-58 with content of sulfur 1%;

Fuel of GOST 305-58 with content of sulfur 0.33% (hydropurified).

b) Oil DS-11 from sulfur-bearing crudes, oil DSp-11 All-Union Government Standard 8581-57 (with 3% additive tsiatim-339).

c) Additive to oil DS-11: vnii np-360, aznii-8, IP-22, PSM_{ya}, BFK-1.

d) Additive to fuel — naphthenate of zinc.

In the factory one full-size motor 2D100 was taken for tests.

The motor was tested on a special stand which included a fuel and oil system, a fresh water system, and an electrical system identical to a diesel locomotive, and had instruments for carrying out all necessary measurements.

Diagram of systems of the testing stand ensured work of the motor under conditions close to those operational on diesel locomotives. This is very important since the variable operating conditions for the motor, characteristic for diesel locomotives, essentially affect results of tests.

For tests a special method was developed, ensuring full comparison of results of tests of oils with diverse variants of additives and the obtaining of corresponding criteria for appraising effectiveness of tested additives. Such criteria were: change in basic parameters of work of motor and physical chemistry indices of oil with additive (by analyses of samples taken from crankcase of motor); state and wear of basic working parts of the motor (cases of cylinders, piston rings, crankshafts, bearings, piston pins, bushings of upper heads of connecting rods, and others); quantity and quality of gum deposit and scale deposit on basic parts (in openings of cylinder cases, on pistons, in systems of filtration of oil and crankcase of motor, etc); state of fuel equipment; change of temperature of piston during tests (for appraisal of degree of scale deposit), and others.

As standard indices were taken results obtained during tests of the 2D100 motor on fuel of GOST 4749-49 and D-11 oil of GOST 5304-54 with 3% additive aznii-7.

For every type of tests was determined a single procedure.

After rolling and regulating tests the 2D100 motor was tested with respect to load characteristics at 850 rpm and operation on oil D-11 GOST 5304-54, fuel of GOST 4749-49, and fuel intended for tests.

Then the motor was sorted in the following order:

a) removed were lower and upper pistons, main bearings of upper and lower crankshaft (without groove of lower crankshaft);

b) purified from scale were exhaust and blow-through openings of cylinder cases, internal surfaces (cooled by oil) of pistons, grooves of compression rings and skirts, and the rotor of the centrifugal filter was washed;

c) micrometrically measured were cylinder cases of main and connecting rod necks of upper crankshaft, all main and connecting rod bearings, compression rings, piston pins, and bushings of upper heads of connecting rods;

d) weighed were piston compression rings, pistons, and the rotor of the centrifugal filter;

e) oil was poured from the motor and oil system of the stand;

f) crankcase and oil system were washed;

g) filters of coarse purification of oil were washed;

h) filters of fine purification of oil were washed and paper filtering packs were replaced. Before installation, new paper filtering packs were moistened in oil with a corresponding additive at a temperature of 50-60° for 10 hours. After runoff of oil, also for 10 hours, packs were weighed.

i) filters of fine purification of fuel were washed and filtering elements replaced. Before installation new filtering elements were moistened for 5 hours in fuel intended for tests. After runoff of fuel during 3 hours filtering elements were weighed;

j) oil system was filled by test oil with additive.

Oil system was filled after mixing oil with corresponding additive in a special 600 kg mixing tank equipped with individual steam preheating of oil and device for circulatory mixing.

Fullness of dissolution of additive in oil was checked by viscosity of oil taken from bottom and from top of mixer.

Preceeding for tests, fuel, oil, and additives were analyzed in the laboratory on all basic indices for conformity to their GOST or TU at each servicing of stand capacities.

Every development type of oil with additive was tested for 600 hours, separately repeating 10-hour stages in conditions close to working conditions of motor during operation of diesel locomotives. At the end of the 600-hour tests load characteristics at 850 rpm were determined.

During every stage of prolonged tests were measured basic parameters of work of motor and analyzed samples of oil taken from crankcase of motor.

During tests of additives aznii-8, vnii mp-360 and standard samples, each 20 hours of motor operation temperature of the bottom of one or two lower pistons was measured by a special thermomeasuring device for appraisal of increase of scale deposit on bottom of pistons. These measurements were produced in conditions of maximum capacity and with the load characteristic at 850 rpm.

Samples of oil for analysis were removed in the following order: first sample before first stage of tests; second — in the beginning of first stage (after 20 minutes of work); subsequent samples removed after every 30 hours of motor operation at maximum capacity at 850 rpm.

In samples of oil there were determined the following physical chemistry parameters: a) kinematic viscosity at 100°; b) acid number; c) ash content; d) content of water; e) mechanical impurities; f) temperature of flash; g) content of barium or calcium; h) content of mineral acids and alkalis.

During prolonged tests after every 30 hours of work, the motor was stopped and oil with additive was added to the necessary level. Quantity of added oil with additive was fixed in order to calculate total expenditure of oil and additive.

Expenditure of oil after every stage of prolonged 600-hour tests was defined as the sum of added oil with additive after subtracting weight of oil in removed samples.

After 600-hour tests motor again was sorted in the following order.

a) Inspected and visually determined were scale and varnish deposit on pistons, in grooves of piston rings, and cavity of oil cooling. Determined were the mobility of piston rings, gum deposit, and coke clogging of compression and oil rings with subsequent purification of scale for its weighing.

b) Inspected were exhaust and blow-through openings of cylinder cases for visual appraisal of scale deposit with subsequent purification of it for weighing.

c) Inspected and checked were burner and fuel pumps.

d) Micrometric measurement was made of cylinder cases, main and connecting rod necks of upper crankshaft, connecting rod necks of lower crankshaft, main and connecting rod bearings, compression rings, piston pins, and bushings.

e) Weighed were piston compression rings, packs of filters of fine purification of oil and fuel, and rotor of centrifugal filter.

All scale deposit was subjected to chemical analysis.

Results of Tests

A. Tests on Nonsulphur-Bearing Fuel of GOST 4749-49 and D-11 Oil of GOST 5304-54 with 3% Additive aznii-7 (Standard Tests)

Results of these tests were the criteria for appraisal of effectiveness of different additives to DS-11 oil (from sulfur-bearing crudes) during work of motor on sulfur-bearing fuel.

Tests showed the following.

1. Basic parameters of work of motor during 600-hour tests virtually were not changed.

2. Internal cooled surfaces of pistons had insignificant scale deposit — on the average 0.67 g for lower pistons and 1.95 g — for upper.

3. In grooves of piston rings scale constituted on the average 6.52 g for lower pistons and 6.7 g — for upper.

4. Babbit surfaces of main and connecting rod bearings were in good condition.

5. Absence of loss of mobility in all piston rings.

6. Small scale deposit on blow-through and exhaust openings of cylinder cases, ensuring stability of basic parameters of motor operation.

7. Moderate wear constituted:

a) for cylinder cases over belts in the region of internal dead points, mm.....0.054

b) for compressor rings near locks:
of lower pistons, mm.....0.273
of upper pistons, mm.....0.375

c) for bushings of upper heads of connecting rods, mm.....0.04

d) for piston pins, mm.....0.08

d) for main and connecting rod bearings, mm.....0.006

Consequently, standard tests showed reliable motor operation.

B. Tests of a Motor Working on Fuel with 1.2% Content of Sulfur

Tested were:

a) DS-11 oil with additive vnii np-360 in concentrations of 6% and 14%;

b) the same with additive aznii-8 in a concentration of 8%;

c) additive of zinc naphthenate to fuel in a concentration of 0.2% in combination with additive to oil vnii np-360.

It is necessary to note that during first tests analysis of oil on degree of wearability of additive showed that content of active barium sharply decreased and already after 200 hours of motor operation it was insignificant, as a consequence of which was observed active scale deposit. In connection with this was revealed the necessity of selecting corresponding concentration of additive to oil.

Tests of enumerated development types showed the following:

1. Comparative tests of a 2D100 motor with respect to load characteristic at 850 rpm on fuel with a 1.2% sulfur content, GOST 305-42, and on fuel of GOST 4749-49 (conducted in beginning of 600-hour tests) revealed that basic parameters of work of motor are changed insignificantly; therefore, for work on sulfur-bearing fuel readjustment of motor is not required.

2. Basic parameters of work of a 2D100 motor, toward the end of 600-hour tests, were changed. During tests of oils with 6% additive vnii np-360 and 8% additive aznii-8 the capacity of the motor decreased by 40-50 hp, and temperature of exhaust gases was increased by 20-40°. These changes were caused by impairment of operation as a result of the decrease in the cross section of exhaust and blow-through openings because of heightened scale deposit during work on fuel and oil from sulfur-bearing crudes.

3. Measuring the piston temperature showed that increase in temperature of bottom of piston during the time of tests is practically equal for all tested samples (including standard) and constitutes approximately 70°.

4. During inspection of dismantled motor after termination of tests, it was established that pistons had the best conditions of external surfaces and internal (cooled by oil) surfaces, as far as scale deposit was concerned, after tests of oil with 14% additive vnii np-360; the least quantity of scale deposit on blow-through openings existed also after tests of oil with 14% additive vnii np-360 (11.7 g), the biggest (31.4 g) -- after tests with 6% additive vnii np-360 (during standard tests 4.13 g).

Least quantity of scale deposit on exhaust openings was after test with 6% additive vnii np-360.

5. Check and inspection of fuel equipment showed satisfactory state of pumps and burners during all conducted tests.

6. Results of micromeasurement showed that least average wear of basic working parts of motor was obtained during tests of oil with 6% additive vnii np-360, and the biggest during tests of oil with 8% additive aznii-8. Thus, for instance:

a) wear of cases along fourth belt (in region of combustion chamber) after tests of oil with 6% additive vnii np-360 constitutes 0.085 mm, with 14% additive vnii np-360 — 0.154 mm, and with 8% additive aznii-8 — 0.246 mm. (During standard tests 0.054 mm);

b) least increase of gap in locks of compression rings was obtained after tests of oil with 6% additive vnii np-360, for upper rings — 0.845 mm, the biggest after tests of oil with additive aznii-8 — 2.55 mm, after tests with 14% additive vnii np-360 increase of gap constituted 1.39 mm (during standard tests 0.79 mm);

c) least wear of pins of lower pistons — after tests of oil with 6% additive vnii np-360 — 0.005 mm, with 14% additive — 0.03 mm (during standard tests 0.01 mm).

Wear of pins of upper pistons after tests of oil with 6% additive vnii np-360 — 0.015 mm, with 14% of this additive — 0.024 mm (during standard tests 0.01 mm);

d) wear of lower main bearings after tests of oil with 6% additive vnii np-360 — 0.007 mm, with 14% of this additive — 0.026 mm (during standard tests 0.006 mm).

Tests of additive to fuel naphthenate of zinc in concentration 0.2% (during simultaneous application of 8% additive vnii np-360 to oil) showed that impairment of basic parameters of work of motor — decrease of capacity approximately by 35 hp and increase of temperature of exhaust gases by 25° was caused by heightened scale deposit on blow-through and exhaust openings of cylinder cases and large quantity

of deposit on surface of nozzle tips of burners. Heads of pistons on the side of the combustion chamber were covered by nonuniform layer of deposit of dark-brown color. The same deposit in large quantity were on nozzle tips of burners.

These deposits were formed under the influence of additive of naphthenate of zinc in fuel;

e) increased 2-3 times the wear of cylinder cases and piston rings of motor as compared to standard tests.

Consequently, conducted tests of additives vnii np-360, aznii-8 and naphthenate of zinc during work of motor on fuel with content of sulfur 1.2% showed that these additives do not ensure completely satisfactory work of motor 2D100; the most effective in washing properties is additive vnii np-360 in a concentration of 14%, and in antiwear properties the same additive in a concentration of 6%.

C. Tests of a Motor Working on Fuel with Content of Sulfur 1.0% and Oil DS-11

During work of motor on this fuel were tested additives vnii np-360, IP-22, PMS_{ya} and BFK-1.

As a result of conducted tests of additive vnii np-360 both in the factory and in VNII NP, optimum concentration of it was found to be 8% in oil. During test of additive of this concentration on motor it was revealed that results of variation in parameters of work of motor, mobility of piston rings, wear of basic working parts -- cylinder cases, piston rings, bearings, and crankshafts, are equivalent to results obtained during standard tests.

Results of these tests, with respect to scale deposit on pistons, blow-through and exhaust openings and cleanness of other parts of the motor, are close to the results of tests of this additive in concentration of 14% during work on fuel with content of sulfur 1.2%.

Additive IP-22 was tested in a concentration of 13.75% at the Kolomenskiy factory and in a concentration of 8% at the factory named after V. A. Malyshev. During test were obtained unsatisfactory results, expressed by impairment in parameters of work of motor, increased wear of working parts and loss of mobility of part of the piston rings.

During test of additive PMS_{ya} in a concentration of 8% (with simultaneous application of additive vnii np-354 in a concentration of 2%) it was revealed that deposit of scale on skirts and internal cavities of pistons, blow-through openings, and on oil rings is absent. This testifies to high washing properties of this additive; basic parameters of work of motor during 600-hour tests were virtually not changed; wear of basic parts of motor (piston rings, crankshaft, bushings of upper heads of connecting rods and piston pins) is equivalent to wear during tests of oil with 8% additive vnii np-360.

Wear of cylinder cases by 20-40% exceeded wear of cases during mentioned tests and could be caused by presence of consolidated deposit on lateral surfaces of heads of pistons (higher than piston rings).

Tests of this additive with decrease of concentration to 5% (during simultaneous application of additive vnii np-354) showed sharp impairment of motor with respect to scale deposit, mobility of piston rings, wear, and other indices.

Test of additive BFK-1 in concentration of 6% showed that wear of cylinders, compression rings, piston pins, bushings of upper heads of connecting rods approximately corresponds to wear observed after test of 8% additive vnii np-360; however, cleanness of basic parts was somewhat worse, therefore, application of additive BFK-1 for motor 2D100 may be recognised as expedient under conditions of a certain improvement in its washing properties.

Consequently, conducted tests of additives IP-22, vnii np-360, PMS_{ya} and BFK-1 to oil DS-11 during work of motor on fuel with content of sulfur 1.0% showed that the most effective additive is vnii np-360 in a concentration of 8%.

Therefore, it is possible to allow 2D100 motors to operate on sulfur-bearing fuel with content of sulfur below 1.0% and DS-11 oil with 8% additive vnii np-360.

D. Tests of a Motor Working on Hydropurified Fuel with Content of Sulfur 0.33% and DSp-11 Oil, GOST 6581-57 (with 8% Additive vnii np-360)

In 1959 a decision was made concerning the temporary (period of one year) application on diesel engines 2D100 of diesel locomotive TE3 of DSp-11 oil. In connection with this, in the factory were conducted 600-hour tests showing a certain impairment of motor condition as compared to standard tests on fuel of GOST 4749-49 and D-11 oil with 3% additive aznii-7. The commission conducting observation of tests considered it possible temporarily to allow use of diesel locomotoves TE3 on above-indicated fuel and oil with additive tsiatim-339 during observance in operation of the following conditions: to remove pistons for purification from scale of external and internal surfaces after running 55-60 thousand km, to change oil, to purify exhaust openings of scale, to replace filters and to purify centrifugal filter after 15-20 thousand km of running; to watch carefully state of motor.

On the basis of these decisions a number of depots were directed to work 2D100 motors on DSp-11 oil, but after operating motors on this oil for 1.5-2 thousand hours of work of diesel locomotives, there began a mass breakdown of connecting rod bearings due to chipping off of the babbit filling.

Up to now the nature of the bearing breakdowns has not been completely studied; therefore, factories and institutes of the petroleum industry should be more energetically involved in the study and removal of this phenomenon. It seems to us that the attempt of VNII NP to negate the harmful influence of DSp-11 oil during prolonged work of motors is unfounded.

In prospect, DS-11 oil with 8% additive vnii np-360 will be introduced into use; therefore, the study of the phenomenon of bearing breakdowns should be a first

priority problem, the more so, because during operational check of DS-11 oil with 6% additive vnii np-360 there also were observed cases of bearing breakdown due to chipping off of babbit.

In connection with this and before the study of the cause of the established defect, it is necessary to stop the operation of diesel locomotives TE3 on DSp-11 oil.

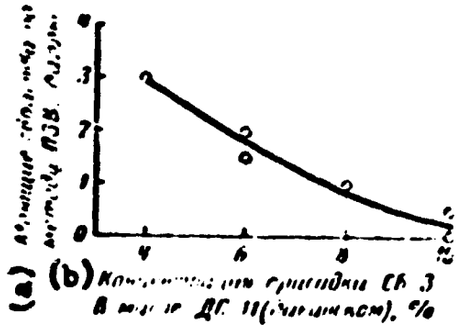
RESULTS OF MOTOR TESTS OF ADDITIVES DEVELOPED BY THE INSTITUTE OF PETROCHEMICAL PROCESSES OF THE ACADEMY OF SCIENCES OF THE AZERBAYDZHAN SSR (INKhP AN AZERB SSR) FOR THE IMPROVEMENT OF OPERATIONAL PROPERTIES OF FUELS AND OILS

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Additive SB-3

Additive of the sulfonate type have a number of essential advantages in comparison with alkylphenol additives released in the USSR on an industrial scale. They give oils high washing properties, are dissolved well in them, and are approximately 3-4 times cheaper. Sulfonate additives are wide spread in other countries where they are applied both in pure form and in combination with other compounds. Sulfonate additive SB-3 was subjected to a complex of motor tests.

On the figure and in Table 1 is shown change of washing properties of DS-11 oil, obtained from Baku oil, depending upon content in it of additive SB-3. As follows from their graph, this dependency has linear form.



Washing properties of additive SB-3 depending upon its concentration in oil.
KEY: (a) Washing properties according to method PZV, points; (b) Concentration of additive SB-3 in DS-11 oil (Baku), %.

Table 1. Results of Test of Oils with Additives According to Method PZV, and on UIM-3 Installation

Tested sample	Appraisal, points	
	PZV	UIM-3
DS-11 NKZ + 3% tsiatim-339.....	1.5	15
The same, Baku + 10% SB-3.....	0--0.5	9.8
The same, NKZ + 6% BFK-1.....	1.0	8.6
The same, Baku + 10% (0.8% SB-3 + 0.2% BFK-1).....	0.5--1.0	5.3
The same, Baku + 10% (0.8% SB-3 + 0.2% vnii np-354	0.5	11.4
The same, Baku + 6% vnii np-360.....	0.5	9.1

During 10% concentration of additive in oil, appraisal by PZV is equal to 0 points. In connection with this, in further tests was applied precisely such a concentration of additive. It is necessary to note that additive SB-3 dissolves very well in oils in any quantity. As a result of 100-hour tests of Baku oil AS-10 with additive SB-3 on motor GAZ-51 (Table 2) it was established that in the otor was kept 100% mobility of piston rings, and varnish on pistons was practically absent. Wear turned out to be the same magnitude as was attained during use of effective additive aznii-8. The same results were obtained during comparative tests of additives SB-3 and tsiatim-339 in lubricating oil AS-9.5 of the Novokuybyshevsk factory (NKZ).

Table 2. Results of Short-Term Tests of Oils with Additives SB-3 and BFK-1 on Motors GAZ-51 and YaAZ-204

Index of appraisal of results of test	AS-10 (Baku) + 3% azni1-8	AS-10 (Baku) + 10% SB-3	AS-9.5 NKZ + 3% tsiatim-339	AS-9.5 NKZ + 10% SB-3	DS-11 NKZ + 8% tsiatim-339	DS-11 (Baku) + 10% SB-3	DS-11 NKZ + 3% tsiatim-339	DS-11 (Baku) + 5% BFK-1
	GAZ-51, 100 hour, gasoline A-70				YaAZ-204, 140 hour, fuel S = 1%			
Wear of piston rings, in weight loss, milligrams:								
compression	10	7.8	16.5	15	188	153	167	125
oil	18	18	45	40	43.6	22	58	40
Wear of piston rings, by change of gap in lock, mk:								
compression	—	—	—	32	151	225	92	72
oil	—	—	—	90	134	84	189	78
Wear of connecting rod bearings, milligrams	69	80	68.6	75	40.4	12.6	90	61
Mobility of piston rings, %:								
free	21	24	24	24	12	13	11	16
tight	3	0	0	0	3	2	5	0
burned	0	0	0	0	1	1	0	0
Total scale, g	5.2	5.6	10.6	11	18.82	14.9	4	5
Including:								
from rings and grooves	2.6	None	2.66	0.1	8	9	—	—
from blow-through openings	—	—	—	—	10	2.8	—	—

On the basis of obtained data a decision was made about carrying out prolonged interdepartmental tests of additive SB-3 in bench conditions. Results of the latter are given in Table 3.

Obtained data very convincingly showed high washing properties of additive SB-3, which ensured 100% mobility of piston rings after 600-hours of work of GAZ-51 motor and insignificant quantity of deposit of carbonic substances on components of piston group (10 times less than during application of additive tsiatim-339). Regarding wear of basic motor parts, it turned out to be smaller than during application of additives tsiatim-339, vnii np-360, and PMS_{ya}.

On the basis of obtained results in 1959-1960 was prepared an experimental lot of additive for carrying out operational tests.

Table 3. Results of Prolonged Interdepartmental Tests of Oils with Additives SB-3 and BFK-1 on Motors GAZ-51 and YaAZ-204

Index of appraisal of results of tests	AS-9.5 NKZ + 3% tsiatim-339	AS-9.5 NKZ + 10% SB-3	DS-11 Baku + 3% tsiatim-339	DS-11 Baku + 5% BFK-1
	GAZ-51, 600 hours, gasoline A-70		YaAZ-204, 600 hours, fuel S-1%	
Average wear of cylinders, mk	9	4	34	22
Wear of piston rings, by loss of weight, milligrams:				
compression	85	52	260	325
oil	90	115		
Wear of rings, by increase of gap in lock, mm:				
compression	0.15	0.07	0.145	0.150
oil	0.21	0.16		
Wear of crankshaft, mk:				
connecting rod necks	5	2	0	0
main necks	6	2	0	0
Wear of bushing, milligrams				
connecting rod	—	—	56	121
main	—	—	240	145
Mobility of piston rings				
free	24	24	16	32
tight	0	0	14	0
burned	0	0	2	0
Total scale, g	6.3	0.68	—	—
Including:				
from rings and grooves	0.13	—	6.25	4.66
from blow-through openings	0	—	—	—

Influence of Additive SB-3 on Operational Properties of Diesel Oils

In 1959 in VNII NP there was conducted a series of brief tests of additives of the sulfonate type on tractor and automobile diesel engines. As a result of these tests, it was established that on the D-35 motor, when using additive SB-3, there is observed a noticeable lowering of wear of basic parts and a decrease in quantity of carbonic deposits as compared to a given application of DSp-11 oil

(with additive tsiatim-339). On two-cycle diesel engine YaAZ-204 also was noted an increase in mobility of rings, decrease in varnish formation while holding wear of parts at the same magnitude as during use of additive tsiatim-339. In connection with the fact that data obtained on motor D-35 cannot be widespread on other types of tractor diesel engines, we considered it expedient to estimate the effectiveness of additive SB-3 on one-cylinder motor UIM-3, representing a section of diesel engine DT-54. Oil was tested on this installation in rigid temperature conditions (t_{cool} = 135°). Results of test are expressed in points, considering quantity, quality, thickness and color of deposit on piston, and also mobility of piston rings. Results of test of different additives are shown in Table 1. It is necessary to consider in examining data of the table that oils without additives on this installation are estimated at 35-40 points.

From the table it follows that if oil DS-11 NKZ with 3% tsiatim-339 has an appraisal at 13.3 points, then with addition of additive SB-3 to the same base oil appraisal is improved to 9.8 points. Additive vnii np-360 corresponds to an appraisal at 9.1 points.

Results of brief tests of additive SB-3 on motor YaAZ-204, represented in Table 2, show that on oils DS-11 (Baku) with additive SB-3 deposit in blow-through openings of cylinder cases turned out to be 3 times less than on standard (DSp-11 NKZ). Magnitude of wear of basic parts of motor and quantity of scale turned out to be either somewhat smaller or identical with standard. Base oil DS-11, worked out basically from oils obtained in trade "shale oils," to which was added additive SB-3, by its motor properties yields oil from sulfur-bearing crudes DS-11 NKZ.

On the basis of obtained data recommendations were made about expediency of carrying out prolonged bench tests of sulfonate additive SB-3 on diesel engines of transport type. Subsequently, work on test of additive SB-3 was conducted in the direction of combining it with other additives to get oil of not only high washing properties, but also increased stability.

Additive BFK-1

In 1959 in INKhP Academy of Sciences Azerb. SSR was completed research work on additive BFK-1, barium salt of a product of condensation of alkylphenol by formaldehyde, the results of which are given in Tables 1-3.

Brief tests of additive BFK-1 on YaAZ-204 showed its high effectiveness in operating conditions of even such a thermally strong motor. Thus, wear turned out to be smaller than during work on oil DSp-11 NKZ; rings preserved 100% mobility, whereas during work on standard 30% of rings turned out to be tight.

During tests of this additive on installation UIM-3, complex appraisal of it according to the NATI method constituted 3.6 points, i.e., better than for SB-3. It is interesting to note that such a difference in appraisal is obtained due to higher mobility of rings. It is possible to assume that even an effective washing additive not as completely prevents formation of deposit in piston grooves. Additive BFK-1, as laboratory data showed, besides other functions, possesses also antioxidant properties. It is possible that this explains the preservation of full mobility of piston rings during work of motor YaAZ-204 on oils DS-11 NKZ with additive BFK-1. For a more detailed check of operational properties of additive BFK-1, there were conducted prolonged (600 hour) bench tests on diesel engine YaAZ-204. As a standard was tested oil DSp-11 NKZ.

From Table 3, in which are given results of test, it follows that at approximately equivalent antiwear properties of standard and tested oils there is obtained a significant difference in mobility of piston rings. During use of additive BFK-1 all rings, without exception, turned out to be free, when during work on oil DSp-11 NKZ only 50% of rings kept their full mobility. It is necessary to note that during tests of oils on motors YaAZ-204 under conditions regulated by method of interdepartmental tests, preservation of full mobility of piston rings during work on high-sulfur fuel is an extraordinarily rare phenomenon even for

140-hour tests using effective additives to oils. For instance, during work of a motor on oil with additive vnii np-360 there was observed a partial scorching of rings already after 140-hour test. This, once again, testifies to high operational properties of additive BFK-1.

Study of Joint Effect of Additives SB-3 and BFK-1 on Operational Properties of Diesel Oils

Peculiarities of the effect of additives SB-3 and BFK-1 (which included giving to oil high washing and antiwear properties when adding to it first additive and increasing resistivity of oil to formation of deposit in piston grooves when introducing into it the second additive) were used for obtaining oil possessing high washing properties and heightened stability. After preliminary experiments it was established that the optimum combination of additives SB-3 and BFK-1 is a mixture containing 80% of the first and 20% of the second. As can be seen from Table 1, with this are kept sufficiently high washing properties (0.5-1 point) and are obtained fully favorable results during tests of this mixture on installation UIM-3, estimated at only 5.3 points. Apparently, such a combination of additives turned out to be correct. Attempt to replace BFK-1 in the mixture by additive vnii np-354 was a complete failure (appraisal 11.4 points), in spite of high washing properties determined by PZV method.

In Table 1 for comparisons are given results of test of effective additive vnii np-360.

At present work on the study of effectiveness of the mixture of additives SB-3 and BFK-1 continues.

Conclusions

1. Additives SB-3 and BFK-1 are new (in native practice) additions, better, to a significantly larger degree, than tsiatim-339 released in industrial scale, the operational qualities of Baku and eastern oils.

2. 10% of additive SB-3, added to oil during prolonged time of work of motors, ensures full mobility of all piston rings and cleanness of parts of native tractor diesel engines and carburetor motors GAZ-51.

3. Additive BFK-1 ensures fully satisfactory work of strong, in thermal respect, diesel engine YaAZ-204 during prolonged time without complications connected with loss of mobility of piston rings and during acceptable magnitudes of wear for given type of motor.

4. Considering the low cost of additive SB-3 and the presence of stabilizing effect in additive BFK-1 it is expedient to apply them in a mixture in a 4:1 ratio for improvement of performance properties of diesel oils.

EXPERIMENT IN USING OIL ADDITIVES FROM SULFUR-BEARING CRUDES IN DIESEL LOCOMOTIVE DIESEL ENGINES

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In 1957-1959 in the TsNII MPS there were conducted operational tests of diesel locomotive engines D50 and 2D100 on oils prepared by the Novokuybyshevsk factory from sulfur-bearing crudes with different additives.

I. Tests on D50 Motors

In D50 motors were tested base oil DS-11 and the same oil with additive tsiatim-339 -- DSp-11, according to GOST 8581-57.

In the process of tests it was necessary to resolve the problem to investigate the possibility of replacing D-11 oil, GOST 5304-54, used in the D50 motor, by oil prepared from sulfur-bearing crudes.

On base oil DS-11 were tested eight diesel locomotives TE1 (eight D50 motors), the pistons of whose motors were supplied with two upper compression rings of trapezoidal cross section.

On oil DSp-11 were tested 10 two-section diesel locomotives TE2 (20 D50 motors), part of whose motors also had piston rings of trapezoidal cross section.

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Testing run of diesel locomotives corresponded to the interval between two large periodic repairs and constituted approximately nearly 100 thousand km.

For each series of diesel locomotives there were two locomotives working for comparison on control oil D-11.

Experimental and control diesel locomotives were supplied with one diesel fuel, GOST 305-42, with variable content of sulfur from 0.10 to 0.7%, where weighted average content of sulfur in fuel, after period of tests, constituted 0.44%.

During inspections of motors after tests on oil DS-11 there were revealed 2.5 times more broken piston rings of trapezoidal cross section as compared to number of broken rings during work of motor on oil D-11 and an almost 4 times larger quantity of burned remaining compression rings.

Addition in this oil of 3% additive tsiatim-339 (oil DSp-11, GOST 8581-57) prevented, to a significant degree,the breaking of piston rings of trapezoidal cross section in D50 motors of diesel locomotives of series TE2 and essentially decreased scorching of rings.

Scorching of piston rings in motors of diesel locomotives TE2, working on DSp-11 oil, decreased approximately twice as compared to work of motors on D-11 oil (even during application of rings of trapezoidal cross section) and by 25% during application of rings of right-angle cross section.

Therefore, in order to avoid scorching of first compression rings, it is necessary not only to select effective additives to oil, but also to select compression rings of corresponding configuration. Inspection of D50 motors working on base oil DS-11 revealed very large scale deposit in body of turbosuperchargers, leading sometimes even to wedging of hub of gas wheel. Analysis of scales from body of blower showed that the quantity of carbons and carboids during application of base oil constitutes 84%, when during work on DSp-11 oil it does not exceed 60%.

Thermal stability of oil, determined by K. K. Papok's method, was 20 minutes for base oil DS-11 and 26 minutes for DSp-11.

Tests showed also that stability of DS-11 oil without additives is insufficient for use of it in diesel locomotive engine D50.

Inserting results on scale deposit are obtained during operation of diesel engine D50 on mixtures of Baku and eastern oils. These mixtures were applied by chance. During opening of motors working on the mixtures, it was revealed that scale deposit and number of burned piston rings was 1.5-2 times larger than during work of motors on each of these oils separately.

Set up in the laboratory of the All-Union Scientific Research Institute, experiments on oxidation of oils D-11, DSp-11 and their mixtures on instrument DK-2 NAMI showed that viscosity and quantity of deposit not soluble in alkylate are higher for mixtures than for individual oils. Consequently, when mixing these two oils, their stability is sharply lowered.

Data determining the wear of first compression rings of a motor working on these oils showed that on DSp-11 oil wear decreases more than twice and on cylinder cases by 25%, as compared to work on D-11 oil. Insignificant decrease in wear of compression rings also is noted, and during work on base oil DS-11 it constitutes nearly 20% of wear on D-11 oil; as it concerns cylinder cases, their wear was increased almost by 40%. Possibly the cause is the massive breaking of first compression rings, observed during work of motor on this oil.

In connection with the unsatisfactory results obtained during test of base oil from sulfur-bearing crudes in motor D50, further works on test of this oil were ceased.

DSp-11 oil, GOST 8581-57, was recommended for application in diesel locomotive engines D50, with content of sulfur in fuel not more than 0.7%.

II. Tests on 2D100 Motors

In 1958-1959 in the All-Union Scientific Research Institute MPS there were conducted operational tests of oil from sulfur-bearing crudes with different additives for the selection of an additive ensuring normal work of a 2D100 motor on sulfur-bearing fuel containing up to 1.0% sulfur.

Comparative tests were conducted on oils with the following additives: with 5% tsiatim-339p (fully replaced by barium), with 3% azniI-7 and with 8% vniI np-360.

Additive tsiatim-339p was tested in oils with viscosity of 11.0 cs and 12.5 cs at 100°. DSp-11 oil (with additive tsiatim-339p) was tested with both sulfur-bearing and low-sulfur fuel.

On each variant of fuel and oil combination worked three diesel locomotives TE3 (6 2D100 motors). As a control (standard) combination of fuel and oil was taken low-sulfur fuel with content of sulfur from 0.2% and D-11 oil, GOST 5304-54. Running of the diesel locomotives corresponded to the interval between two large periodic repairs, taken for diesel locomotives of a given series (approximately 2500 motor hours).

Oils with additives during operational tests were evaluated with respect to washing properties (scale deposit on exhaust and blow-through openings and also in cooling channels of pistons); stability (scorching of piston rings and varnish formation on skirts of pistons) and antiwear properties (by wear of piston rings, cylinders and piston pins). Data on wear of necks of crankshaft, estimated only on upper shaft, did not enter into the final appraisal, since on all fuels and oils this wear turned out to be within limits of accuracy of measuring tool during testing run.

As operational tests showed, additive tsiatim-339p does not possess sufficient washing properties when using it with sulfur-bearing fuel and causes mass scorching of piston oil rings even during work with low-sulfur fuel. During application of additive tsiatim-339p to oil of heightened viscosity (12.5 cs) insufficient washing

properties of the oil show to a larger degree and the number of burned oil rings noticeably increases (from 45 to 65% on lower pistons). These data are given in Table 1.

Worst results with respect to washing properties and scorching of piston rings were obtained on DSp-11 oil with additive aznii-7, in which scorching of oil rings attained 77% on upper pistons and 62% on lower.

Positive results were obtained during work on oil with additive vnii np-360. Results of tests of this oil showed:

a) satisfactory state of exhaust openings, making it possible to preserve existing cleaning periods taken during application of D-11 oil with low-sulfur fuel;

b) somewhat increased quantity of deposit in blow-through openings (Fig. 1);

c) complete removal of phenomena of scorching of oil rings (see Table 1);

d) significant decrease in quantity of deposit in cooling channels of piston (Fig. 2).

During work on oil with this additive there was observed an increase in deposit on heads, especially for upper pistons for grooves under burners (Fig. 3).

Analysis of deposit showed that on 60% it consists of inorganic compounds, components, basically of elements of the additive.

Appraisal of antiwear qualities of oils with tested additives on parts of the cylinder-piston group is presented in Table 2.

From this table it is clear that the greatest wear of compression rings and cylinder cases on sulfur-bearing fuel is observed on DS-11 oil with additive tsiatim-339p, however, during work on oil of heightened viscosity (12.5 cs) with this addition wear sharply decreases and becomes equal to wear during work on standard fuel and oil. Obviously, there was a somewhat greater durability of oil film caused by heightened viscosity of base oil.

Table 1. Scorching of Oil Rings of Motors D50 and 2D100 During Work on Oils with Different Additives

Quantity of motors	Oil and fuel	Pistons	Quantity of burned rings	Burned rings, %
6	Oil D-11, fuel S = 0.2%	Upper Lower	10 25	5.5 13.9
6	Oil DSp-11 (tsiatim-339;), fuel S = 0.2%	Upper Lower	51 99	28.4 55
6	Oil DSp-11 (tsiatim-339p), fuel S = 1%	Upper Lower	66 82	36.7 45.5
4	Oil DSp-13 (tsiatim-339p), fuel S = 1%	Upper Lower	94 118	52.2 65.6
6	Oil DSp-11 (aznii-7), fuel S = 1%	Upper Lower	138 112	76.6 62.2
6	Oil DSp-11 (vnii np-360), fuel S = 1%	Upper Lower	— 2	— 1.1

Note. Percent of burned oil rings is determined by the ratio to their total inspected number of a corresponding number of pistons and group of fuel and oil.

Decrease of wear, observed by us during application of oil with a viscosity of 12.5 cs at 100°, makes it possible to assume that the 11.0 cs viscosity of oil, selected in the Malyshev factory for diesel engine 2D100, is not optimum.

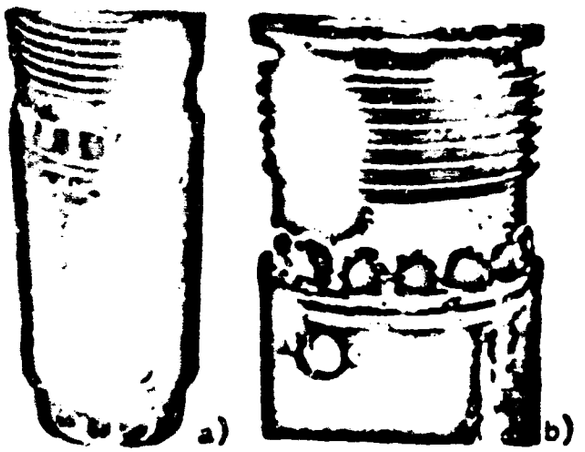


Fig. 1. State of blow-through openings.
a) after work on standard fuel and oil; b) after work on sulfur-bearing fuel and oil with additive vnii np-360.

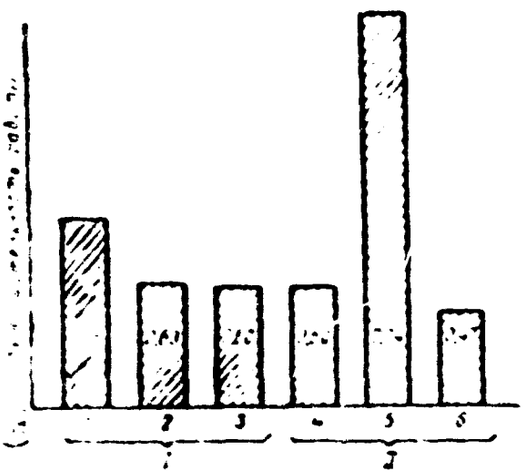


Fig. 2. Average quantity of scale (in grams) in cooling channels of upper pistons (depending upon duration of work of motor).
I) fuel S = 0.2%: 1) oil D-11; 2) oil DSp-11 (tsiatim-339p); 3) oil DSp-11 (tsiatim-339p); II) fuel, sulfur-bearing S = = 0.8 — 1.0%; 4) oil DSp-13 (tsiatim-339p); 5) oil DSp-11 (aznii-7); 6) oil DSp-11 (vnii np-360).
KEY: (a) Duration of work.

During application of DS-11 oil with additive tsiatim-339p on low-sulfur fuel there was obtained minimum wear, significantly smaller than on standard fuel and oil, however, because of much scorching of oil rings it is impossible to recommend this oil as a full value substitute for D-11 oil during work of 2D100 motor on low-sulfur fuel.

Great wear of compression rings was observed also during application of additive aznii-7.



Fig. 3. Upper piston of diesel engine 2D100 with deposit on head after work on oil with additive vnii np-360.

The least wear of compression rings and cylinders of cases during application of sulfur-bearing fuel with DS-11 oil is given by additive vnii np-360. Wear during work with this additive is of the same magnitude

as wear during application of low-sulfur fuel with D-11 oil. In connection with satisfactory results obtained during performance tests with respect to washing properties of the additive, the complete liquidation of the phenomenon of scorching of oil rings and such wear of motor parts as is observed during work on standard fuel and oil, DS-11 oil with 8% additive vnii np-360 is recommended for use in diesel engines 2D100 when running them on sulfur-bearing fuel with content of sulfur below 1.0%.

It is necessary to note that during application of fuels and oils from sulfur-bearing crudes, wear of oil rings, especially for upper pistons, increases as compared to wear observed during work on low-sulfur fuel and D-11 oil, although in absolute values it remains insignificantly small (0.5 g).

The greatest wear of oil rings for upper pistons was observed during application of additive vnii np-360. It is possible to assume that this phenomenon, as also the significant deposit of additive on upper pistons, may be somewhat decreased by introduction of intermediate cleaning of blow-through openings, which will lower the temperature in the region of the upper piston. However, it is necessary also to improve quality of additive and oil.

High wear of oil rings and upper pistons is not accidental, since it, just as washing property of the oil, is well connected with the operational expenditure of oil (Table 3). Expenditure of oil in 2D100 motor is determined by two factors: carbon monoxide and adding for partial refreshment.

Expenditure of oil on carbon monoxide increases with increase in scorching or wear of oil rings, which becomes sufficiently graphic during joint consideration of data in Table 1 (scorching of oil rings) and data in Table 3 (operational expenditures of oil). Increase of expenditure of oil on carbon monoxide during application of additive vnii np-360, in spite of absence of scorching of oil rings, is explained by their increased wear.

Table 2. Average Wear of Basic Parts of 2DISO Motor by Groups of Fuel and Oil, Referred to 10^8 ton km Gross Weight Work of Section TE-3

Worn out parts	Pistons	No. of rings	Oil D-11, fuel S = 0.2% (standard)	Variants of tests of oils and fuels									
				Oil DSp-11 (tsiatim-339p), fuel S = 2%		Oil DSp-11 (tsiatim-339p), fuel S = 0.8 to 1.0%		Oil DSp-11 (tsiatim-339p), fuel S = 0.8 to 1.0%		Oil DSp-11 (vnii np-360), fuel S = 0.8 to 1.0%		Oil DSp-11 (vnii np-360), fuel S = 0.8 to 1.0%	
			Wear, g	Wear, g	Wear in % with respect to standard sample	Wear, g	Wear in % with respect to standard sample	Wear, g	Wear in % with respect to standard sample	Wear, g	Wear in % with respect to standard sample	Wear, g	Wear in % with respect to standard sample
Compression rings	Upper	1	6.46	5.0	77	8.74	135	6.92	107	8.50	132	6.80	105
		2	2.10	1.18	56	2.62	125	1.73	83	2.54	121	1.94	92
Oil rings	Upper	5	0.07	—	—	0.20	286	0.16	229	0.24	344	0.40	571
Compression rings	Lower	1	10.9	7.46	68	13.34	123	8.31	76	11.14	102	9.65	89
		2	4.18	1.48	35	4.54	109	3.96	95	5.68	136	2.45	59
Oil rings	Lower	5	0.20	0.08	40	0.12	60	0.21	105	0.25	125	0.48	240
Wear of Cylinder Cases in a Plane Perpendicular to the Axis of the Crankshaft													
On III belt of measurements			0.048 mm	0.043 mm	90%	0.055 mm	114%	0.051 mm	105%	—	—	0.05 mm	103%

Table 3. Average Operational Expenditure of Oil per 1000 km of Running, by Groups of Fuel and Oil

Quantity of diesel locomotives	Fuel	Oil	Average expenditure of oil in kg per 1000 km of run	
			in partial refreshment	in carbon monoxide
2	Low-sulfur S = 0.2%	D-11, GOST 5304-54	20.6	23.5
3	Sulfur-bearing S = 0.8 to 1.0%	DSp-11 Tsiatim-339p	26.2	27.2
3	Sulfur-bearing S = 0.8 to 1.0%	DSp-13 Tsiatim-339p	15.1	41.5
3	Sulfur-bearing S = 0.8 to 1.0%	DSp-11 Aznii-7	4.06	69.6
3	Sulfur-bearing S = 0.8 to 1.0%	DSp-11 Vnii np-360	26.2	34.7

Expenditure of oil on its partial refreshment is caused by defects inherent in a given motor — dilution of oil by fuel on idling and small loads. This expenditure, to a significant degree, is determined by scale deposit on blow-through and exhaust openings.

Therefore, in those cases when scale formation on exhaust and blow-through openings was increased, blow-through of motor worsened, which caused increase of temperature and increase of pressure in cylinders promoting best evaporation of fuel.

During wide operational check of oil with additive vnii np-360, in the process of which maintenance measures are possible, (cleaning of blow-through openings and others), it will be possible to decrease loss of additive on heads of upper pistons and increased wear of oil rings.

Conclusions

1. On the basis of tests conducted, DS-11 oil with 8% additive vnii np-360 is recommended for application jointly with diesel fuel, containing up to 1.0% sulfur in diesel locomotive engines 2D100.

2. Additive tsiatim-339p and azniI-7 do not ensure normal work of diesel engines 2D100 on sulfur-bearing fuel with content of sulfur 0.8 to 1.0% basically due to increased scale deposit and scorching of oil rings. Wear, obtained during work on oils with these additives, also is higher than on standard fuel and oil.

3. It is necessary to intensify work on creation of effective oil additives which give the possibility of working with sulfur-bearing fuel without shortening the period of service of a diesel engine with sufficient duration of periods of oil service.

THE EFFECT OF MOTOR OIL ADDITIVES ON PITTING (POINT BREAKING-OFF) OF HYDRAULIC LIFTERS

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Contemporary motors are characterized by high thermal intensity: with increase of temperature of combustion in automobile motor from 1500 to 2000° temperature was increased in the lower part of the piston bottom and the oil washing it.

Although for motor ZIL-120 temperature of bottom of piston is 240°, for motor ZIL-111 it attains 300°.

In conditions of such rigid thermal conditions intensity of oxidation and polymerization of oil increases, which causes formation of carbon deposit in zone of piston rings and other motor parts.

Intensity of processes of oxidation and contamination of oil increases also because of increased breakthrough of gases to crankcase, since construction and effectiveness of system of crankcase ventilation in both domestic and foreign motors is practically unchanged.

Thus, according to Larsen, magnitude of breakthrough of gases for motors of models 1950 and 1957 has increased approximately 60%.

In Table 1 are given data on breakthrough of gases to crankcase of ZIL-110 and ZIL-111 motors, from which it is clear that breakthrough of gases in ZIL-111 motor is increased 70%.

Table .

Motor	Breakthrough of gases (l/min) to crankcase of motors at rpm			
	2000	2500	3000	3500
ZIL-110	53	27	27	27
ZIL-111	37	42	46	47

Increase in degree of compression of motors and, combined with this, increase in average effective pressure increased the load on bearings, which made it necessary to use new bearing materials, including plumbous babbit, possessing smaller resistivity to corrosional influence of oil as compared to babbit on a stannous basis. Lubricating oil in these conditions should possess necessary anticorrosive properties.

Increase of capacity and rpm of motors increased not only degree of their compression, but also increased loading coefficient. This in turn caused increase in tightening force of valve springs and sharp increase in inertial force of parts of valve mechanism. Thus, tightening force of the springs constitutes for motor ZIL-110 50 kg and for ZIL-111 85—90 kilograms. Such a force promotes sharp increase of contact stresses of cam-lifter pair, especially during work at little rpm.

High loads on parts of the gas-distributor mechanism, in particular on the cam-lifter pair, especially during work at little rpm, cause their intensive wear.

Besides the general uniform wear of these parts, there is observed catastrophic wear — breaking-off (pitting) — of lifters and cams.

Breaking-off is the most threatening form of wear since it rapidly puts the cam-lifter pair out of service.

This form of wear is met during test of additives tsiatim-339 and IP-22k on motors ZIL-110 after running them 25,000 km, and on new high-revolution V-form motors with hydraulic lifters.

Pitting is a regular phenomenon during work on a new motor, since with this the working conditions of the gas-distributor mechanism sharply worsen. Works on the investigation and removal of pitting have been conducted since 1959.

It is necessary to note that in the United States during transition to contemporary V-form motors with hydraulic lifters, pitting of lifters and cams became a mass phenomenon.

In 1953 - 1954 were started research works in this region.

Pitting on working surface of lifters appears due to fatigue of contact surface of lifter as a result of cyclically repeated load.

Cracks forming in contact surface are disposed approximately in parallel to surface of lifter in loaded state.

Wear and destruction of surface of lifter are insignificant until there sets in the phenomenon of metal fatigue, after which wear of lifter surface is increased, then pitting sets in (point breaking-off) and after that fast wear of cam.

If particles of metal are removed from surface layer as a result of wear before they attain fatigue limit, then pitting, obviously, will not occur.

Application of oils possessing good antiwear properties prevents appearance of pitting.

Consequently, in order to remove pitting, it is necessary, first, to select oil preventing excessive wear of details, secondly, to select corresponding material of lifter and cam shaft.

Thus, for instance, if cam shaft is of steel, and lifters from bleached cast iron, then this pair will be very sensitive to quality of oil.

If, however, cam shaft is of cast-iron heated to red-hot, and lifter is prepared from bleached cast iron, then such a pair will be less sensitive to quality of oil.

Third, it is necessary to facilitate construction of gas-distributor mechanism. This will lower inertial forces and, consequently, decrease contact stresses provoking pitting.

American researchers have established and our experiments confirmed that the phenomenon of lifter pitting during work on oils without additives is not observed, but wear increases.

Only during introduction into oil of washing, thickening and other additives, the phenomenon of lifter pitting very rapidly appears. Therefore, it is necessary to replace mechanism of gas distribution (lifters, cam shafts) in certain cases after running an automobile 1.5—3.0 thousand km.

Consequently, requirements for quality additives ensuring anticorrosive, antioxidant, washing, thickening and antiwear properties of oils, are increased.

I. Selection and Test of Oil Additives Removing Pitting of Lifters

For investigation of the influence of motor oil additives on pitting of hydraulic lifters 24- and 50-hour tests were conducted.

Conditions for the 24- and 50-hour tests were selected on the basis of works on the study of wear of the distributive mechanism, conducted in the United States, where these conditions were selected for lifters from bleached cast iron and steel forged cam shaft.

Tests in the United States were conducted at constant 3150 rpm and 30 hp.

Force of valve springs constituted 75 and 110 kilograms.

To increase rigidity of conditions of tests there was introduced lower and variable revolutions of motor (since low and average revolutions to a larger degree, promote formation of pitting and wear). Motor was equipped with valve springs with a force of 75 and 130 kilograms.

During selection of oil additives the following requirements for oil quality were taken: a) corrosion, according to method DK-2, not more than 5 g/m^2; b) washing properties, according to method PZV, within limits of 1-2 points.

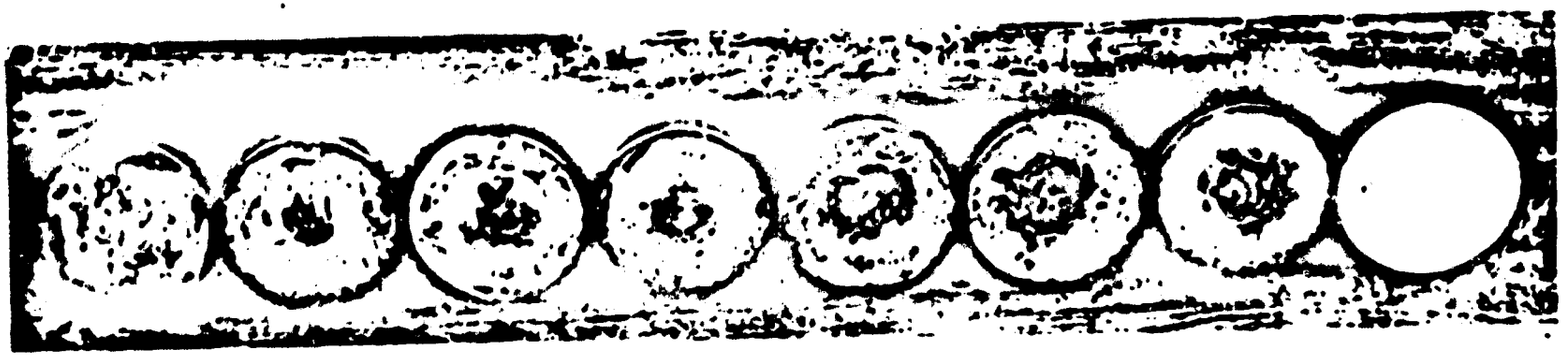


Fig. 1. Influence of SAE-30 oil of the firm "Esso" on pitting of lifters.
(Force of springs 115 — 130 kg).



Fig. 2. Influence of oil CR — 30 HD of the firm "Wakefield" on pitting of lifters.

The following oils and additives were tested.

1. Industrial 50 and DS-8 of the Novokuybyshevsk factory (without additives).

2. DS-8 oil with alkylphenol additives tsiatim-339 and vnii np-371.

3. DS-8 oil with additives containing alkylphenol and a phosphorous component: vnii np-360 and IP-22.

4. DS-8 oil with sulfonate additives PMS_{ya}.

5. DS-8 oil in mixture with dialkyldithiophosphates of barium and zinc (DP-1 and DP-5).

6. Mixtures of barium sulfonate (high-ash sulfonate AzNII) or an alkylphenol component (vnii np-350) with dialkyldithiophosphates 9, DP-10, DP-11) with DS-8 oil.

7. Mixture of low-ash barium sulfonate (washing component aznii-5) or SB-3 in combination with DP-11.

8. Imported oils of the firms "Shell," "Esso," "Wakefield" and "Raven."

During tests of enumerated oils and additives it was seen that additives DP-1, PMS_{ya}, vnii np-371 in mixtures with aznii-tsiatim-1, vnii np-360 (taken in different concentrations -- 3.5 and 7.0%) and oil of the firms "Shell" and "Esso," with respect to pitting of lifters, gave unsatisfactory results (Fig. 1). Good results, with respect to state of lifters, are obtained only on oils Castrol SAE-30 and CR-30 HD of the firm "Wakefield" (Fig. 2).

Additive PMS_{ya}, presenting calcium sulfonate (content of calcium 2.5%), causes very deep pitting of lifters (to 62% of lifters).

It is interesting to note that additive vnii np-360, containing in concentration 7% dithiophosphate of zinc, did not give positive results on removal of pitting, although content of barium, zinc, and phosphorus in oil was the same as in oil SAE-30 Castrol.

This indicates that organic components entering into the composition of additives are different.

To determine direction of further research an experiment was conducted on improvement of antiwear properties of DS-8 oil containing 3.5% additive DF-1, by introducing 0.5% antiwear additive khloref-40 (ether trichloromethaphosphinic acid), developed at the Institute of Oil-Chemical Synthesis of the Academy of Sciences of the USSR.

After test of this sample of oil, pitting was revealed on one lifter out of 16 (6.6%); average and maximum wear of lifters constituted 0.018 and 0.030 mm; wear of cams was, respectively, 0.042 mm and 0.08 mm.

However, this sample of oil turned out to be extraordinarily corrosive; during the test on the DK-2 instrument its corrosiveness constituted 29.3 g/m^2 for 10 hours and 76.6 g/m^2 after 20 hours. Washing properties turned out to be also unsatisfactory — 4 to 4.5 points.

The obtained results of tests showed the expediency of introduction into oil of antiwear additives.

Further work was directed toward search for additives of the dithiophosphates of zinc type.

II. Selection and Tests of Additives Containing Dialkyldithiophosphate of Zinc

Properties of dialkyldithiophosphates of zinc and, in particular, influence of them on operational properties of oils depend on the magnitude and structure of the hydrocarbon radical.

Thus, for instance, additive DF-1, synthesized on a basis of high-molecular alcohols, besides antioxidant and anticorrosive properties, possesses high depressional properties — lowers temperature of thickening of oil from -15 to -36°. Additives prepared on a basis of low-molecular alcohols do not possess depressor properties.

As Larsen shows, during application of dialkyldithiophosphates of zinc as antiwear additives, their antiwear effect is increases with a decrease in

molecular weight of compound, i.e., with decrease in magnitude of radical.

Tests of additives of the dithiophosphate of zinc type began from a check of additive DF-5. DF-5 is a 50% solution in oil of a mixture of dialkyldithiophosphates of zinc, obtained on a basis of technical high-molecular alcohols C_{19} — C_{24}.

DF-5 was tested in mixture with different washing components, and also in mixture with DF-1, taken in different qualitative relationships.

As results of tests showed, additive DF-5 possesses unsatisfactory antiwear properties. Pitting of lifters constitutes 75 — 100%, during a 130 kilogram force of valve springs.

Subsequently tested were the following dialkyldithiophosphates of zinc, synthesized on different alcohols: DF-8 on a basis of secondary n-octyl alcohol; DF-9 on a basis of primary isooctyl alcohol; DF-10 in a mixture of isobutyl and secondary octyl alcohols, taken in equimolecular ratio; DF-11 in a mixture of isobutyl and primary octyl alcohols, taken in equimolecular ratio.

All DF additives were solution of an active component (dialkyldithiophophaste of zinc) in light oil (spindle AU) in 1:1 ratio.

As washing components, as in the first stage of tests, were used: high-ash sulfonate AzNII (1%) and component vnii np-350 (1.5%).

Quantity of washing component was reduced 2 times in connection with the fact that washing properties of these compositions with additives DF-9 and DF-11 were satisfactory (1 —1.5 point).

An exception is DF-10, which, during test on PZV, caused great varnish formation — 5 points.

Concentration of washing component was lowered also due to the fact that high-ash sulfonate has bad solubility in oil.

As a result of 24-hour tests it was established that additives DF-9, DF-10, and DF-11 give satisfactory results with respect to protection of lifters from pitting.

Additive DP-2 caused a sharp increase in pitting of lifters (88%).

However during more prolonged tests (to 50 hours) additive DP-9 also gave an unsatisfactory result (pitting of lifters constituted 37%).

Additive DP-10, during 30-hour tests, gave best results with respect to pitting, however it sharply worsened (to 5 points) washing properties on PZV scale.

Additive DP-11 after 50 hours of tests gave good results both with respect to pitting and washing properties (Fig. 3).

Consequently, in all tests best results are obtained in a triple mixture of additives with DP-11 However, to recommend such a mixture for manufacture of an industrial batch of additive, at present, is not possible, until solubility of high-ash sulfonate has improved.

In connection with this, for further tests, was taken a low-ash sulfonate of AzNII, which has somewhat better solubility and at present is produced on an industrial scale (since there is a washing component of additive azmii-5), and also sulfonate SB-3.

The tested experimental types consisted of 3% low-ash sulfonate AzNII, 2% DP-11 and 4% SB-3 with 2% DP-11.

Test of these samples after 50 hours gave satisfactory results with respect to pitting of lifters and good results with respect to washing properties (0.5 to 1 point).

It is necessary to note that development types of oils prepared with low-ash sulfonate AzNII and with SB-3 in a mixture with 2% DP-11, with respect to state of surface and wear of lifters, are on a level with imported oils Castrol SAE-30 HD and CB-30 of the firm "Wakefield" (see Figs. 2 and 4).

Samples of oils possess good anticorrosive and washing properties.

Prolonged 600-hour tests of DS-8 oil (with 3% low-ash sulfonate and 2% DP-11) and SB-3 (with DP-11) on motor ZIL-375 gave good antiwear and other operational properties of oils.

Basic results of above-mentioned tests are represented in Table 2.

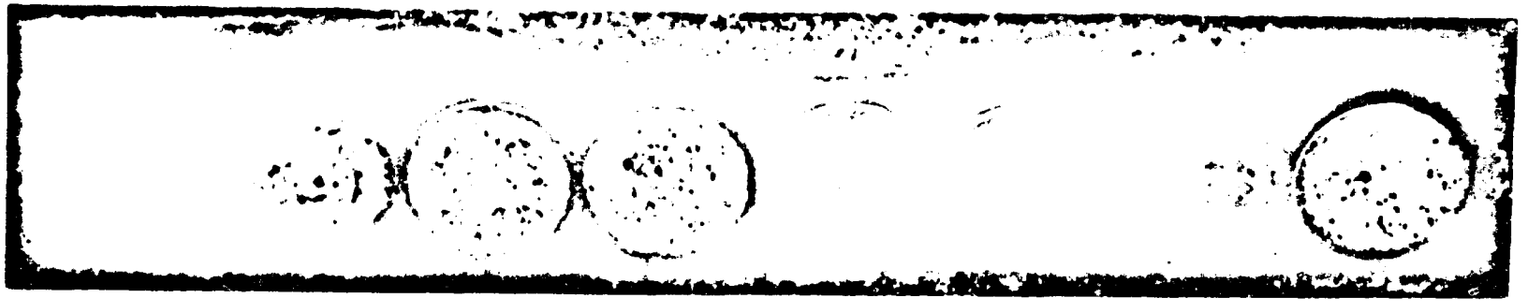


Fig. 3. Influence of DS-8 oil with additive DF-11 on pitting of lifters.

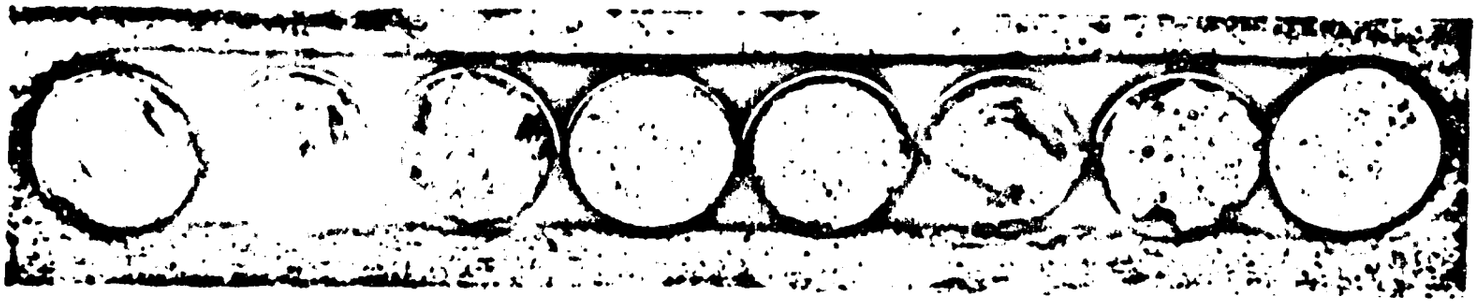


Fig. 4. Influence of DS-8 oil with 3% low-ash sulfonate AzNII and 2% DF-11 on pitting lifters.

Table 2.

Oil	Lifters				Cams		Duration of tests, hours	Note
	With pitting, %	With burr, %	Wear, mm		Wear, mm			
			Average	Maximum	Average	Maximum		
DS-8 without additive.....	12	37	0.032	0.06	0.039	0.097	10	In the table are given data of tests which were conducted on motor ZIL-111 with valve springs force 130 kg
DS-8 with additive:								
3.5% vnii np-360.....	62	—	0.045	0.11	0.044	0.07	from 9 to 26	
7.0% vnii np-360.....	12	81	0.05	0.09	0.028	0.067	24	
3.5% vnii np-371 + 1.2% aznii-tsiatim.....	37	37	0.066	0.09	—	—	24	
3.5% DF-1.....	56	50	0.045	0.060	0.09	0.11	9	
3.5% DF-1 + 0.5% khloref-40.....	6.25	0	0.018	0.030	0.042	0.080	24	
1% DF-1 + 2.5% DF-5.....	100	100	0.023	0.045	0.095	0.145	14	
10% PMS_{ya}.....	62	75	0.040	0.06	0.091	0.144	24	PMS_{ya} — calcium sulfonate VNII NP
2% VZS + 3% vnii np-350 + + 2.5% DF-5.....	50	0	0.032	0.035	—	—	24	VZS—high-ash sulfonate AZNII Vnii np-350—washing component of additive vnii np-360
4.5% PMS_{ya} + 3% vnii np-350 + 2% DF-5.....	75	37	0.045	0.05	0.070	0.117	12	
3% NZS + 2% DF-11.....	6.25	0	0.016	0.025	—	—	50	NZS—low-ash sulfonate AzNII
4% SB-3 + 2% DF-11.....	6.25	0	0.007	0.022	0.196	0.335	50	SB-3—barium sulfonate AzNII
SAE-30 HD Castrol.....	12.5	0	0.014	0.020	0.180	0.298	50	
SAE-30 HD Firm "Shell".....	43.8	87.5	0.020	0.029	0.043	0.100	24	
SAE-30 HD Firm "Esso".....	62.5	75	—	—	—	—	24	
CR-30 Firm "Wakefield".....	0	0	0.016	0.025	0.164	0.335	50	

Conclusions

1. Pitting of lifters from bleached cast iron, working in a pair with a steel cam shaft, to a larger degree depends on quality of applied oil. This is explained by the fact that washing components of additives promote appearance of corrosional fatigue of metal.

2. The most effective additive, preventing pitting of lifters, is DF-11 -- dithiophosphate of zinc, prepared on a basis of primary octyl alcohol (2-ethylhexyl) in a mixture with isobutyl alcohol (Institute of Oil-Chemical Synthesis of the Academy of Sciences of the USSR). This additive is introduced into oil in a quantity of 2%, calculating the content of zinc and phosphorus in oil at nearly 0.1%.

3. For obtaining satisfactory washing properties in oil it is necessary to introduce sulfonate or alkylphenol additives.

Satisfactory qualities of oil all over the complex of requirements (washing, antiwear, and anticorrosive properties) are obtained with the following compositions of additives: a) 3% low-ash sulfonate AzNII with 2% DF-11; b) 3% sulfonate additive SB-3 with 2% DF-11.

4. The selected method of 24- and 50-hour tests on a motor makes it possible to choose best samples of additives, preventing the pitting of lifters and to obtain comparative appraisal of quality of metal applied for manufacture of lifters.

METHOD AND RESULTS OF STAND TESTS OF TRANSMISSION OILS WITH DIFFERENT ADDITIVES

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For the satisfactory work of transmissions of automobiles lubricating oils have to respond to the following basic requirements:

1) possess good antiwear and antiburr properties, ensuring reliable and long-lasting work of gears and bearings;

2) have good viscosity-temperature properties corresponding to operating conditions of the transmission: sufficiently low temperature of thickening which corresponds to the climatic conditions of the region of operation; during starting and work to have viscosity ensuring maximum power losses;

3) stable during work and storage;

4) not cause corrosion of parts;

5) not cause foam formation during work in aggregates.

Mineral oils not containing special antiwear, antiburr and other additives do not satisfy these requirements.

Antiwear properties of oils with additives can be correctly estimated only when testing them in real aggregates of the transmission since existing methods of laboratory tests of oils on different machines of friction do not reproduce real operating conditions of oils with respect to loads, temperatures, and speeds of slip.

Table 1. Conditions of Bench Tests

No. of stage	Time of work from beginning of test, hours	Load on ring gear, kgm	Conformity to torque of motor, kgm	rpm of ring gear	Time of work on given conditions, hours	rpm of motor	Applied transmission
I			Rolling				
	1	300	—	45	1.0	—	—
II			Tests on wear				
	3	200	~30	180	2.0	~1200	IV
	5	300	~24	180	2.0	~2300	III
III			Rolling				
	5.5	500	—	25	0.5	—	—
IV			Tests on wear				
	7.5	400	~31	100	2.0	~1270	III
	9.5	500	~23	100	2.0	~2200	II
V			Rolling				
	10	600	—	15	0.5	—	—
VI			Tests on wear				
	12	600	~28	60	2.0	~1320	II
	13	600	—	120	1.0	—	—

Note. During test, temperature of oil in crankcase, with the help of water cooling, was maintained within limits of 80-85°.

For operational tests of oils are required prolonged runs of several automobiles in identical road conditions.

The method, developed at ZIL, of testing transmission oils in the main transmission of a truck with spirally-conical gears on a stand with power closed contour makes it possible to evaluate transmission oils with respect to antiwear, antiburr, anticorrosive, anti-foaming properties and stability for a relatively small period of time — 13 hours.

Oil was tested in conditfons anticipating speed and loads corresponding to operating conditions of the main transmission of an automobile at different speeds, when the transmission of all the torque of the motor is to one drive axle, where each stage of tests on wear was preceded by a stage of rolling.

Selected conditions of bench tests, given in Table 1, were developed and tested in 1953 and gave positive results during test of experimental transmission oils with additive EZ-5, subsequently standardized.

Each oil was tested on two-three pairs of new (without coppering) spirally-conical gears of the main transmission of an automobile. All gears are consecutively established in the same crankcase of the rear axle. Before installation of each pair of gears the crankcase of the axle is thoroughly washed.

Installation in crankcase of axle and adjustment of gears of main transmission was done in accordance with technical requirements on assembly and adjustment of drive axles of automobile.

After installation of gears in crankcase of gear was additionally washed with light industrial oil. Then into the crankcase was poured test oil on level and it was tested on selected conditions.

Oil was evaluated according to the following indices:

1) state of operating surfaces of teeth of gears after test;

2) wear of teeth of pinion and ring gears (Fig. 1), measured by special method developed at ZIL;

3) change of side play in engagement;

4) quantity of iron removed from friction surfaces after period of test;

5) change of physical chemistry properties of oils, presence of deposits and sediment;

6) presence of corrosion on parts.

By the above-indicated conditions and method, on a stand were tested the following samples of oils:

a) prepared on a base of transmission motor and tractor oil (nigrol cylinder oil) with additives: EZ-5 and LZ-6/9, and also transmission motor and tractor summer oil (nigrol cylinder oil);

b) prepared on a base of extracts of eastern sulfur-bearing crudes with additives: EPO (2 variants), aznii-7 (2 variants), LZ-6/9;

c) prepared on a base of oils of selective purification with additives: khloref-40, molybdenum blue and LZ-6/9, chloroparafin and LZ-6/9, phosphorus-chlorine-sulphurized sperm whale fat, concentrate of sulphurized terpene with octochlorocyclopenta.

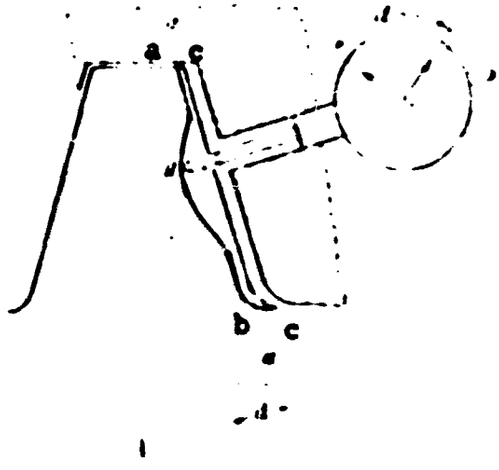


Fig. 1. Measuring diagram for appraising wear of teeth.
aa) line of profile of standard tooth; bb and cc) probable deviations from standard line of profile of gear tooth before test; bob) profile of tooth after test; d) magnitude of wear in mm.

Development types of additives were developed and prepared by the following scientific research institutes and factories:

1) additive LZ-6/9 — Leningrad oil refining factory named after Shaumyan;

2) additive khloref-40 — Chemistry Laboratory of the Institute of Oil-Chemical Synthesis of the Academy of Sciences of the USSR;

3) additive of molybdenum blue -- Laboratory of the All-Union Scientific Research Institute of the Petroleum Industry;

4) additive aznii-9 -- Azerbaidzhan Scientific Research Institute (INKP Academy of Sciences Azerb. SSR);

5) additive phosphorus-chlorine-sulphurized sperm whale fat, concentrate of sulphurized terpene with octochlorocyclopenta -- experimental workshop of the "Neftegaz" factory.

Selection of base oils and additives and the preliminary elimination laboratory tests of development types of them, besides the samples of oils of the "Neftegaz," factory were produced by a laboratory of VNII NP.

Results of comparative tests of samples of transmission oils on the stand are given in Table 2 and in Fig. 2.

From data of these tables can be made the following conclusions.

1) Samples of experimental oils with sulfuric additive LZ-6/9 in antiwear properties somewhat exceed oil with additive EZ-5 and are significantly better than transmission motor and tractor oil. Both residual oils and oils of selective purification with additive LZ-6/9 give identical results with respect to wear of teeth of gears.

2) Development type of oil with additive khloref-40 showed high antiwear properties. Of all tested earlier, xperimental and commodity oils with other additives, additive khloref-40 gave best results.

3) Development type of oil with additives of molybdenum blue and LZ-6/9 (I variant) also showed high antiwear properties, but due to sharp specific odor was removed from tests. II variant of this oil, containing additive of molybdenum blue, prepared on other alcohols, also showed high antiwear properties. However, oil did not possess sufficient stability due to loss of additive of molybdenum blue in deposi..

4) Development type of oil with additives of chloroparafin, LZ-6/9 and

Table 2. Results of Tests of Transmission Oils with Different Additives

Base oil	Designation and quantity of additive	Mean value of tooth wear, mm		Mean value of increase in side play, mm	Mean value of quantity of removed iron, g	Note
		Pinion gear	Ring gear			
Transmission, motor and tractor, summer (Aigrol cylinder oil)	—	0.42	0.24	0.95	16.06	—
Transmission, motor and tractor, (Aigrol cylinder oil), diluted by diesel fuel	3.5% concentrate of sulphurized terpene + 1.5% hexachlorethane	0.20	0.04	1.15	3.7	Oil "overage"
Transmission, motor and tractor, (Aigrol cylinder oil), diluted by diesel fuel	5% L2-4/9	0.04	0.025	0.17	2.06	—
Selective refining from eastern crudes of Ufimsk factory	5% L2-4/9	0.03	0.03	0.19	3.53	—
Mixture of extracts of phenol refining of distillate and residual oils and industrial [illegible]	5% L2-4/9	0.04	0.04	0.13	—	—
Mixture of distillate extract of phenol refining of oils and oil of industrial [illegible]	10% EPO (I variant)	0.04	0.01	0.08	—	Oil with this additive is unstable
Mixture of residual and distillate extracts of phenol refining of oils [illegible] and oil of industrial [illegible]	10% EPO (II variant)	0.17	0.04	0.25	5.7	Oil with this additive is unstable
Mixture of residual and distillate extracts of phenol refining of oils [illegible] and oil of industrial [illegible]	5% anti-9 (I variant)	0.19	0.05	0.42	5.9	Surfaces of gear teeth have unsatisfactory state
Mixture of extracts of phenol refining of distillate and residual oils [illegible] and oil of industrial [illegible]	5% anti-9 (II variant)	0.19	0.03	0.27	—	Oil causes corrosion of reducter parts
Selective refining from eastern sulfur-bearing crudes [illegible]	4% chloref-40	0.02	below 0.01	0.05	0.77	—
Selective refining from eastern sulfur-bearing crudes [illegible]	1.5% molybdenum blue + 3% L2-4/9 (I variant)	below 0.01	0.00	0.10	—	Due to toxicity of oil one reducter was tested
The same	2.5% molybdenum blue + 3% L2-4/9 (II variant)	0.04	0.02	0.05	1.72	—
The same	7% chloroparafin + 3% L2-4/9 + 0.3% phenyl-α-naphthylamine	0.19	0.04	0.28	4.12	—
The same	10% phosphorus-chlorine-sulphurized sperm whale fat	0.04	0.04	0.20	3.03	Oil causes corrosion of reducter parts
The same	3% concentrate of sulphurized terpene +2% octachloropropionate + 5% L2-8	—	—	0.19	5.12	Absolute value of wear is not established due to formation of deposit on non-working surface of teeth. Oil causes corrosion of reducter parts.

phenyl-α-naphthylamine, in antiwear properties, is worse than oil TAp-15 with additive LZ-6/9 and approximately corresponds to oil TAp-15 with additive EZ-5.

5) Development type of oil, prepared on base of extracts, eastern sulfur-bearing crudes with sulfur-phosphorous additive EPO (1 variant) had satisfactory antiwear properties, however, oil was unstable due to loss of additive. Variant II of this oil, with modified technique of manufacture of additive, showed significant impairment of antiwear properties and state of working surfaces of teeth.

6) Samples of experimental oils with additive aznii-9 (I and II variants) in antiwear properties were on the level of oil TAp-15 with additive EZ-5. However, during test of oil of variant I, working surface of teeth of pinion gears had unsatisfactory state (burrs, chipping off). Variant II of oil caused corrosion of reductor parts and working surface of teeth had burrs and coarse furrows.

Results of tests of oils with additives EPO and aznii-9 show that this method of bench tests of oils is sufficiently sensitive to a change in manufacturing technique of additives.

Tests of the remaining experimental oils made it possible to reveal the following.

Sample of oil with an additive of phosphorus-chlorine-sulphurized sperm whale fat caused corrosion of reductor parts and had an inclination toward oxidizing polymerization.

Sample of oil with additives of concentrate of sulphurized terpene, octochlorocyclopenta and IR-8 caused strong corrosion of reductor parts, was marked also by destruction of working surfaces of teeth of pinion gears.

It is necessary to note that during test of all these oils foaming was not observed.

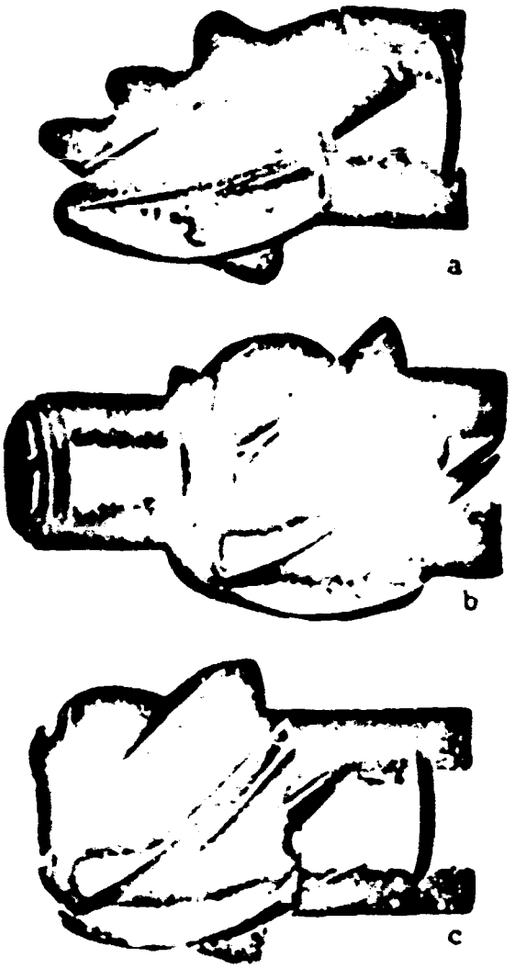


Fig. 2. Pinion gears of main transmission of an automobile after 13 hour stand tests of samples of transmission oils.
a) oil, transmission, motor and tractor, summer (nigrol cylinder oil);
b) oil, TAp-15 with additive LZ-6/9;
c) oil, selective from sulfur-bearing crudes (MKZ) with additive khloref-40.

Conclusions

Bench tests, developed on the ZIL method, of transmission oils make it possible to evaluate oil in antiwear, antiburr, and anticorrosive properties, and also stability and foam characteristics.

These tests make it possible to recommend for production and application TAp-15 oil with additives EP-5 and LZ-6/9, to recommend for further research and

tests on long-term oils additives khloref-40 and molybdenum blue with LZ-6/9, and also to reveal deficiencies of other tested additives.

RESEARCH ON EFFECTIVENESS OF ADDITIVE TSIATIM-339 DURING PROLONGED OPERATION OF HIGH SPEED AND FORCED SHIP DIESEL ENGINES ON SULFUR-BEARING FUELS AND OILS

V. P. Korotnenko

Application on ship diesel engines of diesel fuels with content of sulfur higher than 0.2% and lubricating oils from sulfur-bearing crudes leads to heightened scale formation and increas[illegible] wear of parts of the cylinder-piston group. Degree of increase in scale deposit and wear is not identical for ship diesel engines of different types and depends both on quality of applied commercial fuels and oils and design features of motor and operating conditions. In connection with this our research was conducted on a large quantity of motors of different types and in various operating conditions.

Work conducted before 1957 in different scientific research organizations and factories established that during application in diesel engines of sulfur-bearing diesel fuel with content of sulfur below 1% the most effective additive to oil from those mastered by native industry was additive tsiatim-339.

Research on effectiveness of additive tsiatim-339, during prolonged operation of ship diesel engines on sulfur-bearing fuels and oils, was conducted by us in two stages.

In the first stage (1955-1959) motors were operated on sulfur-bearing diesel fuel of brand C (GOST 305-58) and lubricating oils from Baku crudes with 3% additive tsiatim-339. Duration of operational tests on each type of motor is given in Table 1.

Table 1

Type of motor	Duration of test on each motor, hours	Number of motors on which additive was tested	Type of motor	Duration of test on each motor, hours	Number of motors on which additive was tested
2Ch8.5/11	1500	18	11D	600	6
4Ch10.5/13	2500	22	37D	2000	8
3D6	750	8	M-50	300	24
7D6	1600	10	M-50F	500	24
9D	1200	12	DK-2	750	8

In the second stage (1958-1960) motors were operated on sulfur-bearing diesel fuel of brand C (GOST 305-58) and lubricating oils from sulfur-bearing crudes with 3% additive tsiatim-339. Duration of these tests on each type of motor is given in Table 2.

Table 2

Type of motor	Duration of test on each motor, hours	Number of motors on which additive was tested
2Ch8.5/11	1900	6
4Ch10.5/13	2500	8
9D	1500	6
37D	2000	4
M-50F	500	16
DK-2	750	4

Appraisal of effectiveness of additive tsiatim-339 was conducted according to the following indices:

1) character and quantity of scale and varnish deposit on parts of motors;

2) wear of basic parts of motors;

3) state of working surfaces of parts of motors;

4) intensity of wearability of additive;

5) character of change in physical chemistry indices of working oil in oil system of motors.

Scale Deposit on Parts of Motors

On motor parts working on sulfur-bearing fuel of brand C and oils from Baku crudes with 3% additive tsiatim-339, scale deposit is 5-10% more than during application of low-sulfur diesel fuel DS (GOST 4749-49) and the same oils. Heightened deposit are observed basically in upper part of pistons, including zone of compression rings, on covers of cylinders on the side of the combustion chamber and on rods of valves. Scale formation occurs intensely at the beginning of the work of the motor. Subsequently, during achievement of some critical magnitude, quantity of scale is increased insignificantly. For instance, weight of scale, removed from compression rings of sixth cylinder of motor 37D after 156 hours of work on sulfur-bearing fuel of brand C and oil Dp-11 with 3% additive tsiatim-339, constitute 17.15 g, and after 2000 hours 20 and 30 g, and during work of motors on diesel fuel DS (GOST 4749-49) and oil Dp-11 with 3% additive tsiatim-339 10.25 g and 13.60 g, respectively. This phenomenon is explained, obviously, by development of washing properties of oil with a multi-functional additive. This conclusion is confirmed by the presence of a large quantity of hard particles of scale in oil filters on main pumping line of oil (weight of scale gathered from filters after 200 hours of motor operation constituted, on sulfur-bearing fuel, 141.4 g and, on low-sulfur fuel, 130.1 g).

During work of motors on sulfur-bearing fuel of brand C and sulfur-bearing oil with 3% additive tsiatim-339 the quantity of deposit in the zone of piston rings is 10-15% larger than during work on low-sulfur fuel and Baku oils.

Wear of Basic Parts of Motors

Wear of basic parts of motors during work on sulfur-bearing fuel of brand C and oils from Baku crudes with 3% additive tsiatim-339, and also on oils from sulfur-bearing crudes with the same additive is more than when operating on diesel fuel DS and Baku oils. For instance, for motors 37D after 2000 hours of work on sulfur-bearing fuel and oil Dp-11 (GOST 5304-54) with 3% additive tsiatim-339 maximum wear of cylinder bushings constituted 0.20 mm, maximum gap in locks of piston rings 5.95 mm, and on diesel fuel DS and oil Dp-11 with 5% additive aznii-tsiatim-1 constituted 0.15 and 3.5 mm, respectively. Wear of bushings of cylinders and compression rings of motors during work on sulfur-bearing fuel and sulfur-bearing oil is 20-30% more after 1500 hours of work for motors 9D, 3-5% more after 500 hours for M-50f and 5-7% more after 2000 hours for 37D than during work of enumerated motors on low-sulfur fuel and Baku oils.

Heightened scale deposit and increased wear of parts during work of motors on sulfur-bearing fuel of brand C and sulfur-bearing oils with 3% additive tsiatim-339 testify to insufficient effectivenes of additive tsiatim-339, the application of which does not manage to neutralize harmful influence of products of combustion of sulfur-bearing fuel to the level characteristic for motors working on low-sulfur fuel DS and Baku oils.

Wearability of Additive

Wearability of additive tsiatim-339 was investigated in operational conditions in oil MS-20 from sulfur-bearing and Baku crudes during application on motors M-50f, and in oil DSp-11 from the same crudes during application on motors 37D and 9D.

Research was conducted by means of determining barium content in that part of additive, which was in working oil in initial state. This part of additive was separated from that part where barium is in the form of its solid compounds with products of aging of oil, dissolution of batch of oil in benzene, with subsequent filtration of solution and treatment of filtrate by method presented in GOST 7178-58.

Working oil in motors M-50f was changed after every 60 hours of work, in motors 37D and 9D after 300 hours.

Wearability of additive was studied with and without adding fresh oil to tank of circulatory (working) oil in accordance with effective operating instructions; with the adding of fresh oil content of additive in working oil was kept within limits of 2.0-2.6%.

Results of research of additive wearability without added fresh oils are given in Table 3.

Table 3

Type of motor	Applied oil and fuel	Content of additive in oil (in %) during work in motor, hours				
		fresh	0.5	100	200	300
9D	Oil DSp-11, fuel of GOST 305-58	3.0	2.60	2.53	2.27	2.04
		3.0	2.75	2.49	2.12	1.75
9D	Oil DSp-11, fuel of GOST 4749-49	3.0	2.44	2.30	2.14	1.84
		3.0	2.85	2.66	2.36	2.10
37D	Oil DSp-11, fuel of GOST 305-58	2.90	2.55	2.50	2.21	2.01
37D	Oil DSp-11 with 3% additive tsiatim-339, fuel of GOST 4749-49	2.93	2.59	2.54	2.19	2.00

Obtained data show that additive tsiatim-339 in sulfur-bearing and Baku oils during work of motors on both sulfur-bearing and low-sulfur fuel wears practically equally: toward the end of the work period of the oil, content of it oscillates within limits of 1.75-2.10%.

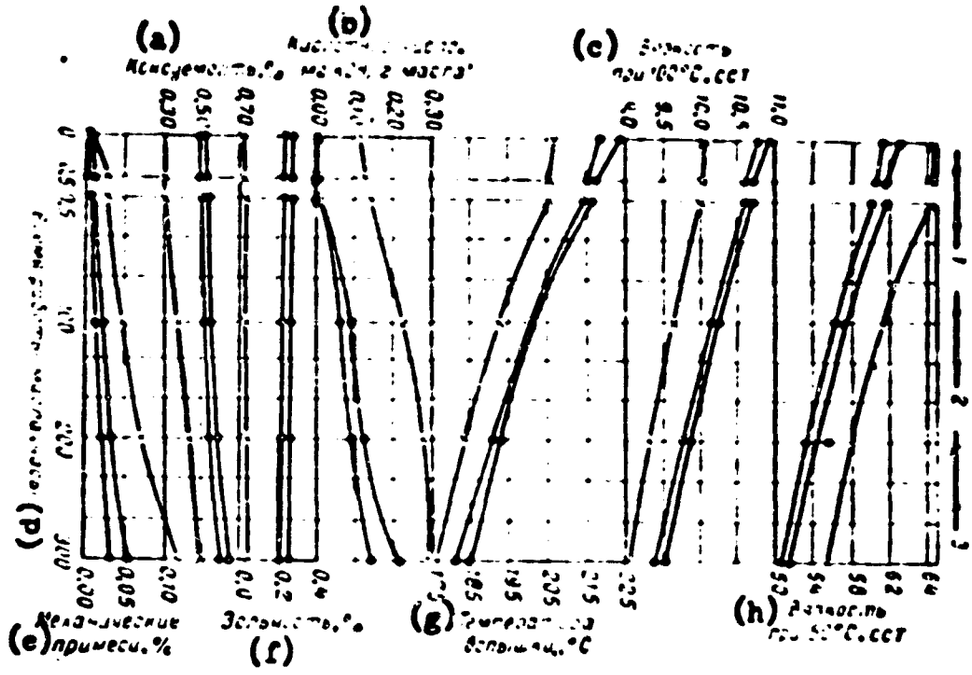


Fig. 1. Change of physical chemistry indices of oils during work in 9D motors.
1) DSp-11 oil (sulfur-bearing fuel, GOST 305-58); 2) DSp-11 oil (low-sulfur fuel, GOST 4749-49); 3) Motor oil T (low-sulfur fuel).
KEY: (a) Coking capacity %; (b) Acid number, milligram KOH/g oil; (c) Viscosity at 100°C, cs; (d) Time of work of oil, hours; (e) Mechanical impurities, %; (f) Ash content, %; (g) Temperature of flash, °C; (h) Viscosity at 50°C, cs.

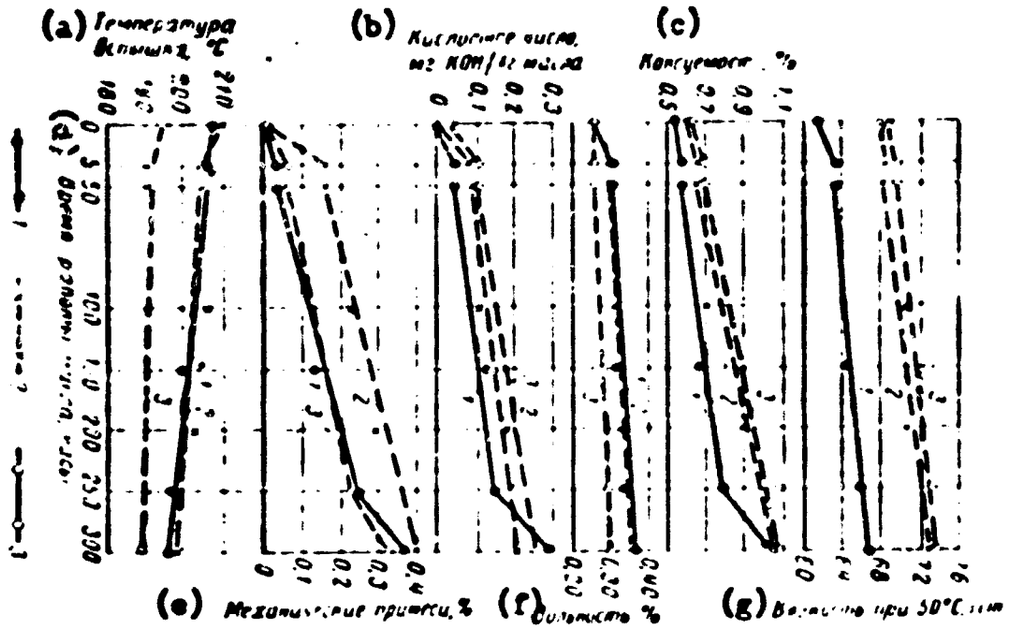


Fig. 2. Change of physical chemistry indices of oils after period of tests on motor 37D.
1) DSp-11 oil (sulfur-bearing fuel); 2) Dp-11 oil (sulfur-bearing fuel); 3) Dp-11 oil (low-sulfur fuel).
KEY: (a) Temperature of flash, °C; (b) Acid number, milligram KOH/1 g oil; (c) Coking capacity, %; (d) Time of work of oil, hours; (e) Mechanical impurities, %; (f) Ash content, %; (g) Viscosity at 50°C, cs.

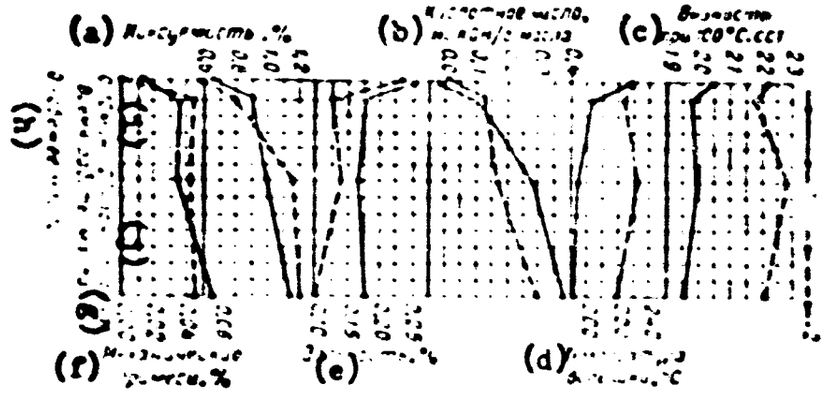


Fig. 3. Change of physical chemistry indices of oils during work in rotors M-50f.
1) MS-20 oil of the Orskiy factory with 3% additive tsiatim-339, fuel of GOST 305-58; 2) MK-22 oil with 3% additive azrii-tsiatim-1, fuel of GOST 4749-49.
KEY: (a) Coking capacity, %; (b) Acid number, milligram KOH/g oil; (c) Viscosity at 100°C, cs; (d) Temperature of flash, °C; (e) Ash content, %; (f) Mechanical impurities, %; (g) Time of work of oil; (h) O-fresh oil; (i) Minute; (j) Hour.

Character of Change in Physico-Chemical Indices of Operating Oil

Character of change in physical chemistry indices of operating oil in the process of prolonged operational tests investigated by means of analysing samples removed from circulatory oil tanks. Results of analysing working oils after one cycle of work in system of motors M-50f, 9D, and 37D shown in Figs. 1, 2, 3 show that the character of change in physical chemistry indices of working oils in oil system of motors both for oils from Baku crudes with additive azniI-tsiatim-1 and with additive tsiatim-339 and sulfur-bearing oils with additive tsiatim-339, during work of motors on low-sulfur and sulfur-bearing diesel fuels is practically identical.

Conclusions

1. Additive tsiatim-339 added to lubricating oils in quantity 3% of weight, during operation of ship diesel engines on sulfur-bearing fuel of brand C (GOST 305-58) and oil from Baku crudes, is sufficiently effective and ensures normal operation of these motors.

2. During application in motors of sulfur-bearing fuel of brand C and sulfur-bearing oils, additive tsiatim-339 turns out to be insufficiently effective and does not ensure neutralization of harmful effect of products of combustion of sulfur-bearing fuel and oils to the level characteristic for parts of motors working on low-sulfur fuel DS (GOST 4749-49) and oil from Baku crudes.

THE EFFECT OF VISCOSITY OF ADDITIVES ON OPERATIONAL PROPERTIES OF OILS

Ye. G. Semenido, V. I. Sharapov, and N. V. Shchegolev

As a result of the application in the last 10-15 years, on carburetor, diesel, and certain other types of motors, of oils with low-molecular basis, limited in fractional composition [1], it became possible to introduce into the production of oils different polymers as viscosity additives.

The most widespread viscosity additives are polyisobutylenes and polymethacrylates, with molecular weight of 15,000-30,000.

Foreign production of viscosity additives has reached 100 thousand t/year [2].

Conditions for application of polymers as viscosity additives and a number of properties of thickened oils are described earlier [3-8]. In this report are considered new data in this region.

Permissible Concentrations of Polymers in Thickened Motor Oils

In standard thickened motor oils AKZp-6, AKZp-10 and MT-14p, prepared on the basis of solar-spindle oil distillates of definite composition, there is 1.8-4.5% polyisobutylene, with a molecular weight of 20,000. So that on the same basis more viscous oils are obtained (type MT-16 and MK-22), large quantities of polymer

(of an order of 6-7%) will be demanded. If, however, as a basis of oils we use diesel fuel, then additive of polyisobutylene will be demanded in a quantity of 8-10%.

It has been important to clarify the character of changes of polyisobutylene during high concentrations of it in oil during the work of thickened oils in motors under the influence of thermal and mechanical factors.

It was established [9] that degree of mechanical destruction of polyisobutylene in thickened oils is determined by level of viscosity of these oils and does not depend on concentration in them of polyisobutylene (Table 1).

Table 1. Change of Viscosity of Thickened Oils as a Result of Mechanical Destruction of Polymer at 20°, in Conditions of the Instrument of K. I. Klimov

Composition of oil	Viscosity (in cs) during experiment, minutes			
	0	30	120	300
1. Turbine oil 22 + 5% polyisobutylene, molecular weight 20,000.....	1148	928	623	423
2. Kerosene + 20% the same polyisobutylene.....	1153	975	646	415

Consequently, thickened oil, possessing sufficient resistance to mechanical destruction at a given level of viscosity, can be obtained with various quantities of polymer by means of change in viscosity of basis of oil.

Resistance of polymers in solution of oils to thermal destruction is ensured by application of stabilizing additives, [8].

Tests on motors of type V-2 (one-cylinder installation) oils with a viscosity of 14 cs at 100°, obtained by thickening with polyisobutylene of solar-spindle oil distillates and diesel fuel, containing 3 and 5.5% polymer, respectively, showed that in both cases molecular weight of the latter was changed approximately equally and to a comparatively small degree (Table 2).

Table 2. Change of Polyisobutylene of Brand P-20 in Thickened Oils (on Various Bases) During Work in Motor of Type V-2

Oil on a basis of solar-spindle oil distillates					Oil on a basis of diesel fuel				
Work, hours	Viscosity at 100°, cs	Content of polymer, %	Molecular weight of polymer	Decrease of molecular weight, %	Work, hours	Viscosity at 100°, cs	Content of polymer, %	Molecular weight of polymer	Decrease of molecular weight, %
0	13.9	3.04	21,800	0	0	13.0	5.50	20,200	0
23	11.1	3.68	19,900	9	10	15.3	6.13	18,700	7
41	11.9	3.56	17,900	18	20	17.5	7.21	18,100	11
					30	20.2	7.54	18,100	11

Increase of quantity of polymer in oils during work occurs due to gradual evaporation of low-boiling fractions of basis of oils. In oil on a basis of diesel fuel this increase, naturally, is larger (from 5.5 to 7.5%). However, it is not accompanied by a sharp lowering of molecular weight of the polymer.

Making the operating conditions of the motor more rugged renders a certain influence on stability of polyisobutylene in working oil (Table 3).

Table 3. Influence of Thermal Operating Conditions of Motor of Type V-2 on Changes of Polyisobutylene in Thickened Oil on a Basis of Diesel Fuel

Characteristic of operating conditions of motor	Characteristic of oil and polymer				
	Work of oil, hours	Viscosity at 100°, cs	Content of polymer, %	Molecular weight of polymer	Decrease of molecular weight, %
High-temperature conditions: temperature of liquid coolant 140°; temperature of oil 100-115°; 1800 rpm	0	10.0	7.4	18,000	0
	5	15.3	—	—	—
	10	23.0	10.9	15,600	13.5
	19	32.9	13.2	15,400	14.5
Normal thermal conditions: temperature of liquid coolant 85-90°; temperature of oil 90-95° 1800 rpm	0	10.0	7.4	18,000	0
	5	12.0	7.0	16,900	6.0
	10	13.6	8.5	16,400	9.0
	20	18.2	11.0	16,700	7.2

Table 4. Characteristics of the Cylinder-Piston Group of a Motor of Type V-2 after 20 hours of Work on Thickened Oil

Characteristic of operating conditions of motor	Deposit, g		Evaluation of piston by PZV, points	Quantity of scale in combustion chamber, g	Mobility of piston rings	Wear of piston rings, g			
	on piston	on piston rings				1	3	4	5
High-temperature conditions	2.96	0.64	4.5—5	1.0	All rings shift in grooves; the 5th ring freely, the remaining ones with a certain effort	0.0012	0.1912	0.0984	0.0122
Normal thermal conditions	1.70	0.21	3—3.5	0.6	All rings shift in grooves; 4th and 5th rings freely, the remaining ones with a certain effort	0.0045	0.0036	0.0077	0.0043

Note. Data obtained jointly with engineer E. G. Kuznetsov.

From the table it is clear that for obtaining thickened motor oils on a low-viscous basis can be applied high concentrations (to 10% and even more) of polyisobutylene, during observance of general conditions developed earlier for thickened oils.

During work of motor on oil with high concentration of polyisobutylene in the presence of additive tsiatim-339, scorching or grabbing of piston rings was not observed even in high-temperature conditions. After work of motor on normal thermal conditions state of cylinder-piston group was better than at high temperature (Table 4). During work of the same motor in high-temperature conditions for 20 hours on MS-20 oil with 3% of the same multifunctional additive, deposit on piston constituted 3.20 g, on piston rings 0.26 g; appraisal of piston by PZV was 3-3.5 points; scale in combustion chamber was 3 g.

The idea existing earlier that heightened content of polyisobutylene causes heightened scale formation was erroneous. Possibility of normal work of powerful motors on thickened oil with high content of polyisobutylene was confirmed by stand motor tests, conducted jointly with V. T. Lomonosov, S. S. Bernshteyn, and A. A. Astanin.

Optimum Molecular Weight of Polymers as Viscosity Additives to Motor Oils

Resistance of polymers to the effect of temperature and mechanical factors, as is known, is improved with a lowering of molecular weight of polymers. However, simultaneous with this increases, is their expenditure. Furthermore, in obtaining thickened oils with polyisobutylene of low molecular weights, as will be shown below, certain exploitational properties of oils worsen.

For polyisobutylene as a viscosity additive an average molecular weight of an order of 20,000 is established; the upper limit of average molecular weight constitutes 25,000. This is explained, basically, by the fact that polyisobutylenes up to a molecular weight of 30,000 preserve the state of viscous mass, and at

higher weight become elastic solid bodies.

Lower limit of molecular weight of polyisobutylenes as viscosity additives is arbitrarily taken as 15,000. At present there are tendencies to lower the average molecular weight of polymers to 10,000. As far this is right, we will consider below.

It is very important that at a given average molecular weight the polymer have sufficiently uniform fractional composition. This, in the practice of production and application of viscosity additives, is allotted, unfortunately, insufficient attention.

The wider the fractional composition of the polymer at a given average molecular weight, the worse the depolymerization resistance, inasmuch as such a polymer, along with low-molecular fractions, includes also high-molecular ones, more inclined to depolymerization.

In conditions of production (Table 5) it is possible to obtain polymers with sufficiently high average molecular weight and comparatively narrow fractional composition (middle polyisobutylenes with molecular weights of 20,000 and 15,000). This is necessary to consider during discussion of lower limit of molecular weight of polymers as viscosity additives.

Table 5. Fractional Composition of Three Industrial Lots of Polyisobutylene

No. of fraction	Polyisobutylene of average molecular weight 30,000		Polyisobutylene of average molecular weight 20,000		Polyisobutylene of average molecular weight 15,000	
	Molecular weight of fraction	Quantity of fraction, %	Molecular weight of fraction	Quantity of fraction, %	Molecular weight of fraction	Quantity of fraction, %
1	61,000	4.92	28,000	43.65	30,000	9.40
2	50,000	32.80	17,000	25.44	25,000	22.27
3	31,000	23.39	13,800	7.78	18,000	27.47
4	25,000	8.91	10,500	9.60	15,200	8.22
5	17,000	7.58	5,500	7.44	13,000	10.71
6	13,000	5.44	Remainder	4.30	9,000	7.61
7	8,500	3.42	—	—	7,000	7.07
8	4,000	10.82	—	—	Remainder	7.16

Oils on a low-viscous basis, thickened by polymers, as compared to the usual distillate, residual, and mixed oils, possess a series of known advantages: small values of index ν_{50}/ν_{100}, significantly smaller viscosity at low temperatures, high viscosity at temperatures higher than 100°, and so forth.

In order to determine what should be optimum average molecular weight of polymers as viscosity additives, it is necessary to clarify to what measure their expenditure and the designated, most important properties of thickened oils (Table 6) will depend on molecular weight of the polymers.

Table 6. Influence of Molecular Weight of Polymers on Viscosity-Temperature Properties of Thickened Oils on a Low-Viscous Basis

Characteristic of polyme.			Viscosity (in cs) at temperature, °C								Viscosity (in poises) at temperature, °C				
Name	Molecular weight	Quantity in oil, %	150	140	130	120	110	100	50	$\frac{\nu_{50}}{\nu_{100}}$ Ratio	0	-10	-20	-30	-40
Polyisobutylene	30,000	4.1	7.75	8.45	9.65	12.60	15.1	18.3	73.0	3.99	12.6	31	81	224	675
	20,000	5.3	7.88	9.12	10.60	12.60	15.1	18.3	76.3	4.17	14.7	38	105	316	1258
	10,000	8.2	7.65	8.90	10.56	12.55	15.2	18.3	81.1	4.43	16.6	48	162	630	2510
	5,000	12.0	7.70	8.88	10.64	12.62	15.1	18.3	84.9	4.63	26.2	68	218	890	3980
Polymethacrylate	18,000	6.6	8.20	9.45	10.70	12.60	15.3	18.3	64.5	3.52	9.5	20	45	120	478
	10,000	9.7	8.20	9.38	10.90	12.80	15.2	18.3	67.5	3.69	10.4	22	56	173	630
Oil basis	—	—	1.67	1.88	2.16	2.48	2.9	3.47	12.1	3.49	--	9	20	54	245

Considering data on ratio ν_{50}/ν_{100} and viscosity at low temperatures for oils equally viscous at 100°, thickened by polyisobutylenes and polymethacrylates (on the same oil basis), we ascertain, as a rule, impairment of viscosity-temperature properties of oil with the lowering of molecular weight of polymers.

Viscosity of thickened oils at temperatures higher than 100° depends on the nature of the polymer and virtually does not depend on its molecular weight.

Polymethacrylates, as compared to polyisobutylenes, ensure best indices on viscosity at low and high temperatures and on ν_{50}/ν_{100} ratio.

During application of polyisobutylenes and polymethacrylates with a molecular weight of 10,000 instead of 20,000, their expenditure is increased, on the average, by 50%. Besides increasing expenditure on thickening, the application of polymers with a molecular weight of 10,000 somewhat worsens low-temperature properties of oil; therefore, optimum molecular weight for polymers as viscosity additives one should consider 20,000. With this, it is necessary that polymers have narrow fractional composition, for which in technical requirements on viscosity additives it is necessary to specify corresponding indices, excluding the possibility of content in polymer of fractions of molecular weight and more than 25-28,000.

Compatibility in Oils of Polymeric, Multi-functional and Other Additives

One of the obligatory conditions of the application of polymers in oils is the addition to them of chemical compounds, including also certain multi-functional additives giving polymers the necessary depolymerization resistance.

With respect to polyisobutylene in solution of oils, known multi-functional additives, according to the decrease in effectiveness of their influence on depolymerization resistance, can be arranged in the following order: IP-22, ZIT-1, aznii-8, tsiatim-339, DF-1, aznii-7, aznii-tsiatim-1, aznii-5, aznii-4.

Antioxidants possessed definite ability to increase depolymerization resistance of polyisobutylene (Table 7).

Hence it is possible to consider established a connection between the antioxidant effect of additives and their ability to improve resistance of a polymer to depolymerization. Therefore, during selection of multi-functional and other additives for oils thickened by polyisobutylene, it is expedient to be oriented to substances possessing good antioxidant properties.

Table 7. Influence of Antioxidant Additives on Depolymerization Resistance of Polyisobutylene (5%) in Solution of Turbine Oil

Characteristic of additive			Viscosity of oil at 100°, cs			Index of stability of viscosity (ISV) $\frac{\nu_{final}}{\nu_{initial}} 100\%$
Brand	Chemical composition	Quantity in oil, %	Initial	After heating at 200°, for 6 hours	After heating at 200°, for 12 hours	
--	--	0	27.6	27.3	25.3	91.7
Topanol A	2.4-dimethyl-6-tert-butylphenol..	2	28.8	28.5	28.4	98.6
Topanol O	4-methyl-2.6-di-tert-butylphenol.	2	29.1	29.5	28.2	96.8
Topanol M	N, N'-di-sec-butyl-n-phenylene diamine.....	2	28.8	28.5	27.7	96.1
FCh-16	Product of processing cheremkhovo coals.....	2	25.8	25.8	25.6	99.3
Brake preparation	Product of dry distillation of birch wood.....	2	28.6	28.8	28.4	99.4
Wood-resinous antioxidant	Product of dry distillation of wood.....	2	28.6	28.7	28.6	100

Experience in application and many-sided research on oils thickened by polyisobutylene convince us that polyisobutylene will combine with all known multi-functional, depressor, antioxidant, and other additives.

The situation is otherwise with polymethacrylates in a solution of oils. It is revealed that these polymeric additives are not compatible with a number of multi-functional additives [8, 10]. Thus, the additives tsiatim-339, IP-22, vnii np-361 and certain others cause a sharp increase in viscosity, up to gelformation of oils thickened by polymethacrylates.

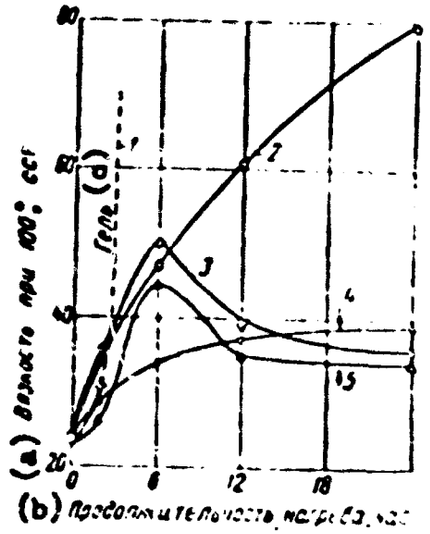
To this or that degree this phenomenon is characteristic also for foreign additives (see figure). It has been important to clarify whether polymethacrylates preserve their depressor properties in the presence of multi-functional additives.

It has turned out (Table 8) that polymethacrylate as a depressor in the presence of a number of multi-functional additives in oil, to a larger or smaller measure, lowers its effectiveness ("effect of suppression" of depressors).

With respect to this property, additive DF-1 profitably differs from others: it does not render negative influence on the depressor effect of polymethacrylate, but, conversely, even somewhat strengthens it.

This was checked also on polymethacrylate of another lot in oil DS-8 NU NPZ. In this case the actual oil had a thickening temperature -14°, with 0.2% polymethacrylate -32°, and after additive of 3% additive DF-1 -37°.

It is noticeable that the basis of the oil, to a significant measure, affects effectiveness of polymethacrylate as a depressor in the presence of multi-functional additives.



Change of viscosity of solutions of additives of viscoplex (polymethacrylate type) in turbine oil 22 during heating up to 200° in the presence of 5% additive vnii np-360.
1) 10.6% HV 2; 2) 15.6% SV 31; 3) 16.4% SV3; 4) 18.4% H-7; 5) 16.2% S1.
KEY: (a) Viscosity at 100°, cs; (b) Duration of heating, hour; (c) Gel.

Oil on a basis of DS-8 with 0.2% polymethacrylate in the presence of additive vnii np-360 (also vnii np-361 and 361a) increased temperature of thickening from -32 to -13°. "Effect of suppression" of depressors constituted 19°.

We will turn to one more interesting fact. Industrial oil 20 obtains temperature of thickening of the order of -36° only in the presence of 1% of polymethacrylate. Addition to oil of 3% additive vnii np-360 does not render a large influence on temperature of thickening. When viscosity of oil was checked, the following was clarified. During introduction into oil of 1% polymethacrylate its viscosity (at 100°) was increased from 5.02 to 7.32 cs. After the addition there too of 3% additive vnii np-360 viscosity of the oil increased to 9.68 cs (industrial oil 20 only with

3% vnii np-360 had viscosity of 5.1 cs).

Table 8. Compatibility of Polymethacrylate (Depressor) with Multi-functional Additives

Oil and multi-functional additive	Content of polymethacrylate, %	Temperature of thickening, °C
Industrial 20 NU NP2	--	-15
	0.2	-38
	0.4	-38
	1.0	-39
Industrial 20 + 3% vnii np-360	0.2	-29
	0.4	-31
	1.0	-36
Industrial 20 + 7.5% SB-3	0.2	-28
The same + 4.5% IP-22	0.2	-27
	0.4	-28
Industrial 20 + 4% aznii-8	0.2	-27
	0.4	-32
Industrial 20 + 3% tsiatim-339	0.4	-32
Industrial 20 + 3% tsiatim-339 + 1% DF-11		
Industrial 20 + additive:	0.2	-27
3.5% DF-11	0.2	-33
3.5% DF-1	0.2	-41
3.5% DF-1	0.4	-42
0.4% depressor aznii	--	-31
3% aznii-tsiatim-1	--	-33
3% vnii np-360 + 1% aznii-tsiatim-1	--	-31

Sharp growth of viscosity of oil (from 5 to 10 cs at 100°) from adding to it only 1% polymethacrylate in the presence of multi-functional additive could have been considered as a positive phenomenon, if viscosity were stable. But after heating such oil at 200° for 1.5 hours its viscosity was lowered to 8.21 cs at 100°.

Influence of Polymers as Viscosity Additives on Antiwear Properties of Oils*

Research was conducted with the help of the method of radioactive isotopes. The motor stand consisted of a ZIL-123F motor and corresponding equipment for

*The work was carried out jointly with L. A. Dem'yanov, P. I. Vorob'ev and M. A. Senichkin.

measurement of the radioactivity of oil. The motor had in each cylinder two activated upper piston rings. On each ring was established eight inserts from Co^{60}. A detailed description of the stand was published earlier [7]. Antiwear properties of oils were estimated by magnitude of tangent of angle of inclination of line of wear (tanα) to axis of abscissas. Appraisal of antiwear properties of oils was conducted on introduced index "relative change of rate of wear," presenting relation tanα of investigated sample to tanα of standard oil. This index was expressed in percents. As standard oil was used industrial oil 50 with 3% additive tsiatim-330 (Table 9).

Table 9. Appraisal of Antiwear Properties of Oils

Oil	tan α	Relative change in rate of wear, %
Sulfurous basis	1.240	111.0
Sulfurous basis thickened by polyisobutylene.	0.687	61.5
The same + 3% tsiatim-339	0.525	47.0
The same + 4% vnii np-360a	0.435	38.9
The same + 3% aznii-8	0.300	26.9
Baku basis	1.950	174.6
Baku basis thickened by polyisobutylene	0.620	55.5
The same + 3% aznii-4	0.550	49.2
The same + 3% aznii-8	0.382	34.2
Industrial oil 50	1.428	127.8
The same + 3% tsiatim-330	1.117	100.0
DS-8 NKZ	0.795	71.2
DS-8NKZ + additive:		
3.5% DF-1	0.778	69.6
5.5% IF-22k	0.605	54.2
3% tsiatim-339 + aznii-tsiatim-1	0.604	54.1
4.5% vnii np-361	0.391	35.0

For comparison are presented also research data of analogous properties of oil compositions on a basis of sulfur-bearing oil DS-8 NKZ*. Inasmuch as works

*According to A. A. Ivanov, A. B. Vipper, P. I. Vorob'ev and K. S. Rybakov.

were conducted on the same motor stand and by the same experimenters, comparison of these data is very expedient.

From data in Table 9 the following conclusions can be made.

1. In antiwear properties (in conditions of the applied method) oils thickened by polyisobutylene exceed oil of the usual method of production, for instance machine oil SU, DS-8 NKZ with additive DF-1, IP-22K, tsiatim-339 + azniitsiatim-1.

2. Sulfur-bearing oils, in the studied properties, are better than Baku oils (middle sulfur-bearing basis and DS-8 NKZ with industrial 50 and others).

3. The studied multi-functional additives manifested an ability to improve antiwear properties of oil.

4. Sharp decrease (2-3 times) tan a of oil bases after their thickening by polyisobutylene is explained, besides the increase in level of viscosity of oil composition, also by the specific influence of viscosity additives on antiwear properties of oil. The latter is confirmed by the practice of using thickened oils.

From the considered multi-functional additive the best turned out to be azniI-8, vniI np-361 and 361a. The last two additives, identical in chemical nature, differ from each other only by relationship of washing and polyfunctional components.

Data on research of antiwear properties of lubricating oils by the method of radioactive isotopes agree well with results of 60-hour bench tests of $AS3_p$-10 oil thickened by polyisobutylene with additive vniI np-361a, and on AK_p-10 oil with additive azniI-8—with the results of operational tests (run 25,000).

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CHAPTER VII

ADDITIVES TO FUELS

ADDITIVES TO LIQUID FUELS FOR GAS TURBINE INSTALLATIONS, PREVENTING DEPOSITS OF ASHES AND VANADIUM CORROSION

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VTI*

During operation of gas turbine installations on petroleum fuels there appear deposits, connected with jam of flow-through part of turbine by deposits of ashes and vanadium corrosion of metal of blades.

Earlier we showed that vanadium corrosion of metals depends on composition of ashes of fuel, temperature of gas and concentration in it of oxygen, and also on chemical composition of steel.

Vanadium corrosion is a process of oxidation of metals, catalyzed, in our opinion, by peroxides and vanadium derivatives in "semiliquid" state.

This work is devoted to test in laboratory conditions and on GTU 60C-1.5 with capacity of 1500 hp of additives preventing deposits of ashes and vanadium corrosion of blades.

Laboratory Tests

In laboratory the effectiveness of action of additives was tested by two methods: static and dynamic.

Essence of static method consists of quantitative determination of corrosion of metal after holding for 60 hr of sample of steel immersed in ashes (in crucible),

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in presence of air, at a temperature from 625 to 800°.

Additives were mixed with 0.8 g of artificial ashes, consisting of 87% V_2O_5 and 13% Na_2SO_4, i.e., in ratio of 3:1 from calculation on weight amount of V_2O_5 (the most aggressive mixture).

Upon completion of experiment for preliminary estimate of ability of additives to prevent deposit of ashes on blades of turbine, state of ashes was fixed; it was conditionally subdivided into three gradations: 1) easily friable, not at all retained on sample of steel; 2) less friable, slightly cohering, not retained on samples of steel; 3) solid, separated from metal with difficulty.

Effectiveness of action of additives with respect to ability to lower vanadium corrosion was determined by loss of weight of sample of steel (after removal of products of corrosion by electrochemical method).

The most promising additives were tested by dynamic method, whose essence consists of introduction with the help of special burner of aqueous or water-alcohol solution of compounds containing vanadium and sodium into oxygen-hydrogen flame. Products of combustion head to warmed pipe, on whose height samples of metals and thermocouples are fixed. Additives are introduced together with aqueous solution. With the use of additive not soluble in water it is fed together with solution in the form of uniform thin suspension during continuous mixing with magnetic mixer. Experiments were conducted for 30 minutes. Quantity of deposits was determined by increase of weight of plates and corrosion by decrease of it after electrolytic purification.

In process of experiments the following additives were investigated.

I. Compounds of alkali earth metals MgO, $MgSO_4$, $MgCl_2$, magnesite (three samples of industrial waste containing up to 92% MgO), calcite $CaCO_3$ and dolomite--general formula $CaMg(CO_3)_2$, contains CaO 30.4%, MgO 21.7, CO_2 47.9%;

II. Al_2O_3 and marshalite--finely powdered variety of quartz (SiO_2).

III. Aluminum silicates:

1) kaolin -- basic silicate of aluminum; general formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ or $Al_4 (SiO_{10}) (OH)_8$, contains Al_2O_3 39.5%, SiO_2 46.5%, H_2O 14%; during heating loses water, in dry form absorbs water;

2) montmorillonite; general formula $\underline{m} \{ Mg_3 [Si_4O_{12}] [OH]_2 \} \underline{P} [Al, Fe]_2 [Si_4O_{10}] [OH]_2 \, 11H_2O$ or $Al_2O_3 \times 4SiO_2 \cdot \underline{m} H_2O$; $\underline{m} : \underline{p} = 0.8—0.9$; chemical composition depends on content of water, in dry weather it returns part of water, in damp -- absorbs it from air; it possesses sharply expressed ability for exchange with cations;

3) gumbrin, Askania clay and bentonite of Askania -- modifications of montmorillonite;

4) halloysite $Al_4[Si_4O_{10}] [OH]_8 \, 4H_2O$ or $Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$. Contains Al_2O_3 34.7%, SiO 40.8%, H_2O 24.5%;

5) Zikeyevo earth, opoka; is widely used in petroleum industry for purification of oils.

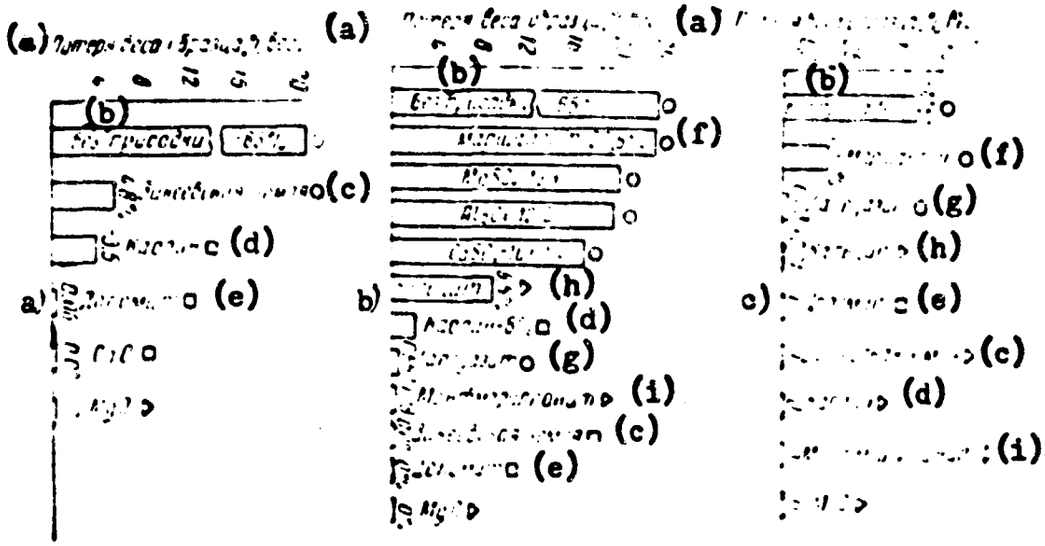


Fig. 1. Action of additives on vanadium corrosion of steel EYalT at a temperature from 625 to 800°C. a) 625°C; b) 750°C; c) 800°C.
Δ— ashes with additive, easily friable, is not at all retained on metal;
□— ashes with additive, less friable, not retained on metal;
O— ashes with additive, hard, separated from metal with difficulty.
KEY: (a) Loss of weight of sample wt %; (b) Without additive; (c) Zikeyevo earth; (d) Kaolin; (e) Dolomite; (f) Marshalite; (g) Halloysite; (h) Calcite; (i) Montmorillonite.

Results of tests by static method at temperatures of 625, 750 and 800° of effectiveness of action of these additives with respect to their ability to prevent adhesion of ashes and to lower vanadium corrosion of steel EYalT are shown in Figs. 1 and 2. Appearance of this steel after 60-hour test at 750° in the absence and in the presence of some additives is presented in Fig. 2.

1. Magnesium, calcium. In whole interval of temperatures and for all grades of tested steel (EI-612, EI-405 and EYalT), the best additive turned out to be magnesium oxide: after experiments ashes were easily friable, metal remained shining, without traces of any corrosion. Calcium oxide turned out to be rather the worst additive: ashes (experiment at 800°) were slightly cohering, although they also did not remain on metal (2-nd gradation), loss of weight after electrolytic purification amounted to 0.02%.



Fig. 2. Influence of additive on vanadium corrosion of steel EYalT at 750°C (60 hr).
a—MgO; b—$MgSO_4$.

Dolomite possesses high effectiveness; calcite is inferior to it.

However, one should refer critically to this estimate, inasmuch as during burning of sulfur fuels oxides of Mg and Ca form sulfates. Therefore, it was interesting to study the effectiveness of action of $MgSO_4$ and $CaSO_4$. The latter, although they also lower corrosion of steel EYalT (from 66 to 20%) are, nevertheless, significantly inferior to activity of oxides.

It is possible to assume that the use of MgO and CaO will have the greatest success during the use of low-sulfur fuel. These assumptions should be checked on real turbine.

2. Aluminum oxide (Al_2O_3) and marshalite (SiO_2) in assumed conditions are insufficiently active additives.

3. Aluminum silicates. Additives of this group deserve special attention during use of sulfur fuel.

They form with V_2O_5 numerous compounds with high melting point and their reaction with sulfates proceeds with yield of oxides of sulfur:

$$Na_2SO_4 + \underbrace{Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O}_{\text{kaolin}} \rightarrow Na_2O \cdot Al_2O_3 \cdot 2SiO_2 + H_2SO_4 \uparrow + H_2O$$

Of this group, montmorillonite (close in effectiveness to MgO gives the best result), then kaolin, bentonite of Askania and Askania clay, the worst - halloysite.

Cost of this group of additives is low and amounts to from 2 to 6 kopecks per 1 t of fuel.

With increase of temperature the ability of additives to prevent adhesion of ashes to metal worsens. At 625° this ability belongs to MgO, montmorillonite, kaolin, Zikeyevo earth (see Fig. 1a); with increase of temperature to 750° (Fig. 1b) this ability is completely kept only by MgO and montmorillonite.

Increase of temperature also worsens the ability of additives to decrease corrosion of metals. Depending on grades of steel the effectiveness of additives changes somewhat. In this respect the most unfavorable is steel EI405.

On the basis of preliminary work on selection of additives and check of best of them by dynamic method, it was recommended for test on GTU 600-1.5 during work on sulfurous black oils additives montmorillonite, kaolin, dolomite, and also MgO, $MgSO_4$ and $MgCl_2$ as the most effective.

Tests On GTU 600-1.5

Experimental operation of GTU 600-1.5 of Nevskiy factory named after V. I. Lenin on different liquid fuels (physico-chemical characteristics of fuels and composition of their ashes see Tables 1 and 2) showed the following.

1) On low-sulfur motor fuel DT-1 and DT-2 turbine works reliably without essential jam of flow-through part of it for 1 month; however, some batches of motor fuel cause jam of turbine after 1 week.

2) On sulfurous black oils 40 and 60 -- directly distilled and containing products of cracking -- combustion chamber works satisfactorily. However, on these black oils turbine rapidly jams in consequence of which run of GTU to lowering of its capacity is twice limited to 1 — 2 twenty-four hour periods.

3) During work of GTU on black oils 40 and 60, containing products of cracking, regular burning of fuel and of separate particles on blades of turbine and wear of burners is observed.

4) Deposits of ashes basically are concentrated on first row of guide (motionless) blades of GTU.

On blades of first row of rotor there are approximately 4 times less deposits than on the guide blades of first row.

5) Deposits on guide and rotor blades (see Table 2) have approximately the same composition as ashes of black oil. Exception is calcium and magnesium oxides, of which in deposits there is 10 times less than in ashes of fuel.

Deposits from regenerative air heater contain little vanadium and sodium; they basically consist of iron sulfates.

6) Deposits on blades of GTU have such a composition that they can be removed without opening the turbine, by means of washing the blades with hot water. Blades after such washing become absolutely clean.

For test of effectiveness of action of additives on GTU special installation was created (Fig. 3), whose purpose is to ensure good mixing of additives (dry,

soluble in water or fuel) with fuel.

Dry additive from bin 1 by means of regulated feeder 3 is fed into mixer of preliminary mixing 4, into which simultaneously through outlying float chamber 5 the fuel proceeds. Paste is fed continuously by plunger pump 6 under pressure of 20 — 40 at into glandless mixer 7, in which is mixed by two turbines with main flow of fuel. In glandless mixer rotor of electric motor revolves in gas pad under pressure of nitrogen.

Liquid additive is fed from service tanks 9 by plunger pump 6 directly into glandless mixer 7.

In 1959 on GTU with use of this installation tests were conducted of effectiveness of action of kaolin during work of turbine on black oils 40 and 60. Physico-chemical properties of these black oils and composition of their ashes are given in Tables 1 and 2 (experiments 1-59, 3-59).

Degree of jam of turbine during work on black oil without additive and with kaolin, expressed in relative decrease of carrying capacity of flow-through part (determined by Flügel's), is illustrated by straight lines shown in Fig. 4.

Duration of work of turbine on black oil with additive without essential jam ranged to be increased from 1-2 to 15 twenty-four hour periods.

Relatively small effectiveness of action of additive, as compared to forecast based on laboratory data, is explained by interruptions in supply of kaolin (malfunctions in work of installation) and by removal of burning particles in flow-through part of turbine (flashes and burning of particles flying through blades were visible through peepholes).

Compounds giving ashes during combustion and contained in burning coke-like high-ash particles, naturally are not able to interact with additive. These heated particles strike relatively cold blades of turbine (600°), and burn on them, forming ash deposits. In these conditions action of additives is hampered.

Table 1. Physico-Chemical Properties of Fuels

Index	Kind of fuel							
	[illegible]	[illegible]	Black oil of commercial	Black oil of commercial	Black oil of commercial (with additive kerite)	[illegible]	[illegible]	Black oil of commercial
	Number of experiment							
	1-57	2-57	3-57	1-58	1-59	3-59	1-60	2-60
Viscosity in °E at:								
20° C	—	[illegible]	[illegible]	[illegible]	—	—	—	—
50° C	—	[illegible]	[illegible]	[illegible]	7.2 - 8.15	6.7 - [illegible] 9.1	—	8.58
100° C	—	1.2	—	4.52	3.0 - 3.4	3.0 - 3.45 3.50	—	3.26
Density, g/cm³	at 20° C		[illegible]	at 20° C	at 20° C			at 20° C
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Ash content, %	[illegible]	[illegible]	[illegible]	0.11	[illegible]	[illegible]	[illegible]	0.11
Amount of mechanical impurities, %	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Flash point according to Brenken, °C	71 - 84	140	157	154	—	—	—	—
Content of water, %		—	[illegible]	0.17	Traces, 1.0	—	Traces	—
Acid point, °		—	[illegible]	[illegible]	— —		—	—
Surface tension, dynes/cm at:								
20° C		[illegible]	[illegible]	[illegible]	—		—	—
50° C	—	[illegible]	[illegible]	[illegible]	— —	—	—	—
100° C	—	[illegible]	[illegible]	[illegible]	— —		—	—
Elementary composition, %								
C		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
H		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
S	<0.5	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
N + O		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Heat of combustion of:								
lowest	-	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
highest		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
by bomb		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Table 2. Composition of Ashes of Fuels and Deposits With GTU 600-1.5

Duration of operation, hr	Position of blades	Ashes and deposits with the use of black oils and diesel fuels of different brands	Composition of ashes and deposits, wt %						
			V_2O_5	Na_2O	SO_3	P_2O_5	CaO	MgO	SiO_2
2-30	183	B-40 of diesel distillation							
		ashes of fuel	9.58	28.84	3.90	1.97	18.8	1.8	2.50
		deposits from guide blades	12.76	19.71	1.16	1.78	3.69	0.35	27.82
		deposits from rotor blades	11.20	23.22	1.32	1.56	4.34	0.44	29.30
9-37	91	B-40:							
		ashes of fuel	18.46	21.3	2.60	1.91	12.60	2.26	26.29
		deposits from guide blades	10.81	20.1	0.75	1.15	9.78	1.99	—
		deposits from rotor blades	11.77	20.10	1.82	1.65	-		
		deposits from regenerator tubes	1.88	1.71	1.83		-	-	
1-28	73	B-40							
		ashes of fuel	18.87	17.87	2.38	2.06	7.85	traces	-
		deposits from guide blades	10.02	20.10	0.66	1.00	4.25		11.20
		deposits from rotor blades	11.06	16.17	0.71	1.10	3.23		19.26
		deposits from regenerator tubes	0.52	1.01	1.11	11.52	0.78		
1-20	284	B-40 with additive							
		ashes of fuel 1	27.06	21.05	2.40	0.22	9.70	1.12	
		" " 2	17.70	11.0	13.20	1.2	10.0	1.20	
		" " (average composition)	24.5	20.83	5.61	0.26	9.0	1.04	
		deposits from guide blades	17.30	22.50	10.85	1.14	3.14	1.03	-
1-20	217	B-40 with additive							
		ashes of fuel 1	1.21	11.70	18.00	1.40	5.0	1.90	14.5
		" " 2	20.6	11.90	10.80	1.14	11.1	2.90	17.0
		" " 3	25.1	16.8	17.70	1.20	10.1	2.80	11.00
		ashes " (average composition)	22.25	13.11	17.65	1.30	7.15	2.11	20.7
		deposits from guide blades	14.31	19.22	19.21	3.10	1.66	1.12	1.1
1-10	140	B-40							
		ashes of fuel	6.70	22.40	1.00	1.20	11.00	0.30	
2-6	140	B-40							
		ashes of fuel	6.46	28.14	1.80	1.10	7.40	2.90	13.6

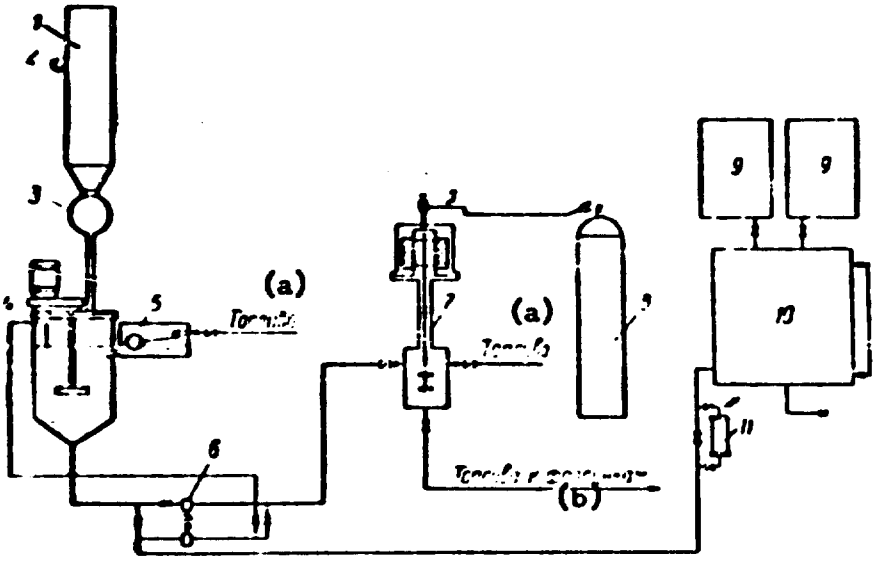


Fig. 3. Diagram of installation for introduction of additive into fuel.
1--bin of feeder; 2--vibrator; 3--feeder; 4--mixer; 5--float chamber; 6--pump; 7--mixer; 8--bottle with inert gas; 9--tanks for preparation of additive solution; 10--service tank; 11--fuel gauge.
KEY: (a) Fuel; (b) Fuel to burners.

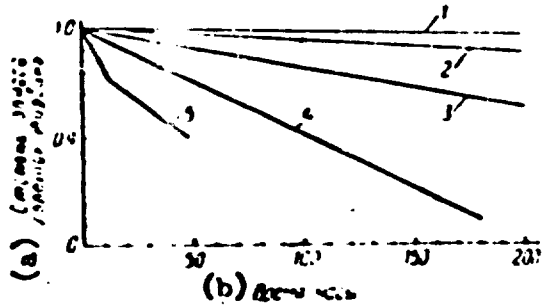


Fig. 4. Rate of jam of turbine during work of GTU on liquid fuel of different brands.
1--experiment 1-59; DT-1; 2--experiment 3-59; M-40 with additive; 3--experiment 1-59; M-40 with additive; 4--experiment 2-59; M-40; 5--experiment 1-59; M-40.
KEY: (a) Degree of jam of turbine blades; (b) Time, hr.

During complete burning of fuel in combustion chamber (when it does not burn on blades) it is possible to expect greater effectiveness of action of additive.

Questions of vanadium corrosion and ability of additive to prevent it were not studied directly on blades of turbine, inasmuch as temperature of gases washing them did not exceed 600°.

For investigation of these questions at GTU 600-1.5 special stand was created (Fig. 5). Gases from combustion chamber at 900° through intake pipe 1 pass water-cooled valve 2 and are divided into three flows. Each of them is cooled to

given temperature in mixer 3 by air and heads to chamber 4, in which in speci pack are placed samples of metals to be tested. Then gases through second v[illegible] 5 head to collector, where they are additionally cooled by air and enter chimne

Temperature of gases in packs is recorded by electronic potentiometer E[illegible]09 and is checked with the help of electronic regulators of VTI construction an[illegible] remote control columns with accuracy ± 5%.

First preliminary experiments on stand showed that during operation of G even on motor fuel DT-2 (Tables 1 and 2, experiment 1-40), containing less t[illegible] 0.002% V_2O_5 during only 100 hr, there is clearly expressed vanadium corrosion [illegible] steel EI405, EI612 and EYaIT at a temperature of 700 and 800°.

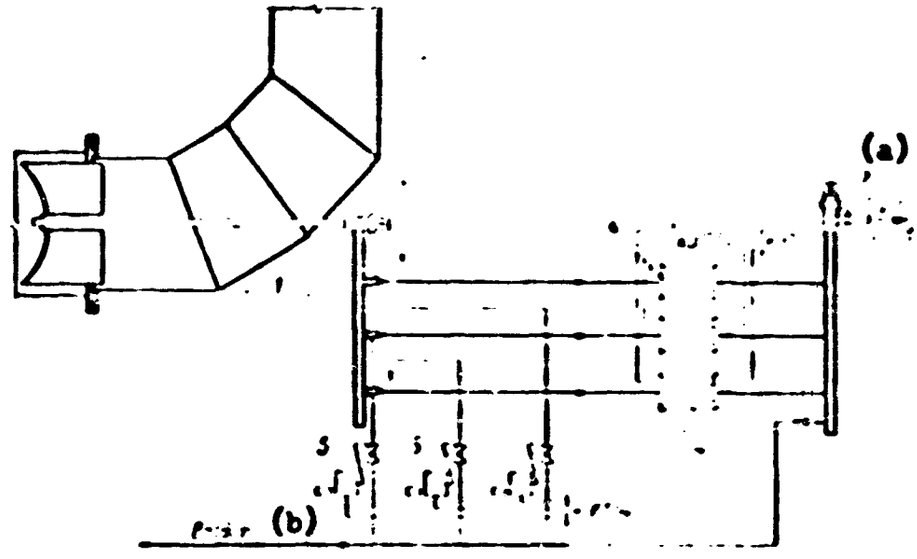


Fig. 5. Diagram of stand for vanadium corrosion.
1—gas intake pipe; 2—valve; 3—mixers; 4—chambers with samples; 5—remote control columns.
KEY: (a) Gas discharge; (b) Air.

Subsequent tests of certain fuels on GTU with use of stand give possibi[illegible] to definitize norm with respect to content of vanadium in gas turbine fuels.

During operation of GTU on the same motor fuel with additive of kaolin vanadium corrosion was not observed on one of tested metals.

During work of GTU on black oil 40 (Tables 1 and 2, experiments 2-40) th danger of vanadium corrosion was revealed in still greater degree.

At 600° the surface of metals was covered by large deposits, but corrosion was not observed. At 700° there were less deposits, but some metals (EI405) were corroded 30% and more. At 800° there were almost no deposits; corrosion was so great that some metals were completely turned into products of corrosion.

Conclusions

1. In laboratory conditions the effectiveness of action of around 20 substances as additives to fuel, preventing deposit of ashes in flow-through part of turbine and vanadium corrosion of blades of turbine was studied by static and dynamic methods.

The best of them were recommended for operational tests — montmorillonite, kaolin, dolomite, magnesium oxide and sulfate.

2. Experimental operation of gas turbine installation with capacity of 1500 hp on motor fuel DT-1 and DT-2 and on sulfurous black oils 40 and 60 was conducted.

Motor fuel containing around 0.002% vanadium pentoxide causes noticeable corrosion of steel EYalT, EI405, and EI612 at a temperature of 700° and above.

Normal work of GTU on black oil does not exceed 2 twenty-four hour periods due to fast jam of flow-through part of turbine by deposits.

According to preliminary data, kaolin, added in concentration of 0.2 wt.% to black oil, lowers jam of turbine, and in motor fuels prevents vanadium corrosion of indicated steel at a temperature of gas of 700°.

SOME DATA ON THE USE OF ANTICORROSIVE ADDITIVES TO RESIDUAL FUELS CONTAINING VANADIUM AND SULFUR

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B. I. Komarov, and G. I. Levinson
VNII NP*

In connection with development of oil-extracting industry chiefly in eastern regions of the country it is possible to expect that chief mass forms of gas turbine fuels will be obtained from sulfurous oils, which contain significant quantity of vanadium.

In residual oil products obtained at oil refining factories, content of vanadium is approximately the following: in naval black oil FS-5 (All-Union State Standard 1626-57) and in furnace black oil 20 0.003-0.007%; in black oils 40, 60, 80 — from 0.008 to 0.012 and in cracking-residual up to 0.020%.

Distillate fuels, obtained from sulfurous crudes (with end point around 480-500°), do not contain vanadium in noticeable quantities; however, content of sulfur remains significant in them. For instance, coking distillates, evaporating within limits of 150-500°, contain sulfur up to 2.5-2.8% and vanadium to 0.001%.

Such distillate fuels apparently can be used as gas turbine and motor fuels

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with use of additives removing sulfur corrosion.

One of the directions of work on lowering of gas corrosion during burning of heavy fuels is introduction of anticorrosive additives to fuels.

In this work are presented results of research of corrosion aggressiveness of ashes of different crudes of eastern deposits, and also the influence of addition agents containing basically magnesium, silicon and aluminum.

Study of Corrosion of Steel In Laboratory Conditions

In laboratory experiments samples of steel prepared in the form of plates with dimension around 10 X 10 X 4 mm were investigated. Plates were placed in quartz crucibles and heated in muffle furnace (control experiments). In that same furnace were placed crucibles with plates immersed in ashes, and also crucibles with plates, ashes and anticorrosive additive. Experiments were conducted at a temperature from 500 to 800° for 10 hr and in separate cases 50 hr. Ratio of weight of metal to weight of ashes amounted to approximately 10:1.

Scale and products of corrosion were removed from plates by electrochemical method in melt of alkali and soda (40% NaOH and 60% Na_2CO_3) at a temperature of 450-500°.

Corrosion was expressed by loss of weight of plates in g/m^2 hr and in wt. % with respect to weight of initial sample.

In laboratory conditions the intensity of corrosion of steels EI481, EI417 and EI607 was investigated (and also some others used for study of corrosion in gas flow). Steel plates of needed dimensions were cut by cold method without forging from metallic rods 250-300 mm in length.

As corrosion medium ashes of four oils were investigated, differing among themselves in chemical composition: 1) high-sulfur Yada crude, 2) sulfurous Romashkinskiy, 3) somewhat less sulfurous Tuymazy and 4) low sulfur Zhirnovsk crude with low content of vanadium. Research of corrosion action on metals of

ashes of sulfurous furnace black oil 60, which is prepared basically from cracking-residuum was started also.

Results of spectral analysis of ashes of petroleum residua are given in Table 1.

Table 1. Composition of Ashes of Petroleum Residua on the Basis of Spectral Analysis*

Element	Ashes, %				
	Romashkinskiy crude (V:Na= = 1:5.7)	Tuymazy crude (V:Na= = 1:1.7)	Zhirnovsk crude (V:Na= = 1:17.3)	Furnace black oil 60 (V:Na= = 1:2.6)	Rada crude (V:Na= = 1:1.5)
Sodium.....	20	8.5	16	15	17
Chromium.....	0.0033	0.008	0.0015	0.006	—
Aluminum.....	0.26	1.01	1.1	0.44	0.55
Strontium.....	0.097	0.015	0.018	0.1	0.012
Nickel.....	0.78	1.7	0.3	1.3	1.6
Magnesium.....	0.85	0.83	1.1	1.3	0.54
Manganese.....	0.15	0.069	0.020	0.021	0.12
Silicon.....	0.69	3.25	1.1	0.63	0.165
Tin.....	—	0.13	0.06	0.03	—
Lead.....	—	0.26	< 0.12	—	—
Calcium.....	4.4	3.4	4.5	6.2	2.0
Vanadium**.....	3.5	5.1	0.92	5.8	11.1
Copper.....	0.033	0.066	0.051	0.26	0.06
Zinc.....	—	0.78	—	—	—
Cobalt.....	0.057	0.125	0.039	0.13	0.12
Indium.....	—	0.1	—	—	—
Iron.....	1.4	8.3	2.6	1.4	1.5
Silver.....	—	0.0045	0.008	—	—
Titanium.....	0.01	0.04	0.03	0.03	0.023
Molybdenum.....	Not found				

*Carried out in laboratory of spectral analysis VNII (All-Union Scientific search Institute for Oil and Gas Refining and the Production of Synthetic Liquid Fuel).

**Determined by analytic method.

As anticorrosive additives clays were used: Crimean Keel, Troshkova, dolomite, kaolin, and also silicon dioxide, magnesium oxide, magnesium sulfate, polyalkylsiloxane and others.

All additives were thoroughly ground, dried at a temperature of 150° and sifted through sieves of 150-270 mesh.

Additives were taken in three concentrations by weight with respect to ashes 1:1, 1:2 and 1:3.

From the above-mentioned additives first of all compounds of magnesium in the form of magnesium oxide and magnesium sulfate were checked (the latter can be used in the form of aqueous solutions). Investigation of anticorrosive influence of magnesium sulfate in laboratory conditions at temperatures of 800° will not completely reflect its behavior in conditions of combustion of fuel, which occurs at significantly higher temperatures (temperature of decomposition of magnesium sulfate with formation of magnesium oxide is equal to 1124°). It is possible to assume that in conditions of gas flow the behavior of additives (in the form of magnesium sulfate and magnesium oxide) is identical.

Compounds containing silicon also are of great interest, since they do not form sulfates during addition to sulfurous fuel, and significantly increase the melting point of ashes of fuels containing vanadium.

Natural clays, investigated as additives to petroleum ashes, contained the following amount (on the basis of heated substance) of silicon dioxide: Crimean keel of Kurtsevo deposit up to 62% (and around 20% aluminum oxide); sample of Troshkova clay of Irkutsk region 50.5% (and aluminum oxide 45%); kaolin up to 40%. In experiments technical silica gel ASK was used also.

For comparison and estimate of separate components entering into the composition of natural clays, synthetic silicon dioxide and additives containing aluminum oxide 5 and 25% were investigated.

If additive possesses good anticorrosive properties, then after heat treatment mixture of ashes and additives is not sticky, light and loose.

Results of experiments on the study of corrosiveness of petroleum ashes on heat-resistant alloy steels and influence of used anticorrosive additives with

ratio of ashes to additive, equal to 1:3, are given in Table 2 and in Fig. 1.

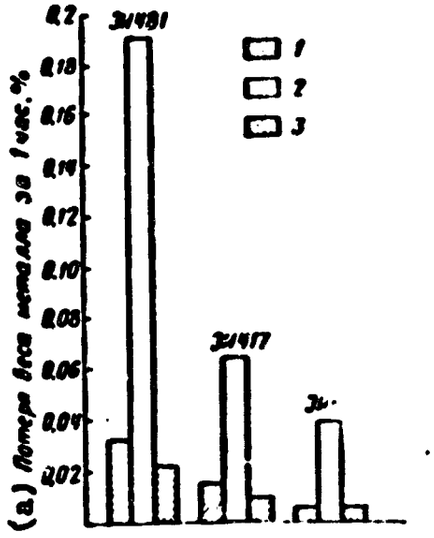


Fig. 1. Influence of addition of clay Crimean keel on lowering of corrosion.
1—control experiment; 2—ashes; 3—ashes and keel (1:3).
KEY: (a) Loss of weight of metal after 1 hour, %.

As results of experiments showed, corrosive action of ashes on alloys is lowered with addition of magnesium oxide to ashes in amount 1:1 by weight.

Steel EI417 contains large amount of chromium as compared to other samples, whose resistivity to vanadium corrosin. apparently is high.

Good results were obtained with the use of clay keep and kaolin, amount of which for complete removal of corrosive action of ashes is sufficient from 1:1 to 2:1 with respect to ashes.

With the use of synthetic silicon dioxide or silicon dioxide with aluminum oxide as additives, results were almost the same as with the use of clay keel or kaolin; optimum ratio of additive to ashes will be 3:1.

Consequently, it is more expedient to use cheap natural clays with high content of silicon dioxide and some content of aluminum oxide, and there is no necessity to obtain for this purpose purer products of synthesis.

During comparison of obtained data(from approximately 15 experiments on the average) on the corrosive action of ashes of Romashkinskiy crude on different alloys, it is possible to say that for steel EI481 average loss of weight of metal after 10 hr of tests at a temperature of 800° amounts to 1.92% instead of 0.33%, obtained in control experiments. For steel EI417 average loss of weight of metal in the same conditions during action of ashes is approximately 3 times less and amounts to 0.66% (and in control experiments 0.16%). The least losses of metal were obtained for steel EI607 — 0.35% with ashes and 0.06% in control experiments.

Table 2. Influence on Corrosion of Steel of Ashes of Romashkinskiy, Tuymazy, Rada and Zhirnovsk Crudes and Anticorrosive Additives*

Medium, in which sample was tested	Change of weight of plate					
	Steel EI481		Steel EI417		Steel EI607	
	g/m² hr	%	g/m² hr	%	g/m² hr	%
With ashes of Romashkinskiy crude (vanadium 3.5%, sodium 20%)						
Control experiment	2.5	0.33	1.3	0.16	0.6	0.06
Ashes	16.3	1.92	5.9	0.66	3.5	0.35
Ashes + keel	2.0	0.23	0.2	0.01	0.6	0.06
Ashes + kaolin	1.4	0.16	0.9	0.11	0.8	0.08
Ashes + synthetic silicon dioxide	3.7	0.43	0.9	0.10	0.5	0.05
Ashes + silica gel ASK	7.9	0.67	2.2	0.20	—	—
Ashes + dolomite	8.3	0.97	1.5	0.17	1.3	0.14
Ashes + magnesium oxide	3.0	0.35	1.5	0.15	0.3	0.03
Ashes + crystallized magnesium sulfate	4.0	0.36	1.8	0.18	—	—
Ashes + Troshkova clay	7.0	0.89	0.5	0.04	0.9	0.07
Ashes + silicone	9.5	1.33	4.5	0.48	0.9	0.15
Ashes + synthetic additive, %						
a) silicon dioxide 75 aluminum oxide 25	—	—	2.2	0.2	—	—
b) silicon dioxide 92 aluminum oxide 8	—	—	—	—	0.5	0.05
With ashes of Tuymazy crude (vanadium 5.1%, sodium 8.5%)						
Control experiment	1.3	0.15	0.6	0.05	0.7	0.05
Ashes	15.0	1.86	0.7	0.72	5.2	0.50
Ashes + keel	0.7	0.12	0.2	0.016	0.7	0.07
With ashes of Rada crude (vanadium 11.1%, sodium 17%)						
Control experiment	2.3	0.27	0.8	0.09	4.3	0.04
Ashes	24.9	3.09	1.0	1.10	9.8	0.95
Ashes + keel	2.2	0.27	2.5	0.26	8.4	0.081
With ashes of furnace black oil 40 (vanadium 5.8%, sodium 15%)						
Control experiment	1.1	0.13	0.4	0.04	0.4	0.04
Ashes	19.9	2.40	3.5	0.37	6.5	0.67
Ashes + keel	1.0	0.22	0.6	0.97	0.5	0.05
With ashes of Zhirnovsk crude (vanadium 0.92%, sodium 16%)						
Control experiment	1.6	0.29	0.7	0.07	0.5	0.05
Ashes	13.7	1.52	8.1	0.92	6.7	0.67
Ashes + keel	3.8	0.44	5.2	0.40	1.2	0.12

*Temperature 800°. Duration of experiment 10 hr. Ratio of additive to ashes 3:1 by weight.

Under the action of ashes corrosion of metals as compared to control experiments increases on the average 6 times for steels EI607 and EI481 and 4 times for steel EI417.

Increase of time of experiment from 10 to 50 hr leads to lowering of corrosion, calculated per unit of time.

Study of Corrosion of Steels in Gas Flow

Work has been started on study in gas flow of corrosive action of vanadium, sodium and sulfur, available in residual fuels, and also anticorrosive additives to fuel on materials used for manufacture of blades of turbines and on other materials.

At first stage work was conducted on sulfurous diesel fuel with additives of elements artificially introduced into it, both causing gas corrosion of material of blades of turbines, and also anticorrosive.

As raw material was used summer diesel fuel with content of sulfur of 1.0-1.6%.

Vanadium was fed into combustion chamber in the form of aqueous solution of vanadyl sulfate $VOSO_4$ in amount necessary for obtaining concentration of it in fuel to 0.02-0.04%.

As anticorrosive additive was added aqueous solution of magnesium sulfate $MgSO_4 \cdot 7H_2O$.

Weight ratio was studied V:Mg = 1:1.5 and 1:3.

Diesel fuel with these additives was burned in special installation, equipped with small-size combustion chamber and attachment with plates of materials to be investigated, fixed in flow of gases on exit of combustion chamber.

For approximation of conditions of action of products of combustion of fuels on plates of the materials to be investigated to the conditions of work of blades of GTU, plates are secured to rotor, mounted on ball bearings. During test rotor with plates revolves, in consequence of which local overheating (possible with

motionless plates) of separate plates because of irregularity of temperature field of flow of gases proceeding to plates is removed, and identical action of products of combustion of fuels on all plates fixed in attachment is ensured.

Diagram of installation is shown in Fig. 2. In diagram of small-size combustion chamber and attachment with plates are shown system of supply of basic fuel, including fuel tank 1, filters of coarse and fine purification 2 and 10, fuel pump 5, fuel preheater 9 and instrument 3 for measurement of fuel consumption; systems of supply of aqueous solutions of additives to fuel and directly to combustion chamber (shown by dotted line), consisting of dosage pump 6, consumption 8 and mixing 4 tanks and burettes 7, serving for adjustment and checking of supply of additive by dosage pump; systems of supply, consisting of compressor 11, oil separator 12, receiver 13 and standard measuring washer for measurement of air consumption 14; attachment with plates 15 and combustion chamber 16 with starter 17.

During test aqueous solution of additive by dosage pump was fed to mixing tank, fixed on line of suction of fuel pump. Surplus of fuel was dumped through reduction valve into mixing tank; thus, during work of installation part of fuel circulated through closed contour, which ensured good mixing of fuel with additive.

However, during test of diesel fuel with additive of vanadium in amount of 0.04% with respect to fuel, there occurred intense corrosion of mouth of atomizer of burner, which caused impairment of atomization of fuel and correspondingly, increase of deposit of scale in chamber and in flow-through part.

Therefore, it was necessary to refuse introduction of this additive into fuel. During further tests additive was injected directly into heat pipe of combustion chamber.

Corrosion aggressiveness of fuels is determined on installation with small-size combustion charber by the following method.

1. Plates of materials to be tested were weighed on analytic scales and secured in attachment.

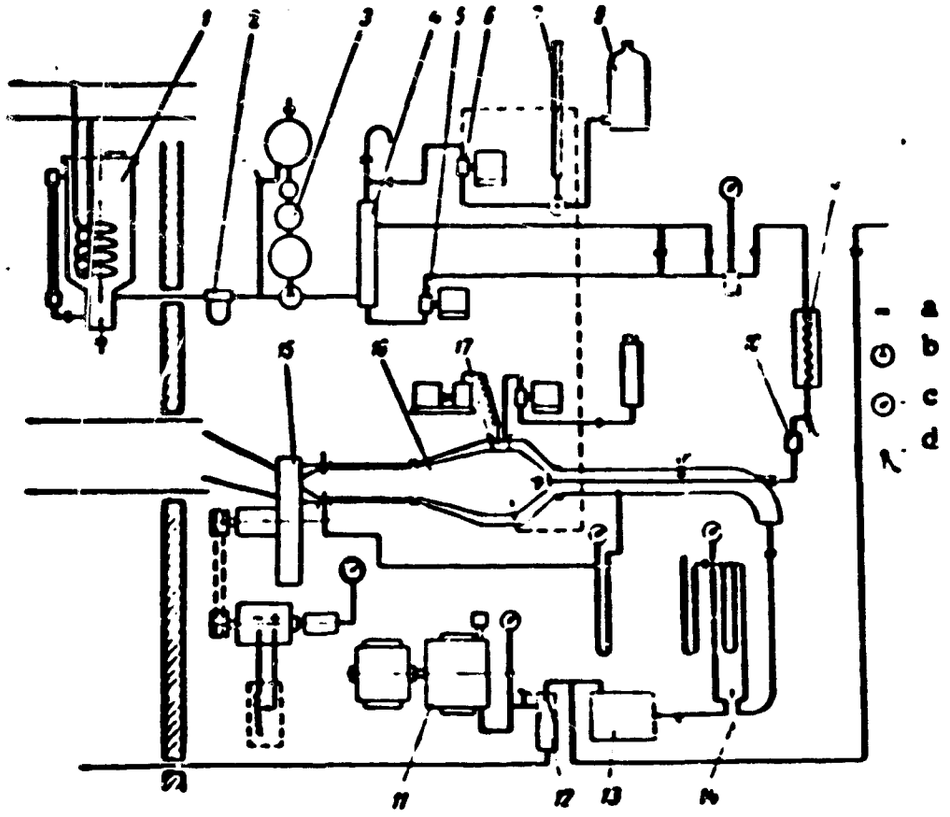


Fig. 2. Diagram of installation with small-size combustion chamber. a—valve; b—three-way cock; c—indicating manometers; d—point of measurement of temperature.

2. Regime of small-size combustion chamber on fuel to be tested (on diesel fuel with additive) established the following.

Consumption of air, kg/sec	0.25
Temperature of air on entrance into chamber, °C	80
Temperature of fuel before burner, °C	100
Number of turns of rotor of attachment with plates of materials to be tested, rpm	1500
Temperature of products of combustion before attachment with plates, °C	750

On this regime installation worked for the given prolonged time in 5 hr stages.

3. Corrosion aggressiveness of fuel and action of additives are estimated by loss of weight of plates during the test.

Data on corrosion aggressiveness of diesel fuel with additives are given in Table 3.

As follows from Table 3, products of combustion of sulfurous diesel fuel with vanadium additive in amount of 0.02% with respect to fuel at a temperature of 750° cause loss of weight of plates due to gas corrosion.

Table 3. Influence of Magnesium Sulfate on Change of Corrosion of Different Metals in Gas Flow on Small-Size Chamber Installation*

Brand of steel	Change of weight of plate after experiment in the presence of					
	Vanadium		Vanadium and magnesium (1:1.5)		Vanadium and magnesium (1:3)	
	%	g/m^2	%	g/m^2	%	g/m^2
EI81	0.170	20.7	0.039	4.6	0.037	4.2
EI607	0.096	11.8	0.040	4.9	0.052	6.0
EI417	0.160	18.6	0.120	14.2	0.067	7.8
EI612	0.066	8.6	0.042	5.6	0.033	4.3
EI726	0.058	7.2	0.028	3.4	0.040	4.9

*Time of experiment 30 hr. Temperature of experiment 750°.

Addition of magnesium sulfate lowered loss of metal 2-4 times, which corresponds to data obtained in stationary conditions. Increase (by weight) of amount of magnesium sulfate with respect to vanadium 2 times did not essentially change the obtained results.

During test in conditions of action of centrifugal forces on plates, plate of steel EI417 turned out to be less stable to gas corrosion. Besides increased loss of weight of plates of this steel, on their shafts deep cavities were formed, causing break of blades.

Results obtained during work of installation are preliminary; however, they confirm the above-stated results of anticorrosive action of magnesium sulfate during burning of fuels containing vanadium.

At Kolomenskiy diesel locomotive building factory together with VNII NP was studied the influence of high-sulfur fuel with small content of vanadium (less than 0.005%) on corrosion wear of steels of different brands.

One of such fuels is distillate of contact coking, recommended by VNII NP as gas turbine fuel for transport installations.

For clarification of corrosive action of gases obtained during burning of tested fuel, on unilocular stand behind combustion charber were placed samples of metallic plates of steels EI481, EI607, EI417 and EI723. Degree of corrosive wear of samples was determined just as in laboratory experiments -- by loss of weight of plates, expressed in wt.%. Data showed that corrosive wear after 100-hour test was insignificant.

Degree of corrosion did not exceed magnitudes which were obtained in laboratory conditions at a temperature of 800° in medium of air and were close to data obtained during work on diesel fuel on small-size chamber installation.

Conclusion

Compounds of magnesium and silicon are recommended as anticorrosive additive for wide stand tests during burning of sulfurous residual gas turbine fuels.

USE OF NEUTRALIZING SUBSTANCES IN MOTORS WORKING ON HIGH-SULFUR DIESEL FUELS

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For "neutralization" of aggressive oxides of sulfur to sulfurous fuels it was suggested to add salts of alkali metals and weak organic acids, zinc naphthenate and certain other products, in particular colloidal copper and organic phosphites and amines [1]. The opinion was declared that the action of amines is based on their ability to form during combustion ammonia, binding oxides of sulfur [2].

In foreign literature in recent years there have appeared many reports of advertising and patent character about additives to high-sulfur fuels.

There are data that the majority of these additives are complicated mixtures of aromatic hydrocarbons, more frequently homologues of naphthalene, with different metalorganic compounds or amines, easily soluble in fuel [1].

Authors conducted prolonged tests of diesel fuels containing up to 1.25% sulfur, with additive 0.5–0.8% of mixture of organic amines (content of nitrogen 11–14%). Experiments showed the ability of amines to lower corrosive wear and varnish-deposit in motors during their operation on high sulfur fuel; however, practical significance of this method is small, since organic amines, as other additives to fuel, are effective only when their content in fuel reaches 0.8–1.0%, which is absolutely unacceptable.

Proceeding from the evident position that effective beginning in organic amines is amine group, authors suggested to introduce ammonia or some ammonium salts directly into suction system of motor*.

First experiments, conducted in 1956 on motor $1Ch^{-10.5/13}$, working on fuel containing 1.25% sulfur, with supply into suction system of 20% aqueous solution of ammonium carbonate (0.03% of fuel, on the basis of $(NH_4)_2CO_3$), gave very favorable results — lowering of wear 2-3 times and complete prevention of scale and varnish-formation and sticking of piston rings. Later these experiments were repeated on a number of motors working on fuels containing up to 1.6% sulfur, with supply to suction system of from 0.08 to 0.16% (by weight to fuel) of gaseous ammonia.

Obtained curves of dependence of wear of motor $2Ch^{-8.5/11}$ with radioactive piston rings working on fuel containing 1.6% sulfur, on concentration of additives in oil and amount of ammonia supplied, show (Fig. 1) that the use of ammonia (0.08% of fuel) lowers wear to the magnitude which is observed during work of motor on low-sulfur fuel. For achievement of such a result with the help of the most effective additives to oil (IP-22 and VNII NP-360**) it is necessary to use them 10-12 wt.% of oil. If we take the average consumption of oil, equal to 5% of fuel, then consumption of these additives will amount to 0.5-0.6 wt.% of fuel, i.e., 6-7 times more than consumption of ammonia.

In Fig. 2 is shown the kinetics of wear of motor during work on oil AS-9.5 with different additives and on the same oil without additive, but with supply of ammonia.

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*Author's certificate No 115811, issued by Committee on Matters of Inventions and Discoveries attached to the Council of Ministers of USSR by declaration No 571926 of 25/IV, 1957.

**Additive designated by number and name of institute, All-Union Scientific Research Institute for Oil and Gas Refining and the Production of Synthetic Liquid Fuel.

Analogous data were obtained on motors IT-9-3 and 1Ch$^{10.5/13}$.

Simultaneously the formation of varnishes and scales sharply decreases and sticking of piston rings completely is prevented.

Increase of consumption of ammonia to 0.16% of fuel leads to further improvement of antiwear effect (Fig. 1).

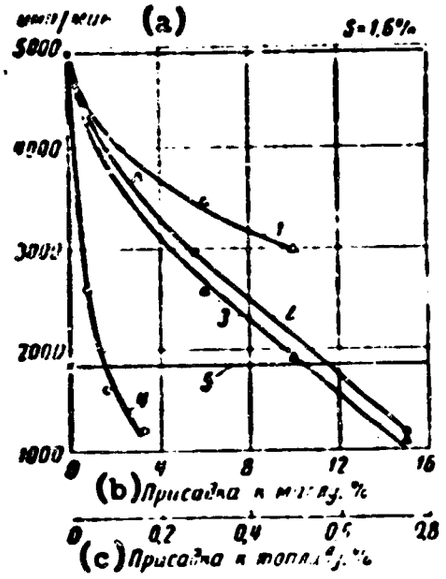


Fig. 1. Average rates of wear of piston rings of motor 2Ch$^{8.5/11}$ during work on oil with different additives.
1--Tsiatim-339*; 2--IP-22$_{to}$; 3--VNII NP-360; 4--NH_3; 5--DS, All-Union State Standard 4749-49.
KEY: (a) Imp/min; (b) Additive to oil, %; (c) Additive to fuel, %.

*Additive designated by name of institute, Central Scientific Research Institute of Aviation Fuel and Oils

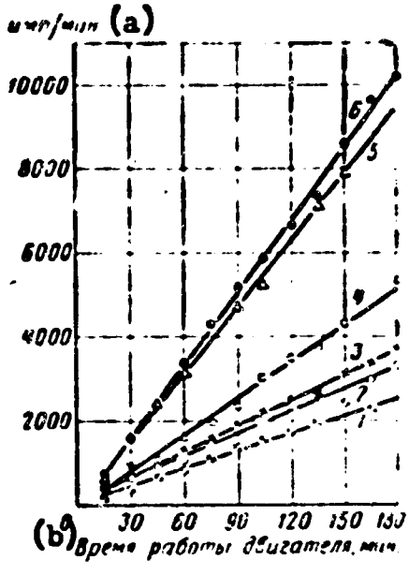


Fig. 2. Rate of wear of piston rings of motor 2Ch$^{8.5/11}$ during work on oil AS-9.5 with different additives (fuel containing 1.57% sulfur).
1--ammonia, oil without additive; 2--fuel according to All-Union State Standard 4749-49, oil without additive; 3--oil with 6% additive VNII NP-360; 4--oil with 3% additive DF-1; 5--oil with 3% additive Tsiatim-339; 6--oil without additive.
KEY: (a) Imp/min; (b) Time of work of motor, min.

Prolonged tests of engines ZD-6 and M-50f on fuels containing 1.20 and 1.57% sulfur with supply of ammonia completely confirmed its effectiveness. Some results of these tests are presented in Tables 1 and 2.

In TSNII MPS (Central Scientific Research Institute of Ministry of Railroads) 600-hour tests were conducted of engine 2D100 on fuel containing 1.1% sulfur, with supply of 0.14% ammonia, which also gave satisfactory results (Tables 3 and 4).

Table 1. Average Wear of Main Parts of Engine ZD-6 After 500-Hour Tests

Wear of parts of motor	During work of motor		
	On sulfurous fuel S = 1.25% and oil MK-22 with 3% tsiatim-339	On fuel S = 1.2% with supply of ammonia 0.16% and on oil without additive	On fuel S = 1.57%, with supply of ammonia 0.16% and on oil without additive
Pistons, mm.....	0.078	0.034	0.021
Cases of cylinders, mm.....	0.026	0.011	0.027
Main journals of crankshaft, mm..	0.008	0.004	—
Connecting rod journals of crankshaft, mm.....	0.006	0.004	—
Piston rings:			
average loss of weight, g.....	0.170	0.077	0.080
average increase of gap, mm....	0.120	0.110	0.100
loss of electricity, kg.....	0.210	0.050	0.130

Consequently, use of gaseous ammonia, fed together with air directly into chylinder of engine, is in principle a new and extraordinarily effective means of surmounting difficulties appearing during use in engines of high-sulfur fuels.

Tests of engines M-50f and 2D100 showed expediency of supply of ammonia with use of oil with commercial additive tsiatim-339 during work of engine on fuel containing more than 1% sulfur.

Analysis of exhaust for content of SO_2 and SO_3 during work of engine on sulfurous fuels without supply of ammonia and with ammonia showed sharp decrease of content of SO_3 in the second case with simultaneous proportional increase of share of SO_2 in exhaust gases, as is shown in Figs. 3 and 4.

Sharp decrease of content of sulfuric anhydride with simultaneous proportional increase of quantity of SO_2 in products of combustion completely explains (in the case of use of ammonia) how significant is decrease of wear of motor, and also decrease of formation of scale and varnishes observed with this on hot parts of motors, simulated in absence of ammonia by sulfuric anhydride dissolved in oil.

Table 2. Average Wear (in mm) of Main Parts of Engine M-50f

Wear of parts of engine	After tests of engine	
	on sulfurous fuel S = 1.2%, with supply of ammonia 0.15% and on oil MK-22 with 3% tsiatim-339	on nonsulphurous fuel and on oil MK-22
Cases of cylinders.....	0.027	0.037
Pistons.....	0.038	0.045
Average increase of gap in lock of piston ring.....	0.06	0.10
Main journals of crankshaft....	0.0026	0.0030
Inserts of main supports.....	0.021	0.015
Connecting rod journals of crankshaft.....	0.0023	0.003
Inserts of connecting rods.....	0.010	0.008
Bushing of piston head of connecting rod.....	0.017	0.018

Table 3. Wear of Main Parts of Engines 2D100 after 600-Hour Work

Wear of parts of motor	Cylinder	After tests on diesel fuel All-Union State Standard 305-58, S = 1.1% and	
		On oil DSp-11 All-Union State Standard 8581-57	With supply of 0.14% NH_3 and on oil DSp-11 All-Union State Standard 8581-57
Wear of pins, mm	Lower Upper	0.043 0.051	0.035 0.036
Increase of gap of first compressor rings	Lower Upper	0.990 0.625	0.800 0.305
Wear of first compressor rings on radius at 1-st point	Lower Upper	0.510 0.240	0.330 0.160
Decrease of weight of first piston rings, g	Lower Upper	8.120 4.550	6.850 3.390
Wear of journals of upper crankshaft, mm	Main and connecting rod bearings	0.033 0.009	0.028 0.009

Table 4. Scale and Varnish-Formation in 2D100 Engines after 600-Hour Work

Amount of deposit and state of rings	With supply of ammonia	Without supply of ammonia
Quantity of scale in exhaust collector, g....	1558	2146
Quantity of scale in exhaust windows, g.....	575	1018
Weight of deposits in centrifuge, g.....	1025	2080
Piston rings, piece:		
burning.....	1	9
dense.....	-	4

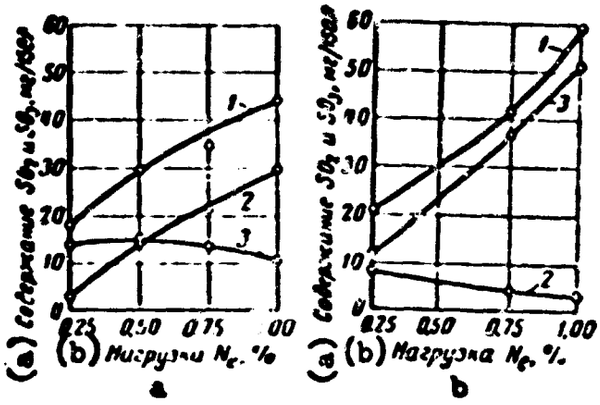
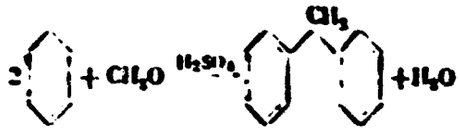


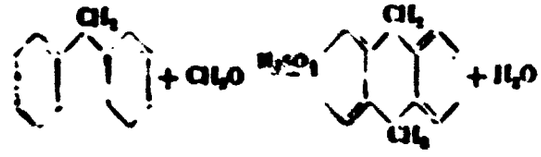
Fig. 3. Content of SO_2 and SO_3 in exhaust gases of engine 1Ch-10.5/13. a—fuel with content of 1.6% sulfur, without supply of ammonia; b—fuel with content of 1.6% sulfur with supply of ammonia (3 liters/hr). 1—SO_2 + SO_3; 2—SO_3; 3—SO_2. KEY: (a) Content of SO_2 and SO_3, mg/150 liters; (b) Load N_e, %.

In first approximation processes of formation of varnishes and scales, stimulated by SO_3 or sulfuric acid, can be subdivided into two types.

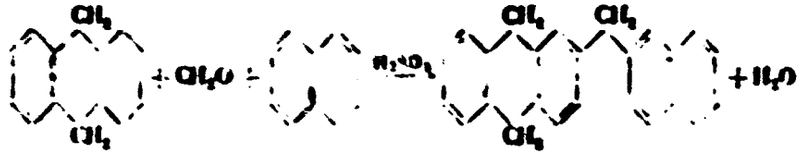
1. Condensation, involving aromatic hydrocarbons, aldehydes and peroxide, for instance according to diagram of Kastyukov [3, 4]:



(1)



(2)



(3)

Oxidation and further condensation of formed naphthene aromatic structures should proceed easily and rapidly with formation of high-molecular-weight annulated oxygen-containing compounds.

2. Formation of diarylsulfones, occurring as a result of interaction of sulfuric anhydride, sulfuric acid and sulfonic acids with aromatic hydrocarbons according to diagram:

$$SO_3 + ArH \rightarrow ArSO_3H \quad (4)$$

$$H_2SO_4 + ArH \rightarrow ArSO_3H + H_2O \quad (5)$$

$$ArSO_3H + ArH \rightarrow ArSO_2Ar + H_2O \quad (6)$$

During liquid-phase oxidation of sulfurous diesel fuels the authors experimentally separated sulfonic acids [5] and showed that their concentration in oxidized products depends on the content of sulfur in initial samples.

Investigation of deposit obtained after liquid-phase oxidation of Tuymazy diesel fuel containing 1% sulfur showed that it in significant part consists of compounds with general formula $C_nH_{2n-6} \cdot SO_2$ [5].

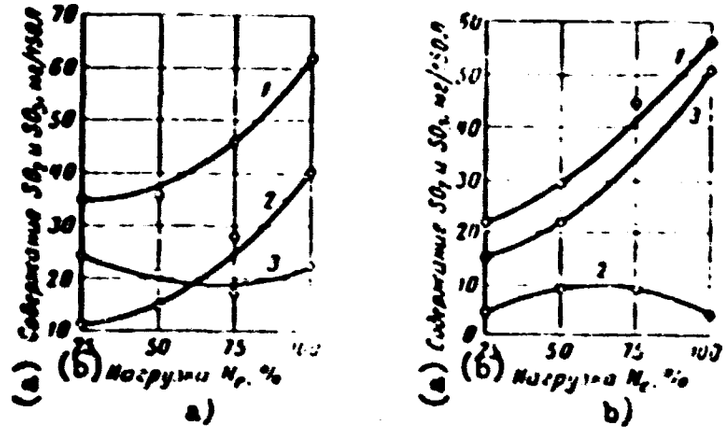


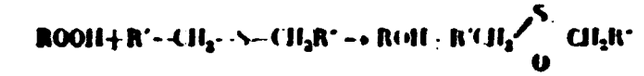
Fig. 4. Content of SO_2 and SO_3 in exhaust gases of engine 2Ch-8.5/11.
a—fuel with content of 1.25% sulfur without supply of ammonia; b—fuel with content of 1.25% sulfur with supply of ammonia (3 liters/hr).
1—$SO_2 + SO_3$; 2—SO_3; 3—SO_2.
KEY: (a) Content of SO_2 and SO_3, mg/150 liters; (b) Load N_e, %.

This confirms the significant role of sulfonic acids (and, consequently, SO_3) in the process of formation of deposits in oil and cylinder of engine. Consequently, with the use of sulfurous diesel fuels success in struggle with clogging of engine in significant measure depends on effectiveness of means preventing appearance of SO_3.

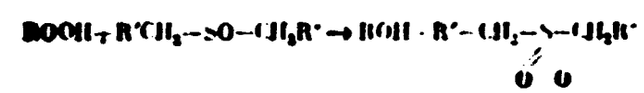
Obtained results (Figs. 3 and 4) indicate, apparently, the ability of ammonia to retard oxidation of SO_2 into SO_3.

For formation of SO_3 from SO_2 a significant energy content and presence of catalysts is required.

During combustion of sulfides, comprising larger part of sulfurous compounds of diesel fuels, CO_2, H_2O and SO_2 are easily formed. However, this direction of reaction is not the only one; during liquid-phase oxidation of sulfur-containing diesel fuels sulfides are turned into sulfoxides and sulfones according to the diagrams [6, 7, 8]:



(7)

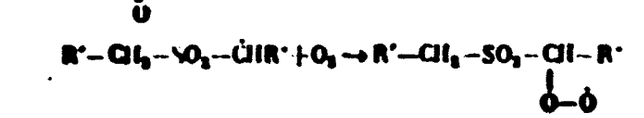


(8)

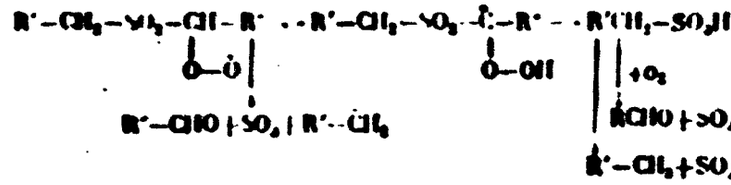
Sulfones do not destroy peroxides and are oxidized by molecular oxygen with formation of sulfonic acids or with direct yield of SO_3, which should be observed during high-temperature oxidation:



(9)



(10)



(11)

Formation of SO_3 from sulfide is facilitated if in pre-ignition period the latter succeeds in being oxidized into sulfoxide or sulfone.

Direction of attack of oxygen on CH_2 — group, adjacent to SO_2 group, is in accordance with idea about great mobility of its hydrogen atoms.

In this case, apparently, selective oxidation will be observed, leading to first formation of SO_3, still before complete combustion of all fuel occurs. Consequently, in cylinder of engine situation is created with which duration of stay of SO_3 is greater than of other intermediate products of reaction, which ensures possibility of interaction of SO_3 and H_2SO_4, formed on cooled surfaces, with oil and products of oxidizing decomposition of hydrocarbons, as was shown above.

From the suggested mechanism of appearance of SO_3 it follows that for retarding the process of its formation it is necessary to prevent oxidation of sulfides. It is necessary to assume that larger part of sulfones and their peroxides (or peroxide radicals) will be formed during high-temperature oxidation of drops of atomized fuel. Consequently, it is necessary to ensure destruction of peroxides (or their radicals) of sulfides, sulfoxides and sulfones in vapor phase.

Action of ammonia is connected, apparently, with its ability to react with peroxides of sulfur compounds and their radicals and thereby to prevent oxidation of sulfur to sulfuric anhydride. Action of ammonia presumably can be described by following diagrams of radical reactions:

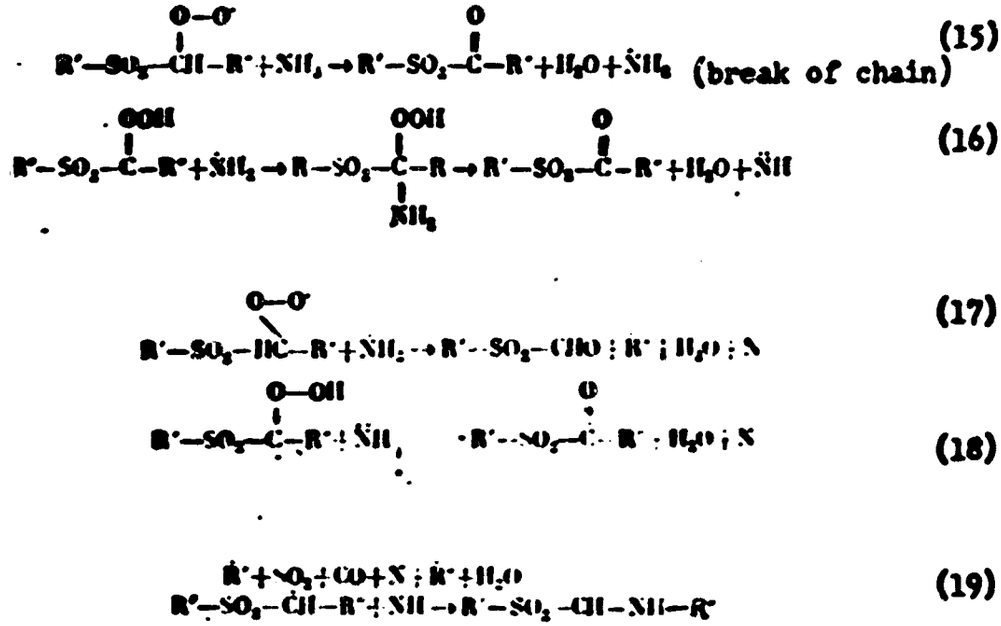
$$R'-SO_2-CH-R' + NH_3 \rightarrow R-SO_2-CH_2-R' + NH_2 \qquad (12)$$

(break of chain of oxidizing process)

$$R'-SO_2-CH-R' + NH_2 \rightarrow R'-SO_2-CH-NH_2-R' \qquad (13)$$

(break of chain of oxidizing process and formation of molecule of antioxidant)

$$R'-SO_2-CH-R' + NH_3 \rightarrow R' + SO_2 + R'CHO + H_2O + NH \qquad (14)$$



From the given diagram it is clear that the action of ammonia is not a monophasic process. Radicals $\ddot{N}H$ and $\dot{N}H_2$, formed in the process of reaction, play role of active inhibitors of vapor phase oxidation of sulfones, undergoing in usual conditions in cylinder of engine oxidizing decomposition earlier than hydrocarbons.

In the suggested diagram ammonia fulfills functions analogous to functions of antiknock compounds of motor fuels.

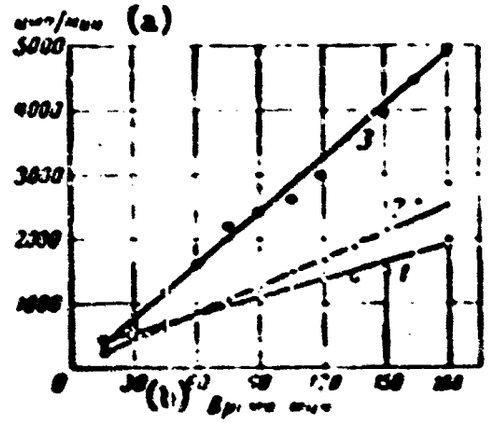


Fig. 5. Rate of wear of piston rings of engine 2Ch-8.5/11 during work on fuel with addition of T.E.L.
1—diesel fuel DS, All-Union State Standard 4749-49; 2—sulfurous diesel fuel with addition of 0.2% T.E.L.; 3—the same fuel without addition of T.E.L.
KEY: (a) Img/min; (b) Time, min.

Proceeding from what has been described, it is possible to assume that introduction of strong antiknock compound into sulfurous diesel fuel should effectively promote decrease of concentration of SO_3 in products of combustion. This position was confirmed by experiments: introduction of 2 ml of liquid P-9 (0.2% T.E.L.) per 1 kg of fuel containing 1.57% sulfur lowered 3 times the concentration of SO_3 in exhaust gases of engine

$2Cn^{-8.5/11}$ (from 22 mg to 6 mg per 100 liters of gases). With this the share of SO_2 was increased correspondingly.

On the same motor with radioactive piston rings during addition to fuel of T.E.L. kinetics of wear of piston rings was established (Fig. 5).

Diagrams of wear were removed during work of motor on fuel containing 1.57% sulfur, on the same fuel with addition of 0.2% T.E.L. and with low-sulfur diesel fuel DS, All-Union State Standard 4749-49 (0.15% sulfur).

As can be seen from Fig. 5, addition per 1 kg of fuel of 2 mm of liquid P-9 lowers rate of wear of piston rings approximately 60%. Exceeding of degree of wear of rings obtained on low-sulfur fuel DS, All-Union State Standard 4749-49, amounts to in this case 30% as against 150% during work without addition of T.E.L.

What has been said confirms explanation of mechanism of formation of SO_3 in diesel fuel and action of ammonia as means retarding the process of formation of SO_3. Simultaneously, the new (in principle) direction in the solution of problem of the use of high-sulfur fuels in engines was established.

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ANTIOXIDANTS FOR FUELS

I. V. Rozhkov, Z. A. Sablina, A. A. Gureyev, and Ye. N. Kornilova

Antioxidants are necessary for automobile gasolines containing components of thermal and catalytic cracking, for ethylated aviation gasolines of direct distillation, for jet propellants, tractor kerosenes and diesel fuels.

Needs of practice make it necessary to study peculiarities of action of inhibitors of oxidation depending on properties of the oil product, which should be protected from oxidation by molecular oxygen.

The influence was investigated of certain inhibitors on kinetics of oxidation of kerosene fraction of fuel containing 5.5% unsaturated hydrocarbons (fraction 150-250 of synthine). Fuel (50 ml) was oxidized at 130° by atmospheric air without mixing. Antioxidants (diphenylamine, paraoxydiphenylamine, α-naphthylamine, hydroquinone, β-naphtol, "Ionol") were introduced into fuel both up to beginning, and also in process of oxidation.

K. I. Ivanov and Ye. D. Vilyanskaya [1-3] on the basis of research on oxidation of petroleum oils suggested to divide antioxidants into three groups depending on action on kinetics of oxidizing process in its different stages (classification of antioxidants is listed in given collection in article of K. I. Ivanov, Ye. D. Vilyanskaya and A. A. Luzhetskiy, see p. 239).

Conducted research showed that, according to the character of influence on oxidation of synthine, all investigated antioxidants should belong to group III.

Effectiveness and mechanism of action of inhibitors of oxidation are not determined only by structure of the inhibitor itself, but depend on a number of factors, in particular on type of oxidized hydrocarbons. This conclusion agrees well with positions of theory of chain reactions [4]. In a decisive manner the mechanism of action of inhibitor depends on chemical composition of fuel to be oxidized also when oxidation of the latter is initiated by nonhydrocarbon additive contained in fuel. For instance, during oxidation of aviation gasolines containing around 0.1% molecular (0.33 wt.%) tetraethyllead (T.E.L.), initiation and development of oxidizing process in significant degree are determined by free radicals of two types, supplied by T.E.L.

$$Pb(C_2H_5)_4 \rightarrow Pb(C_2H_5)_3^{\cdot} + C_2H_5^{\cdot}$$

It was established [5] that antioxidants of phenol type, able effectively to retard oxidation of fuels containing unsaturated hydrocarbons, and also sulfanilamide compounds and disulfides (which are exclusively effective antioxidants for oils) do not at all retard the process of decomposition of T.E.L. in ethylated aviation gasolines. This fact is explained, apparently, by incapability of shown antioxidants to localize alkyl lead radicals.

Significant effectiveness is possessed by shielded alkylphenols (for instance, "Ionol") and aminophenols. Representative of the latter — paraoxydiphenylamine, found practical application as anticxidant for native ethylated aviation gasolines.

Additives, distinguished by mechanism of action on oxidation of hydrocarbons in absence of T.E.L., during liquid-phase oxidation of ethylated gasolines all belong to retarders only of group II [6]. This is explained by the fact that in conditions of liquid-phase oxidation T.E.L. decomposes with formation of active products easier than peroxides of hydrocarbons of saturated structure, and initiates decomposition of peroxides. Influence of peroxides on kinetics of oxidation of

aviation gasolines is not determining. Main role is played by active products of decomposition of T.E.L., identically formed both in the beginning and also during development of oxidation. Therefore, antioxidants effective for ethylated aviation gasolines are not distinguished by kinetic mechanism of their action.

For stabilization of ethylated aviation gasolines usually is taken 0.004-0.005 wt. % of paraoxydiphenylamine. According to All-Union State Standard 1012-54, the period of stability of aviation gasolines after addition of paraoxydiphenylamine should be not less than 8 hr, which ensures possibility of storing them without loss of condition for 3-4 years.

For checking the chemical stability of aviation gasolines with respect to the period of stability, we developed a special method [6].

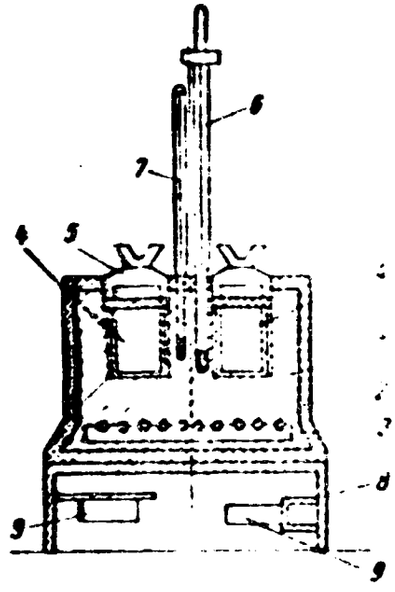


Fig. 1. Instrument for determination of stability of fuels.
1—aluminum bath; 2—insulation; 3—electrical plate; 4—little bombs; 5—cover over little bomb; 6—contact thermometer; 7—checking thermometer; 8—support; 9—relay.

In 1960 a new instrument was designed for determination of periods of stability of aviation gasolines, used simultaneously for checking the stability of ethyl liquid and thermal stability of jet propellants. This instrument (Fig. 1) is a thermostat, having aluminum bath, in hollows of which are inserted four little bombs of stainless steel. Little bombs have threadless self-sealing locking device. Fuel (25 ml) is poured into small glass beakers, placed inside the little bombs. Operating temperature (110°) is maintained with accuracy ±1°.

For thrifty expenditure of antioxidants, correct selection of their concentrations has great value. Antioxidants, besides their own direct purpose -- break of chains of oxidation, are expended on side reactions. In particular, impractical expenditure of antioxidants essentially is influenced by metals, especially copper and its alloys [11]. The higher the initial concentration of antioxidant, the greater amount of it is expended on side reactions. The most economical method of stabilization of fuels is continuous introduction into fuel of liquid antioxidant in small doses, or submersion in volume of fuel of definite quantity of slightly soluble solid antioxidant [11].

In recent years for obtaining of automobile gasolines products of catalytic processes have been used more widely. Autogasoline A-72 contains around 70% of component of single-stage catalytic cracking and has high induction period (500--1200 min).

However, in "strict" conditions of storage this gasoline is oxidized very rapidly (for instance, at 45-50° after 40 days of storage the content of actual resins in gasoline was increased from 4 to 36, and after 85 days -- to 1200 mg/100 ml). Therefore, gasolines of catalytic cracking, as is also done abroad, must be stabilized.

Of substances investigated by us, the most effective turned out to be antioxidant FCh-16; addition of this antioxidant in concentration of 0.03 wt % allows us to obtain completely stable gasoline of single-stage catalytic cracking.

Antioxidant FCh-16 is phenols, extracted from waters of semicoking of Eremkhovskiy coals; content of phenols in commercial product is more than 85%.

According to laboratory research [8, 9], FCh-16 for fuels containing unsaturated hydrocarbons (gasolines, kerosenes, components of diesel fuel), is the most effective antioxidant, exceeding (during comparison in practically used concentrations) wood-tar antioxidant, "Ionol" and paraoxydiphenylamine.

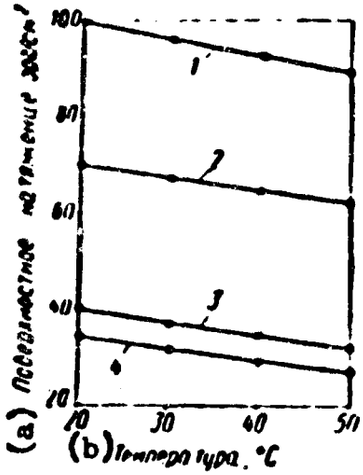


Fig. 2. Influence of antioxidants on surface tension of fuel of expanded fractional composition (60-260°).
1--fuel without additive; 2--with 0.05% FCh-16; 3-- with 0.05% "Ionol"; 4--with 0.01% paraoxydiphenylamine.
KEY: (a) Surface tension erg/cm^2; (b) Temperature, °C.

Automobile gasoline containing 71.2% component of thermal cracking, and aviation fuel containing 30% cracking component, were stabilized by addition of FCh-16 (respectively 0.065% on cracking component and 0.05 wt.% on prepared fuel) and were placed in storage in real conditions in southern zone in region of Baku. During 2.5 years of storage rise of actual resins and increase of acidity in fuels was not observed. These data, obtained during experimental storage of fuels in real conditions, once again indicate that product FCh-16 is highly effective antioxidant for fuels containing unsaturated hydrocarbons.

For fuels of expanded fractional composition antiwear properties, have great operational value since these fuels have lower "lubricating ability" than kerosenes [10]. Antiwear properties of fuels render significant influence on period of service of fuel pumps [10].

Additive FCh-16, just as other industrial antioxidants -- paraoxydiphenylamine and "Ionol", is surface active material (Fig. 2) and increases antiwear properties of fuels.

Antioxidants are necessary not only for jet propellants containing components of thermal cracking, but possibly also for jet propellants obtained by direct distillation. At high temperatures (150-200°), characteristic for conditions of supersonic flight, in aviation kerosenes insoluble deposits are formed. These deposits are products of oxidation, mainly of nonhydrocarbon (sulfur, nitrogen,

oxygen and other) compounds contained in fuels of direct distillation. Stability of fuels against influence of high temperatures obtained the name of thermal stability.

During prolonged storage of fuels their thermal stability worsens; analogous effect is observed also during artificial "aging" of fuels.

Addition to fuels of antioxidants protects them from aging in process of storage and allows us to preserve initial level of thermal stability of fuels (Fig. 3).

Some antioxidants (for instance, "Ionol") can not only preserve the thermal stability of fuels during storage, but during addition in increased (around 0.5%) concentrations also increase it. However, "Ionol" effectively delays formation of deposits in fuels only up to a temperature of 150°.

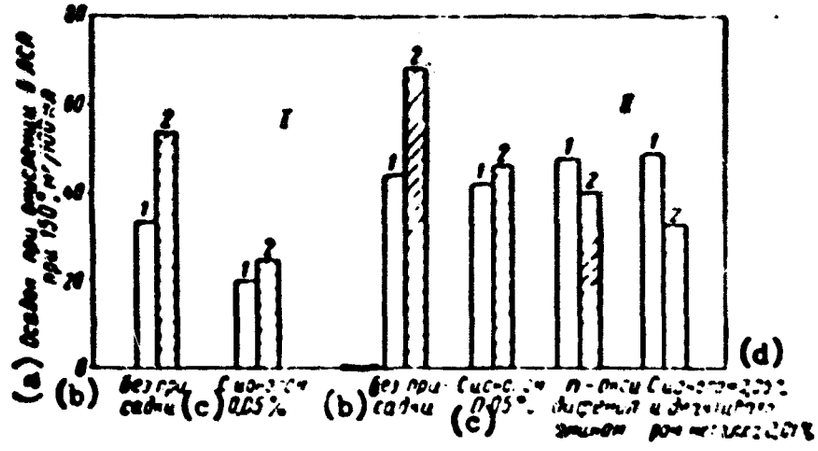


Fig. 3. Influence of antioxidants on thermal stability of fuels during their "aging" (temperature 50°, period of storage 4 months).
I—fuel T-5; II—fuel T-1; 1—up to storage; 2—after storage.
KEY: (a) Deposit during oxidation in LSA at 150°, mg/100 ml; (b) Without additive; (c) With "Ionol" 0.05%; (d) paraoxydiphenylamine with Ionol 0.05% and deactivator of metal 0.01%.

Additives, possessing not only antioxidant, but simultaneously also dispersive (peptizing) properties, most effectively increase the thermal stability of fuels, (see table).

Influence of Stabilizing and Dispersion Agents on Increase of Thermal Stability of Fuels

Fuels	Test temperature, °C	Thermal stability, min	
		without additive	with addition of stabilizing and dispersion agent
T-5	180	90	>300
T-5	200	240	>300
Sulfurous diesel	160	10	>300

Thermal stability of fuels in Table 2 is expressed as time (in minutes) of clogging by deposits of filter of laboratory installation, simulating fuel system of motor.

Conclusions

1. Effectiveness and mechanism of action of inhibitors of oxidation are not determined only by structure of the inhibitor itself, but depend on type of oxidized hydrocarbons and presence in fuel of monhydrocarbon additions (for instance, T.E.L.).

2. For fuels containing unsaturated hydrocarbons, the most effective antioxidant, exceeding wood-tar antioxidant, "Ionol" and paraoxydiphenylamine, is product FCh-16. Additive FCh-16 simultaneously increases also the antiwear properties of fuels.

3. Antioxidants are necessary also for some fuels of direct distillation (for instance jet), to prevent significant lowering of "thermal stability" of these fuels during prolonged storage.

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