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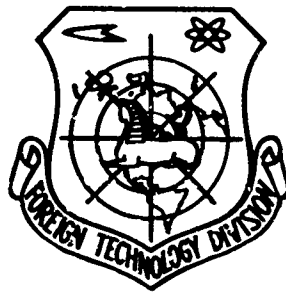
FOREIGN TECHNOLOGY DIVISION



ADDITIVES TO OILS TO LOWER FRICTION AND WEAR

By

I. E. Vinogradova



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EDITED MACHINE TRANSLATION

ADDITIVES TO OILS TO LOWER FRICTION AND WEAR

By: I. E. Vinogradova

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TRANSLATION DIVISION
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I. E. Vinogradova

PRISADKI K MASLAM DLYA SNIZHENIYA TRENIYA I IZNOSA

Pod redaktsiyey doktora tekhn. nauk
professora S. E. Kreyna

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ABSTRACT: The book covers antifriction, antiwear, and antiseizure additives to lubricants. The book is based on Soviet and foreign literature and includes some new experimental data obtained at the All-Union Scientific Research Institute for Oil and Gas Refining and the Production of Synthetic Liquid Fuel (VNIINP). Part I of the book is devoted to the various types of defects and their origins. The main requirements set forth for various additives are also listed in this chapter, which includes a detailed review of the U. S. gear lubricants. Part II covers the classification, properties, preparation, function, selection, and application of additives according to the type of equipment and the working conditions. The effect of various additives on the friction coefficient and surface wear is discussed in Ch. 1 of Part II. Data on 10 Soviet and 35 foreign lubricant additives containing S, P, Cl, and Zn are tabulated. The Soviet additive MDS (alkyl dithio esters of fatty acids) is listed as an effective antiwear additive. Sulfur-treated terpenes are used as multifunctional (antiwear and anticorrosive) additives under the trade name of VTU MNP564-55 (known in the United States as "Stain Add" and "Amoco-48"). Barium and zinc dialkyldiaryldithiophosphates (DF-1, DF-11, "vniinp-354," V-501, LZ-317, and others) are the anticorrosive, antiwear motor oil additives widely used in the USSR. The Soviet additive EZ-2 (castor oil treated with P_2S_5) is described as a

valuable antiwear and antifriction additive. Among others, the following antiseizure Soviet additives are listed: LZ-6/9 (ethylene dibutyl xanthate); LZ-24 (ethylene diethyl xanthate); LZ-23 (ethylene diisopropyl xanthate); and LZ-19 (ethylene diisoamyl xanthate). Among the chlorinated paraffins, the Soviet additive "nami-T-122" (containing 40% Cl) is recommended as an antiscuff additive to gear box lubricants. The Soviet additive EZ-5 is listed among the sulfur-chlorine-containing additive with high antiseizure properties. The use of MoS_2 as an antiseizure and antiwear additive to lubricants applied at high temperature and of other metal-containing additives is discussed in Ch. 7 of Part II. The book discusses the function of additives, including the reaction between the additive and a metal under various conditions, surface film formation, stability of the film, and the effect of various substituents in organic phosphorus- and chlorine-containing additives. A new mechanism of the MoS_2 function is proposed, which is based on experimental data obtained by the author in collaboration with Ye. I. Petyakina. Recommendations are given for selecting additives to lubricants for automobiles, turbines, milling equipment, metal-cutting equipment, and textile machinery. Tabulated information on the type of additive recommended for various automobile parts is presented. English translation: 96 pages and 114 references: 36 Soviet and 78 non-Soviet.

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U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere.
 When written as ѣ in Russian, transliterate as yě or ě.
 The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

↓
THE
ANNOTATION

~~This~~ book is devoted to oil additives for lowering friction, wear and preventing of jamming of friction surfaces.

CONSIDERATION
IS GIVEN TO
THE ~~This~~ book contains materials on antifriction, antiwear and antiburr additives to oils, about contemporary methods of selecting additives and about the mechanism of their action. ~~We consider~~ the principles of selecting oil additives for specific types of equipment and requirements for additives taking into account the conditions of work of machines of different assignment.

This book is designed for engineering technicians and scientists, studying the questions of application of lubricating materials in various areas of technology.

INTRODUCTION

At the XXII Congress of the Communist Party of the Soviet Union and the November (1962) Plenum of Central Committee of the Communist Party of the Soviet Union special attention was allotted to questions of increasing the productivity of labor, technical progress, economy of means and materials.

Additives to lubricating oils, by improving the conditions of friction, promoting the lowering of wear of friction details and preventing the jamming of surfaces, should be considered as a means of fighting for economy of metals and increase of between repair runs of equipment. The interest in additives increases in connection with increase of loads and forcing of operating conditions of machines and mechanisms. However, one should not consider that additives can serve as universal means for all forms of damage of friction surfaces. In connection with this in first part of book we consider the types of damages to surfaces and the causes of their appearance. We also indicate in what cases one or another oil additive can be expediently applied.

The basic part of this book contains information about the types of antiburr and antiwear oil additives, on the contemporary view of the mechanism of their action, the knowledge of which allows us to correctly approach the selection of additives, which improve the condition of work of mechanisms.

It is necessary to turn special attention to the contradictory nature of the basic requirements presented to antiburr additives, from one side, they have to have maximum chemical activity with respect to metals to create films preventing the jamming of surfaces, from the other side, they should not evoke

metal corrosion. This obliges us in developing antiburr additives to study their properties and influence on friction from all sides to confidently select those compounds which satisfy such complicated, contradictory requirements.

The problem of scientific selection of oil additives is still far from solved and a number of positions and terms also remain debatable. However, the latest works on synthesis and investigation of oil additives by Soviet and foreign scientists discovered much in the nature of these processes occurring during friction, and to a significant degree they allow us to depart from the emirics existing till now in development and selection of additives.

This book contains recommendations on selection of additives according to the types of equipment and separate mechanisms of machines.

The book is basically built on literary material, but also contains data which are the result of joint works of collective of [VNII NP] (ВНИИ НП):

Ye. I. Petyakina, F. Ya. Shames, V. P. Karamnova and the author of this book.

I: REQUIREMENTS FOR ADDITIVES TO IMPROVE THE CONDITIONS OF FRICTION

I.1. ROLE OF ANTIBURR AND ANTIWEAR ADDITIVES TO OILS IN DIFFERENT WORKING CONDITIONS OF FRICTION PAIRS

Additives to lower wear and friction and prevent jamming of surfaces cannot be universal means equally effective in all operating conditions of friction pairs. It is necessary to introduce additives into oil to improve the conditions of friction only in absolutely definite cases of abnormal and unsatisfactory work. Due to this the selection of oil with additives should be based on an analysis of the conditions of friction and the character of damage to surfaces, which determines the expediency of application of oils with this type of additives. Random selection of additives may cause not a positive, but a negative effect, unexpected by increasing wear or rendering an undesirable influence on the physicochemical properties of oils. Because of this, before formulating the requirements for additives to improve the conditions of friction, it is necessary to consider the characteristics of the conditions of friction and types of damage to surfaces.

During liquid friction the surfaces are completely separated by the lubricant, and a relative shift occurs between its layers. Wear of surfaces is absent, and friction, except for mechanical parameters, geometry of contacting details and expenditure of lubricant, is determined only by the viscosity of the lubricant at the operating temperature and does not depend on its polar or chemical activity.

Liquid friction can most easily be ensured in the case of contact of bodies with small distinction of surface curvature, e.g., for shaft in a slip bearing.

However, it can also appear during contact of bodies with great differences curvature, e.g., in toothed gears, roller bearings, etc., and so forth, if these friction pairs work at very high speeds.

During liquid friction it is no longer necessary to use additives to lower friction and wear.

During semiliquid friction, although the basic load is carried by the oil film, nevertheless surface contact is observed, always accompanied by wear of surfaces. Semiliquid conditions of friction are observed in most slip and roller bearings and also in gear transmissions. In those mechanisms, which during steady-state operation work in conditions of liquid friction, semiliquid conditions also exist during starts.

Because of this during semiliquid conditions of friction in a number of cases it can appear expedient to apply additives to lower wear and friction.

Mixed friction is called semidry, dry and liquid with predominance of dry contact. Semidry friction is characterized by high wear of surfaces, in a number of cases leading to jamming. Here we need to use additives to lower wear and prevent jamming of surfaces. During application of surface-active additives adsorbed on surfaces in the form of a film with an oriented molecular structure there occurs a transition into conditions of threshold friction, at which the surfaces are separated by a layer of lubricant so thin that its properties differ from the volume properties of the lubricant. The oriented molecular structure determines the ability of such films to lower friction independent of viscosity properties ("oiliness") and increase the load of jamming of surfaces ("durability of film"). However, from the point of view of preventing of jamming, chemically effective antiburr additions are more effective: on the metal surfaces they form compounds of lowered durability, easily destroyed during grasping of surfaces.

Analyzing the character of damages to surfaces allows us to establish that this friction regime limits their efficiency. In investigating the character of damages it is often possible to recognize the cause of their appearance and to find methods of their removal [1].

The state of surfaces can change from slightly rough in ordinary operation conditions to completely destroyed as a result of causes determined as wear.

plastic flow, jamming, contact fatigue, corrosional chemical influence and other damages appearing during incorrect treatment of details.

Of all the enumerated types of damages to friction surfaces only wear and jamming can appear in conditions of imperfect friction, i.e., at semiliquid, semidry and threshold conditions. These types of damage to surfaces are characteristic for heavily loaded gear transmissions, especially for hypoid automobile transmissions, for slip bearings, working in conditions of poor lubricant or made of materials with low antifriction qualities, and also in roller bearings during unfavorable operating conditions, especially in the presence of preliminary deformation of rollers.

The appearance of fatigue phenomena very little depends on the lubricating regime. Fatigue painting of surfaces can appear during liquid conditions of friction under the affect of hydrodynamic pressure in the oil film and its sharp breakdown upon getting out of the contact region which is accompanied by overstrains of the material of slip or roller details [2], leading to contact fatigue and painting. In absence of lubricant during point and linear contact of surfaces fatigue painting rarely appears only because this is prevented by progressive wear and jamming of surfaces, which are continuously renovated.

Fatigue painting is the most wide-spread type of damage to heavily loaded surfaces and limits the efficiency of gear transmissions and roller bearings most. The properties of the lubricant can affect the appearance and development of fatigue painting. It is known that increasing the viscosity of the lubricant increases the limit of contact fatigue of surfaces [3], lowering the coefficient of friction acts in that same direction, but the chemical action of active antiburr additives can lead to lowering the limit of contact fatigue [4,5].

Correctly selected antiburr additives should not evoke corrosion of metal surfaces, however, if specially strong antiburr properties are required, it is necessary to compromise and put up with moderate corroding action of antiburr additives.

Thus, we cannot expect that antiburr additives will prevent all types of damage to surfaces. The basic assignment of antiburr and antiwear additives to lubricating oils is to prevent jamming and lower the progressive wear of surfaces. These additives can also affect other types of damages, however, in

such cases their role is secondary and can be either positive or negative.

Let us consider the principles of selecting oil additives for specific types of friction nodes.

As a rule, roller bearings do not need oils with antiburr additives.

Slipping between rollers under high contact loads is small, in consequence of which the local contact temperatures are low. This explains the fact that cases of jamming in roller bearings are not wide-spread.

The most wide-spread type of damages in roller bearings is fatigue painting, or pitting. When the rollers accomplish only small oscillatory movements the characteristic type of damage to surfaces is fretting corrosion, or brinelling.¹

In connection with this when selecting oils for roller bearings one should first of all be careful to ensure maximum contact durability of rollers, and for oscillatory movement of bearings, prevent fretting corrosion. In the first case it is recommended to apply high-viscous oils, which according to available information [3,4,5], increase the limit of contact fatigue. In the second case one should ensure abundant feed of oil to surfaces to remove abrasive oxidation particles from the region of friction in good time.

When roller bearings have the same lubricating systems, as gear wheels working in specially heavy conditions and requiring antiburr additives, we must consider that the latter affect pitting of balls in a different manner. From strong antiburr additives containing several active elements, one should sooner expect a negative action on contact fatigue of surfaces than a positive one.

Table 1 gives the results of Scott's experiments [4] on the effect of additives in a paraffin base oil on ball pitting. The tests were conducted on a four-ball machine, where the lower balls freely roll in a cup during rotation of upper ball with speed of 1500 RPM. The load on the upper ball was 600 kg.

¹The process of fretting corrosion during small oscillatory movement the oxidized particles of metal wear are not removed from the region of friction and, having higher hardness than the initial metal, act as an abrasive producing local holes.

Table 1. The Effect of Additives and Fatigue Painting of Palls

Additive	Concentration of additive in oil %	Average time before beginning of painting, min
Without additive	-	41
Disbutylphosphite	1	42
"	10	8
Tricresyl phosphate	1	40
"	10	43
Elementary sulfur	0,4	58
Elementary sulfur + lead naphthenate	10	50
Chlorinated paraffin	1	35
"	5	14
"	10	6
Graphite	1	109
Molybdenum disulfide	1	79

From the table it is clear that phosphorous esters either affect fatigue durability of surfaces very little (tricresyl phosphate) as compared to pure mineral oil, or even lower it (dibutylphosphite); the elementary sulfur additive evidently increases contact durability somewhat, chlorinated paraffin lowers it, and such additives as graphite and molybdenum disulfide sharply increase the time before the beginning of pitting.

We must note that graphite and molybdenum disulfide simultaneously lower fretting corrosion somewhat, but they are comparatively weak antiburr additives.

Gear wheels most frequently fail due to painting of the working surfaces of teeth.

At specially high contact loads on teeth and sufficiently high relative speeds of slip of the surfaces the efficiency of gear wheels is limited by jamming of teeth surfaces. In this case it is necessary to add antiburr additives to oils.

Low efficiency is characteristic for worm transmissions, which taking into account losses on friction in transmission supports is equal to 0.7-0.9 depending upon the number of approaches of worm, angle of ascent of the screw line and other factors.¹ Connected with this is the significant heat emission during operation of worm transmissions and their inclination to jamming as a

¹The efficiency of gear transmissions is 0.96-0.99.

result of disturbance of the oil film under the effect of friction temperature.

In an overwhelming majority of cases worm transmissions fail due to jamming of the working surfaces of the worm pair (worm and worm wheel). This makes it necessary to use antifriction material for worm wheels (most frequently bronze).

Light jamming appears in the form of the bronze smearing on surface of steel worm. During heavy jamming burrs appear on the working surfaces of worm pair simultaneously accompanied by increase of coefficient of friction in engagement.

An increase in efficiency of worm transmission, i.e., lowering of losses on friction, can be attained in two ways: 1) by guaranteeing liquid friction due to more favorable kinematics and geometry of engagement or due to application of high-viscous oil; and 2) by lowering the coefficient of friction as a result of application of special antifriction additives to oils. Application of antifriction, polar-active materials to oils for worm transmissions is also expedient because during starting and stopping a mixed character of friction is always present. To prevent wear and jamming of working surfaces it is necessary to combine antifriction additions lowering friction with antiburr components in oils for worm transmissions.

Slip bearings most often fail as a result of wear and jamming of surfaces, although correctly designed, well prepared and normally exploited bearings can work for a very long time.

Wear of bearings appears mainly during starting and stopping of shaft, when the friction regime is the heaviest due to the hydrodynamic wedging effect of the oil film being absent or very small then. Because of this, to lower friction in moments of starting and stopping, and also to create a good threshold film it is recommended to add antifriction and antiwear additives to oils for slip bearings.

Jamming appears during overheating of bearings caused by intensive formation of heat of friction during operation. In this case antiburr additives are ineffective. Overheating may be eliminated only by correct selection of oil viscosity and increasing its flow through the bearing.

In conditions of threshold friction, at small speeds of relative slip of slider along the guide, it is important to guarantee constant and low coefficient

of friction. The independence of coefficient of friction from speed removes the possibility of appearance of undesirable relaxation oscillations (jumps during friction).

In these cases it is expedient to apply antifriction additives to oils [6, 7]. Such additive can simultaneously lower wear of guides at small slip speeds of sliders.

Absolutely analogous conditions exist in lubricated friction clutches, where it is also necessary to guarantee a coefficient of friction that does not change with speed. Here, as above, antifriction additives, stabilizing friction are used [8].

I.2. Classification of Oil Additives to Improve Conditions of Frictions, Their Requirement and Areas of Application

Oil additives to improve conditions of friction can be divided into three basic types according to their character: 1) antifriction, 2) antiwear and 3) antiburr.

The basic requirements for these additives are the following.

Antifriction additives have to lower and stabilize the coefficient of friction; antiwear additives should eliminate progressive wear of surfaces during moderate and high loads; antiburr additives should increase load of jamming and soften the process of jamming, decreasing surface damage and friction.

However, in a number of cases there should be specific requirements and, furthermore, we should add to them a number of secondary ones, without observance of which normal exploitation of oils with additions is impossible.

1. By preventing jamming of surfaces, antiburr additives whose mechanism of action consists of chemical reaction with the metal surface should not increase wear at moderate loads as compared to wear on pure oil, i.e., should not be chemically aggressive. When the antiburr additive by itself cannot ensure this condition, a special antiwear component, preventing progressive wear of surfaces should be provided.

2. Additives should not evoke corrosion of steel and nonferrous alloys at operational temperatures of oil and rusting of steel surfaces in conditions of heightened humidity. If, however, the additive cannot ensure this condition,

a special anticorrosive component preventing aggressive action of the additive should be added.

3. Additives have to possess stability of properties in operation in accordance with their special purpose assignment, i.e., should not lose antiburr ability, antiwear or antifriction properties as a result of reaction with metal or any other transformations.

4. Additives have to be thermally stable in a given range of temperatures, should not decompose and should not precipitate.

5. Additives have to be soluble in base oils and stable in solution during storage. If the additive gives a colloidal solution in oil, it should not be soluble in water, specially when due to operating conditions water can get into the lubrication system.

6. Additives should not negatively affect any of the physicochemical properties of the base oil, should not worsen its thermal stability, viscosity-temperature properties, should not lower the temperature of flash or increase the temperature of thickening, etc.

7. It is desirable that the additive not have a sharp odor since this will prevent its use in oils used in closed locations.

8. Additives should not destroy lining materials (rubber, leather, etc.).

9. If additives that improve friction promote oil foaming or worsen its demulsifying ability components preventing these phenomena should be provided (antifoam or demulsifier).

10. The technology of producing additive should not be too complicated, and the raw materials should be sufficiently accessible.

11. Antiburr additives to oils for hypoid automobile transmissions have to ensure the work of gear teeth surfaces without jamming on very different regimes: both at high contact loads and low speeds and at high speeds and impact loads on gear teeth.

As additives to lower shading and wear and prevent jamming the following types of compounds are applied in pure form and in combination:

- 1) Animal or vegetable fats and fatty acids;
- 2) Organic compound of sulfur;
- 3) Organic compounds containing halides (mainly chlorine);

- 4) Organic compound of phosphorus;
- 5) Organic compound of nitrogen;
- 6) Different compounds of metals (e.g., lead soaps, oxidized and sulfur compounds of molybdenum, sulfur compounds of tungsten, organic compounds of zinc, colloidal iron and others);
- 7) Compounds containing several active elements in one molecule (sulfur, chlorine, phosphorus and others).

All these additives have the ability to simultaneously lower friction and wear, and also to prevent jamming, but in different degrees depending on the character of the compound and its concentration in the oil.

The first of six enumerated types of compounds lowers friction most and prevents jamming least. Thus, an additive of this type, having high surface-active properties, can practically be considered antifriction, but not antiburr.

At the dawn of development of technology animal and vegetable fats were the first lubricating means. At present they are applied only as additives to mineral oils for heavily loaded slip bearings and worm transmissions. They are rejected as additions to oils for lubricant of cylinders of piston engines (with the exception of steam engines), compressors and engines of internal combustion inasmuch as they lower the resistance of oils to oxidation.

Antiwear additives are applied in oils to lubricate mechanisms whose surfaces do not carry high loads, but because of unfavorable kinematic or temperature conditions, due to poor lubricant or chemically aggressive influence of medium are subjected to progressive wear. Bearings of semiliquid friction, pairs, performing return - forward movements - piston groups of internal combustion engines, operate in these conditions.

Antiburr additives of average activity are applied in oils to lubricate heavily loaded industrial gear transmissions, where heightened wear is observed and cases of jamming of gear teeth surfaces are met. Among such transmissions are reducers and gear cages of mechanisms of rolling mills, automobile power transmissions (with the exception of hypoid transmissions, for which strong antiburr additives are needed), etc. In these cases sufficiently effective one additives, constituting a compound with one active elements (sulfur or chlorine).

Of the three enumerated types of additives antiburr are used most; the basic region of their application is automobile transmission.

Antiburr additives were first applied in the 1920's in connection with the use of hypoid transmissions on automobiles. The additives were selected purely empirically, and only in the last two decades have a number of works appeared dedicated to the mechanism of action of antiburr additives and theoretical foundation of their application. Although hypoid transmissions have a large advantage from the point of view of simplicity of teeth and construction possibilities, according to conditions of friction the work of teeth of such gears is significantly complicated. The high contact pressures and slip speeds cause intensive heat emission, which for hydrodynamically unfavorable geometry of teeth and relatively high actual (but not nominal) area of contact leads to disturbance of the oil film and intensive development of the process of jamming. Therefore, exploitation of hypoid transmissions is impossible without application of oils with strong antiburr additives.

The high effectiveness of strong antiburr additives is ensured by presence of several active elements. This may be attained by application of a composition of a number of compounds, each of which contains only one active element, or one compound with several active elements in its molecule. The effectiveness of these additives depends, of course, on the character of the compounds; however, selection of components of strong antiburr additives will be successful when a composition of compounds containing different functional groups supplementing one another can thus be obtained.

Strong antiburr additions should not be applied at moderate conditions of friction, when there is no danger of appearance of jamming of surfaces, since, being aggressive, they can evoke heightened wear and corrosion of metal. For instance, it is not recommended to apply in automobile transmissions boxes oils with strong antiburr additives intended for hypoid transmissions.

The first oils for gear transmissions were high-viscous oil products, containing an additive of active sulfur. In 1937, 90% all lubricants applied in hypoid transmissions belonged to the type of lead soaps with active sulfur.

During the Second World War in the United States and England it became necessary to create universal oils with additives, which could be applied not

only in hypoid transmissions of passenger automobiles, but also in transmissions of other types of self-propelled and other equipment. In connection with this it was undertaken to develop additives of a new type in exchange for lead naphthenate and sulfurized fat additives.

From 1940 foreign technicians began to introduce chlorine compounds into oils containing additives of lead soaps and sulfur, these oils are applied even till now mainly for hypoid transmissions of trucks.

It was found that additives consisting of organic compounds of sulfur and chlorine possess greater universality than additives containing lead soap. Therefore up to 1945 oil with sulfochloro-containing additives were widely applied, but after 1945, besides compounds of sulfur and chlorine, compounds of phosphorus were introduced into antiburr additives [9].

The introduction of frictional mechanisms of block differentials lubricated from one system with gears and having frictional disks made from materials destroyed under the action of certain chemically active additives, and also necessity of guaranteeing a constant coefficient of friction (independence of it from speed and exclusion of jumps during friction) even more complicated the question of selecting additives to oils for heavily loaded transmissions. In connection with this, starting from 1953 and up to 1960, in foreign lands work was conducted to create a new type of additive to automobile transmission oils [10, 11].

The fruit of this work was GL-4 oil, as was assumed, universal for all operating conditions and for all forms of automobile and other self-propelled equipment. According to the patent data the additives to this oil are multicomponent. They include an antiburr additive, (sulfur- and chlorine-containing compounds), an iwear component (zinc dialkyldithiophosphate acid is also simultaneously an anticorrosive and antifriction component [12,13,14]. Depending upon the intensity of operating conditions of transmissions the concentration of additives in the oil can change from 3 to 15%.

Let us give the results of appraising the behavior of old and new types of additives in oil according to the methods of the United States at different

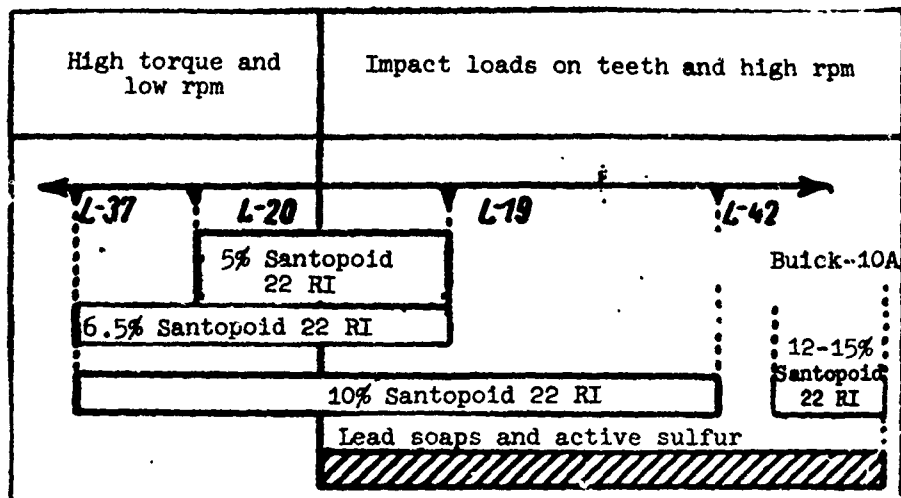


Fig. 1. Regions of regimes of satisfactory work of additives containing lead soap and active sulfur and additives containing a sulfur-chlorine component gray-chloric horse-nt and zinc dialkyldithiophosphate (Santopoid 22 RI and Santopoid 23 RI).

test regimes in near axles of automobiles (Fig. 1): 1) at high moment and low speeds (CRC L-20 and CRC L-37) and 2) at high speeds with sharp braking, provoking impact load on teeth of gears (CRC L-19 and CRC L-42) [10, 11].

The CRC L-20 method, fulfilling the specifications of the US Department of material supply of troops (MIL-L-2105) recently was replaced according to specifications MIL-L-002105A on GL-4 oil by a new, more rigid method, CRC L-37.

Impact high-speed tests are calculated to evaluate the behavior of oils in transmissions of light automobiles, for which a ride with sharp braking in the city is characteristic. According to the old specifications MIL-L-2105 the CRC L-19 method consisted of rolling and two impact high-speed cycles of tests. At present for GL-4 oil according to MIL-L-002105A this method is replaced by the more rigid CRC-L-42, which consists of three cycles. Even more rigid impact high-speed tests are conducted according to Buick-10A method.

Successive trials at different conditions allow revealing the differences

in behavior of additives in oil depending upon test conditions in transmissions of automobiles; this is illustrated by the data of Figure 1. The region of satisfactory work of oil with additives of lead soaps and active sulfur is limited by the shaded band; oil with Santopoid 22 RI acts differently depending upon concentration of the addition (see in Figure 1 the white bands with indication of percent of additive in oil) [14]. To the right in order of increasing rigidity of tests are located the regimes of high-speed tests, to the left in order of increasing rigidity of regimes (from right to left) are represented the tests at high torque and low speeds.

As can be seen from Figure 1, oil with additive of lead soaps and active sulfur acts satisfactorily during regimes of impact high-speed tests characteristic for ride of passenger automobiles in cities, and does not pass the tests at high torque and low speeds. Oil with small concentration of Santopoid 22 RI additive (5%) satisfactorily passes the CRC L-19 and CRC L-20 tests, i.e., corresponds to the old specifications on oils MIL L-2105. At concentration of 6.5% the additive also satisfies the more rigid, CRC L-37 method. Increasing the concentration to 10% gives positive results of testing by the CRC L-42 impact high-speed method, i.e., satisfies the new specifications of the US Department of Material Supply of Troops MIL L-002105A on automobile transmissional oils. Finally, for the oil to pass the test according to the Buick-10A method, it is necessary to bring the concentration of addition Santopoid 22 RI in oil to 15%.

In this the remaining new additives also act: already in small concentration they are effective during work at high torque and low speed, corresponding to the conditions of ride of trucks: but to guarantee the work of transmissions at impact high-speed regimes of passenger automobiles a sufficiently high concentration of these additives is required in the oil.

In metallurgical machine building to lubricate roller gears and power reducers of rolling mills, carrying high impact loads, usually oils with additives of lead soaps and sulphurized fats are applied. Lead soap, besides good antiburr properties, possess high demulsifying ability, which is very important, since water frequently gets into lubricating systems of mechanisms of rolling mills, this water is passed under high pressure to knock the sinter

from the rolled metal.

In recent years antiburr additions for turbine transmissions were also developed.

Because turbine oils move to turbine mechanisms from a single circulatory system of lubricant and simultaneously service power reducers and bearings of liquid friction with babbit filling, they have to possess heightened antiburr properties and should not evoke corrosion of nonferrous alloys or wear of slip bearings. This last condition is especially important, since an aggressive action on the working surface can lead to increase of gaps in bearings and disturbance of their hydrodynamic characteristics.

Hydrotransmissions united with toothed transmissions in diesel locomotives, automobiles and the like, recently obtaining wide use, made it necessary to develop oils with antiwear additives.

For such additives for this goal the most useful turned out to be bimetallic salts of dialkyldithiophosphoric acids (salts of barium and zinc), since the barium salts ensure the necessary washing properties, and zinc dialkyldithiophosphates possess the best antiwear properties and simultaneously increase the load of jamming of surfaces.

In textile machine building antifriction additives are mainly applied to spindle and machine oils. In such a way power consumption is lowered, which to a significant degree determines the price of textile production. Recently there have been attempts to increase the stability of spindle oils, in order to increase the periods of continuous work of spindles. Stoppages of machines during production of yarn to replace the oil and wash the step bearings of a large quantity of spindles sufficiently increases the cost of production. In connection with this stabilizing and washing additives are now introduced into spindle oils in combination with antifriction additives.

For ringspinning machines it is important to lower the friability of thread, connected with jamming between ring and runner due to insufficient antiburr and antifriction properties of lubricating materials or due to the presence of deposits on ring surfaces. Therefore the development of oils for these mechanisms goes towards selecting the appropriate additives and improving the stability of oils.

Gears of metal-cutting machines do not carry high loads. Therefore, selecting antiwear additives to oils for gear transmissions of machines is not necessary. Development of oils for metal-cutting machines was conducted in direction of selecting antifriction additives, ensuring smoothness of movement of supports or face plates along the guides of machines [6].

Methods of testing oils with additives are illuminated in literature [7], therefore in this book the author does not consider them.

II. SELECTING OIL ADDITIVES TO IMPROVE CONDITIONS OF FRICTION

II. 1. CONTEMPORARY DIRECTION IN SELECTING ADDITIVES TO IMPROVE CONDITIONS OF FRICTION

A. Antifriction Additives

As was indicated above when friction surfaces are operating it is important to: 1) lower friction; 2) lower wear; and 3) prevent jamming of surfaces.

These conditions are not always directly interconnected, i.e., maximum lowering of friction will not always be followed by minimum wear of surfaces and, conversely, maximum lowering of wear is not necessarily accompanied by minimum losses of power.

In most cases it is most important to prevent damage to the surface, however, there is also a need in selecting oil additives to stabilize lower friction. Such antifriction additives or additives improving oiliness are ce-active materials.

Especially high surface-active properties are possessed by fatty acids adsorbed on the metal surface in carboxyl groups and capable of a light shift between the facing radicals of neighboring molecules.

The ability of polar-active organic compounds with long chains to lower friction was first investigated by Gardi, who found that with increase of the hydrocarbon chain length the coefficient of friction drops and that the lowest coefficients of friction drops and that the lowest coefficients of friction are obtained during lubrication with fatty acids, and the largest during lubrication

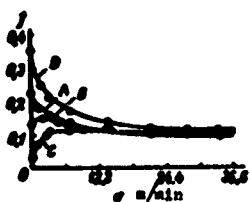


Fig. 2. The effect of anti-friction additives on change of coefficient of friction (f) with slip speed (v). A) 0.6% sulphurized sperm oil; B) 5% sulphurized sperm oil; C) 0.6% limiting fatty acid with long chain; D) mineral oil without additive.

with paraffins.

Good anti-friction and additives are the natural fats of animal and vegetable origins, constituting esters of glycerine and high-molecular fatty acids.

Other types of surface-active materials containing carboxyl groups are resinous acids. Tall oil applied for production of additives improving the conditions of friction is a mixture fatty and resinous acids and is a byproduct sulfate cellulose production.

Finally, a third type of surface-active material containing carboxyl group are the naphthenic acids; these are monobasic acids containing alkylated cyclopentane rings.

The average esters of polybasic acids or polyatomic alcohols to a significant degree lose their anti-friction properties due to their molecules being adsorbed on metal in a lying position [20]. In connection with this incomplete esters preserving carboxyl or hydroxyl groups are more effective anti-friction additives.

Among the anti-friction additives of this type, used in foreign lands, is, e.g., pentaerythritol monooleate.

Figure 2 gives the results of Sprag and Cunningham's experiments on the effect of anti-friction additives to mineral oil on change of coefficient friction with speed [8]. This research was conducted to develop a fluid with special anti-friction characteristics preventing vibration during friction at the moment of starting disk friction clutches.

Pure mineral oil gives a coefficient of friction strongly changing due to slip speed (see Figure 2). As a result relaxation oscillations appear, i.e., jumps during friction at the moment of braking. A somewhat more sloping characteristic is obtained with a 0.6% sulphurized sperm oil additive. The addition of 5% sulphurized sperm oil and, to an even larger degree, 0.6% limiting fatty acid with a long chain lowers the static coefficient of friction (see the start of curves at $v = 0$) in comparison with the kinetic. Certain anti-friction additives in combination with antioxidants (for instance, with zinc dialkyldithiophosphate lose their anti-friction properties during friction in the presence of copper alloys.



Fig. 3. Lowering the coefficient of friction of cork and plumbous bronze on steel depending upon the additive applied to oil. Dotted line — coefficient of friction for mineral oil without additive; C) steel; B) cork; B) bronze (8% Pb); C) additive of sulphurized sperm oil; D) additive of zinc dialkyldithiophosphate.

oil applied for removal of jumps during friction in guides of metal-cutting machines [VNIINP: All-Union Scientific Research Institute for Processing Oil and Gas and Production of Artificial Liquid Fuels]. Figures 4 and 5 give the

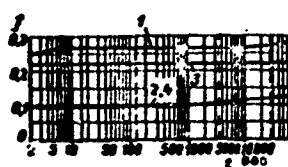


Fig. 4. Dependence of coefficient of static friction of cast iron on cast iron on the duration of motionless contact during lubrication by different oils. 1) industrial oil 45; 2) industrial oil 45 + 3% oleic acid; 3) industrial oil 45 + 10% chloroparaffin; 4) VNIINP-401 oil.

As can be seen from Figure 3, zinc dialkyldithiophosphate, which is an inhibitor of corrosion and oxidation, does not affect the coefficient of friction of cork on steel lubricated by oil with sulphurized sperm fat additive, but brings to zero the antifriction effect of this additive during friction of bronze on steel. This result is natural, inasmuch as in presence of such active metals as copper alloys sulphurized sperm oil acts not so much as an adsorptive, but as a chemisorbative.

Among the salts of fatty acids able to stabilize the coefficient of friction one should mention aluminum stearate, contained, e.g., in [VNIINP-401] (ВНИИП-401)

results of testing different oils in guides of metal-cutting machines [6]. VNIINP-401 oil with aluminum stearate additive gives the lowest value of the coefficient of static friction depending upon duration of surface contact (Fig. 4) and the most constant coefficient of friction depending upon slip speed (Fig. 5).

At high specific loads on the surface polar-active antifriction substances evoke heightened wear of surfaces due to dispersive action, i.e., the penetration of surface-active molecules in microscopic cracks, spreading under influence of internal pressure of the oil film (Rebinder effect).

This explains the results obtained by Larso and Perry [16], who investigated the effect of polar-active additives to SAE-10 oil on wear of friction surfaces.

The test was conducted on a four-ball machine (rpm of upper sphere 700, constant load on upper sphere 7 kg, temperature of oil 130°C) according to the following method.

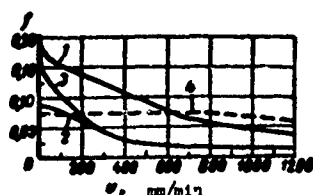


Fig. 5. Dependence of coefficient of friction of cast iron on cast iron on the slip speed during lubrication by different oils. Conditional designations, see Fig. 4.

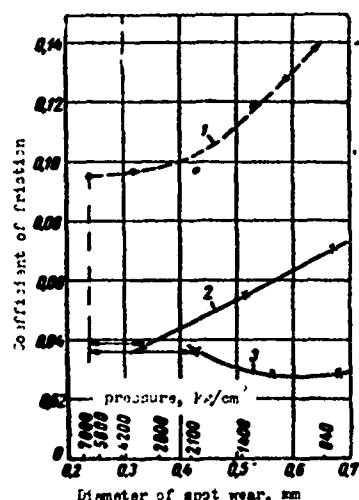


Fig. 6. The affect of polar-active materials on friction and wear of steel surfaces. 1) mineral oil SAE-10; 2) palm oil; 3) mineral oil SAE-10 with 1% oleic acid.

as compared to pure mineral oil, with the exception of lead naphthenate, which in general somewhat lowers friction.

Lecithin, a mixture of esters of fatty acids and phosphoric acid, also lowers friction.

The dependence of the coefficient of friction on concentration of polar-active substances at specific load of 1000 kg/cm^2 is shown in Fig. 8.

To preclude the effect of lubricants on flow of spot wear in the first period of tests, on surface of balls a hole was produced under, lubrication by the same SAE-10 oil for 1, 5, 15, 30, 60 and 120 minutes. After each such period of processing pure oil was poured out and the cup was filled with the test lubricant. Then the machine was operated until the coefficient friction became constant, for which a 30-minute test was sufficient.

Figures 6 and 7 give the results of tests by this method. The pointers in Fig. 6 indicate increase of spot wear of the sphere in the test oil after processing on SAE-10 oil for 1 minute. In the order of sequence from left to right the experimental points for each curve correspond to a period of processing in SAE-10 oil for 1, 5, 15, 30, 60 and 120 min.

The curves give the dependence of coefficient of friction on diameter of spot wear or on specific load on contact surface.

These curves show that fatty acids (specially unsaturated) maximally lower friction, but strongly increase surface wear, the investigated salts and esters of fatty acids increase friction and wear

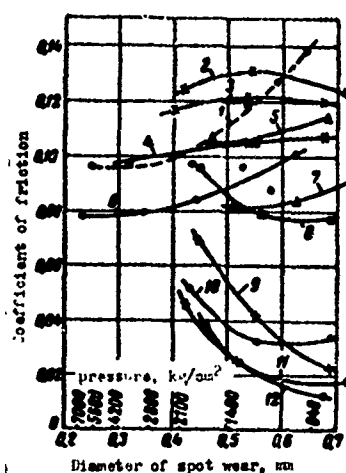


Fig. 7. The effect of additives of fatty acids, esters and soaps on friction surface wear. 1) mineral oil SAE-10; 2) the same with 5% oleate sodium oleate; 3) the same with 5% methyl oleate; 4) the same with 5.6% lead naphthenate; 5) the same with 10% palmitin; 6) the same with 1% soy lecithin; 7) the same with 5% elaidic acid; 8) the same with 5% stearic acid; 9) the same with 5% heptene acid; 10) the same with 5% oleic acid; 11) the same with 5% undecenoic acid; 12) the same with 5% acids from castor oil.

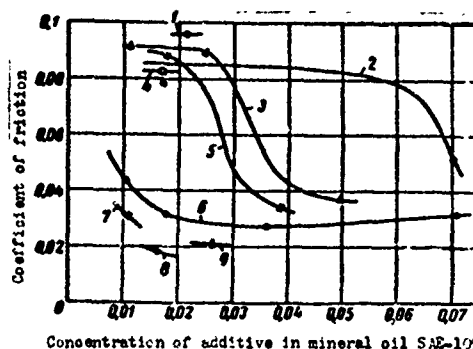


Fig. 8. Dependence of coefficient of friction of steel on steel on the concentration of fatty acid additives in mineral oil. 1) α -mercaptolauric acid; 2) stearic acid; 3) lauric acid; 4) elaidic acid; 5) heptene acid; 6) oleic acid; 7) benzoyl nonylenic acid; 8) fatty acids from castor oil, 9) undecenoic acid.

B. Antiwear Additives

In conditions of low loads, very low speeds and static friction the same polar substances possessing antifriction

properties can serve as antiwear additives. However, at high loads they, conversely, increase surface wear, and under the influence of temperature lose the ability to be adsorbed on surfaces [21].

1. Antiwear Additives Containing Elements of Group V

The strongest antiwear properties belong to certain compounds of phosphorus, arsenic and antimony. Derivatives of phosphoric and phosphorous acids. Their neutral and acid esters and salts of acid esters have obtained wide application as antiwear additives to oils [22, 23, 25]. As a rule, these compounds have weak antifriction properties, i.e., they very little or almost do not increase the load of friction surfaces as compared to pure oils. At the same time these compounds often are not only antiwear additives, but also lower the oxidizability of oils and their corrosional aggressiveness and improve their washing properties.

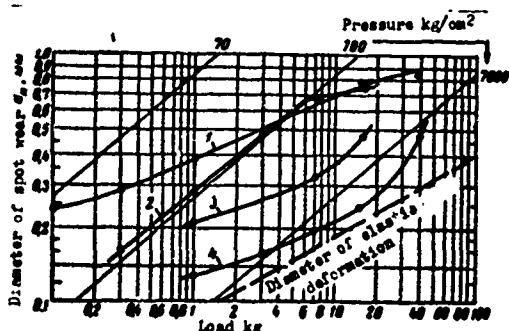


Fig. 9. Lowering surfaces wear under the effect of sulphurized sperm oil and tricresyl phosphate additives in mineral oil. 1) motor oil SAE-20; 2) aviation oil SAE-120; 3) SAE-20 with 1% sperm oil; 4) the same with 1% tricresyl phosphate.

Among such compounds are tributyl, triphenyl, tricresyl phosphates and other similar products. For instance, the known antiwear additive santolube-31 is a phosphorous ester of alkylated phenol. Adding this additive to oil in quantity of 0.25-1%, besides improving antiwear properties, also improves the thermooxidizing stability of oil [22].

In patent literature we encounter in practice as antiwear additives compositions of phosphoric esters and

fatty acids and their esters (including with fatty oils), ketones and compounds of an unsaturated character [24].

Lecithin, which, as noted above, can serve as an antifriction additive, also possesses good antiwear properties (Figs. 7 and 10). However, the application of this product for this goal is very limited.

Similar compounds in combination with fatty acids in solution of vaseline oil were investigated by Beeck and co-authors [26] on a four-ball machine. Test conditions: balls with copper covering, constant load on upper ball 2.2 kg, rpm of upper ball 120.

It was found that a combination of additives - tricresyl phosphate, triphenyl phosphate or triphenyl arcine with fatty acids, their esters and salts in petroleum oil - gives especially significant effect of lowering wear as compared to wear in pure oil. The authors explained this effect by joint "chemical polishing" action of phosphoric compounds and the wedging action of polar-active materials, ensuring a "quasihydrodynamic" action of lubricant in conditions of threshold friction.

Larson and Perry investigated the influence of phosphoric compounds on surface wear on a four-ball machine [16].

The dependence of wear of balls on load on upper ball is shown in Fig. 9. From the curves it is clear that oil with 1% tricresyl phosphate substantially lowers wear as compared to pure mineral oils and as compared to oil containing

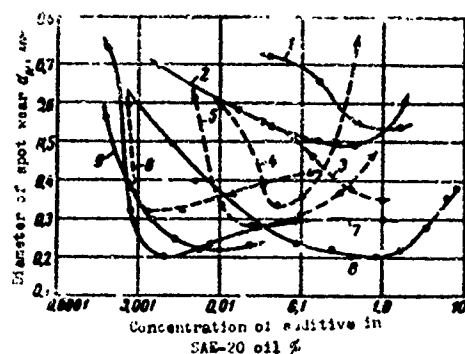


Fig. 10. Influence of concentration of esters and acids in SAE-20 oil on wear of balls under small load (7 kg) on the upper ball (for oil without additive $d_n = 0.7$ mm). 1) methylchlorostearate; 2) dichlorostearic acid; 3) dilauryldisulfyl; 4) free sulfur; 5) sulphurized sperm oil; 6) mercaptolauryc acid; 7) dilaurylphosphate; 8) tricresyl phosphate; 9) soy lecithin.

1% sulphurized sperm fat, although the last one also acts as an antiwear additive.

The results of research on the effect of concentration of various esters and acids on wear of balls under constant load of 7 kg on the upper ball and at oil temperature of 130°C are shown in Fig. 10.

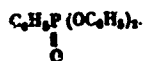
The test lasted 2 hours. Minimum wear was again obtained for phosphor - containing products - tricresyl phosphate, dilaurylphosphate and natural lecithin.

The optimum concentration of phosphoric esters is approximately 1% in mineral oil, corresponding in viscosity to SAE-20 oil.

For lecithin the concentration in oil which

gives a minimum wear is 100 times lower.

Peal and colleagues [27] investigated the antiwear properties of a number of esters of phosphoric and phosphinic acids. The authors report that these compounds simultaneously possess high antiburr properties. However, esters of phosphine, and even more so oxyphosphoric acids, are insufficiently stable, with the exception of more or less stable aromatic phosphines. Thus, Radmer [24] indicates the effectiveness of Müller's additive, - diphenyl ester of phenylphosphonic acid



applied during the war as an antiwear additive to oils.

The research of phosphoric esters conducted by P. I. Sanin, Ye. S. Shapovalova and others [28] was essentially dedicated to study their antiburr, not but/their antiwear properties, and showed that the antiburr effectiveness of esters of phosphoric, phosphorous and phosphinic acids is low. Phosphorus esters and antiburr properties to increase the load of jamming, but does not prevent jamming. The esters of phosphinic acids, having hydrocarbon radicals, and, combined with phosphorus, are significantly more active than esters containing only the alkoxy groups, e.g., esters of phosphorous acid. So the

length of the hydrocarbon chain of esters of alkylphosphinic acids increases their antiburr properties increase.

2. Sulpur-Containing Antiwear Additives

Sulpur-containing organic compounds can simultaneously serve as antiwear and anticorrosive additives to oils.

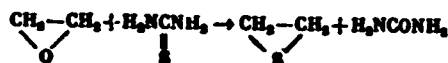
As Ya. M. Slobodin and others [29] established, esters of β, β' -diethanoldisulfide and fatty acids, depicted by the general formula



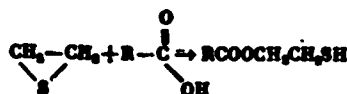
(where R is the alkyl radical), have good antiwear and anticorrosion properties.

Synthesis of the product consists of three stages.

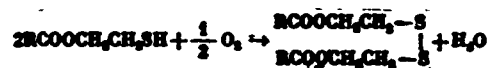
1. Synthesis of ethylene sulfide from ethylene oxide and thiourea:



2. Synthesis mercaptoethyl ester from ethylene sulfide and fatty acid:

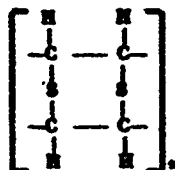


3. Oxidation of mercaptoethyl ester by atmospheric oxygen in presence of traces of Fe^{+2} :



The obtained product called [MDS] (MDC), is an effective antiwear additive and a weak antiburr one. To lower wear the additive is introduced into oil up to 5% by weight.

During sulfurization of fatty oils sulfur is joined in places of unsaturated bonds, forming high-molecular compounds of the type



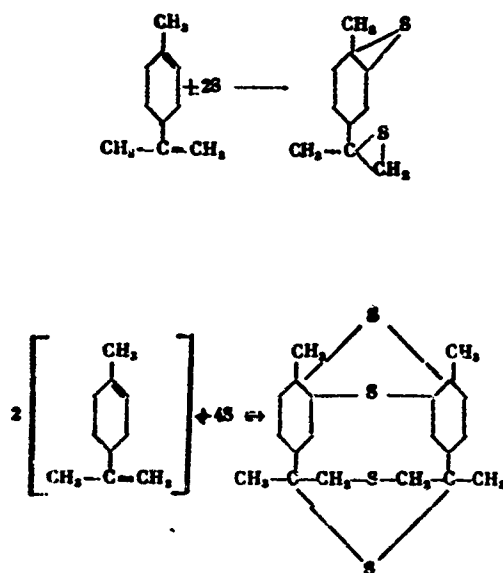
These products possess good antiwear, antifriction and anticorrosion properties and, in a number of cases, stabilize oil against oxidation.

Since in bridges sulfur is sufficiently durably combined, compounds of such type do not substantially affect antiburr properties of oils, even when added to them in significant quantities.

Sulfurized terpenes and olefins have attained propagation as antiwear additives [30].

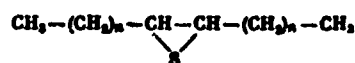
Sulfurized terpenes are multifunctional additives [VTU MNP 564-55] (BY MNP 564-55), which are simultaneously antiwear and anticorrosion additives. They are a brown liquid with molecular weight near 400, viscosity of 23-25 centistokes at 100°C, with sulfur content of about 30%.

During sulfurization of terpene a reaction between dipentene and elementary sulfur occurs, which, as is assumed [31], can pass according to one of the following diagrams:

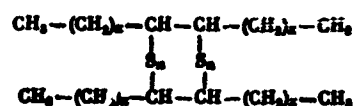


"Sulphurized Terpenes" are applied in foreign lands as an antiwear component of motor oils, and also as an inhibitor of corrosion and oxidation; they are produced by "Standard Oil" under the name "Stain add" and by "Amoco Chemical" under the name "Amoco-43". This additive is added to motor oils in quantity 0.1-0.6%.

Sulphurized olefin hydrocarbons utilized as antiwear additives have the general formula



or

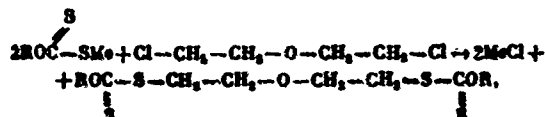


Patent literature describes sulfurization of unsaturated fatty acids and their esters [32], and also olefin hydrocarbons and their polymers, polyisobutylene, linear polymer of methylpentadiene, olefins with aromatic, radical, styrol, stilbene, mono- and dephenylbutadiene [33].

Calaysts are used to obtain sulphurized olefin hydrocarbons with durably combined sulfur: sulfide of alkali metals, aluminum chloride, oxide or hydroxide of metals, amines or amonia [34]. Sulfurization is conduct by elementary sulfur, carbon bisulfide, hydrogen sulfide and mercaptans [35]. In most cases mercaptans, 2-mercaptobenzothiazol and its derivatives, and also dithiocarbamates are applied as accelerators of sulfurization or passivators, removing corrosion ability of the sulphurized product.

Depending upon the durability of the sulfur bond and the length of the molecule's hydrocarbon chain the additive may be slightly active, only lowering wear during moderate conditions of friction, or active, having high antiburr properties.

Ethyl ethers of β, β' -dialkylxanthogenate, "xantbols" synthesized by the Shaumyan Lenigrad Oil Refinery [36] from Chlorex (β, β' -dichloroethyl ether and xanthogenate according to this diagram



are weak antiburr additives, but can be applied to lower wear during moderate conditions of friction. They are added to oil in quantity of about ~0.1%.

Certain sulfurous compounds containing aromatic cycles also have antiwear properties. Such compounds in a number of cases have antioxidant and anticorrosive properties to a greater degree than antiwear properties. For instance, sulfurized alkylphenols, in which sulfur is combined with the aromatic cycle, are more effective as inhibitors and less are effective as antiwear agents in contrast to aromatic sulfides of the dibenzylsulfide, in which the sulfur is in the alkyl group and which possess the best antiwear properties.

3. Sulfur-Phosphorus Containing Antiwear Additives

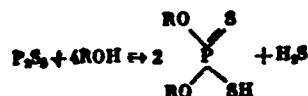
Thiophosphoric compounds, as a rule, are effective additives to oils for lowering surface wear under moderate loads.

To obtain thiophosphoric compounds having antiwear properties, most frequently the reaction of phosphorus sulfide (basically P_2S_5) with organic compounds having mobile hydrogen, and double bonds or containing oxygen is used.

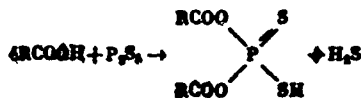
The reaction of P_2S_5 with products having mobile hydrogen

Among these compounds are alcohols, phenols, acids, and amines [37].

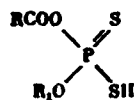
As a result of action of P_2S_5 on alcohols and phenols



we obtain acid esters of dithiophosphoric acid. Analogous products are obtained by the reaction of P_2S_5 with acids:



In certain cases a mixture of alcohols or phenols with monobasic acids is used, and the obtained acid esters correspond to the formula



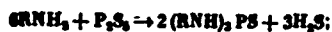
Among the alcohols used to obtain esters of dithiophosphoric and phosphorous acids various aliphatic, aromatic and alicyclic alcohols, alcohol-esters and glycols, but from and among the phenols, - phenol, alkylated phenol, napht. etc., and patented [26].

As a result of the action of P_2S_5 on amines the following types of compounds can be obtained, depending upon the conditions of the reaction and the character of the amines [25].

a) For primary amines: diamidodithiophosphoric acids



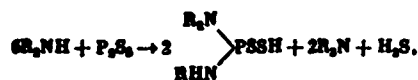
or neutral triamide



b) For secondary amines: monoamidodithiophosphoric acids



or diamidodithiophosphoric acids



or (during prolonged heating) triamide

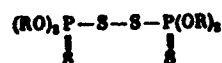


Acid esters cannot be used as oil additives since they are unstable and easily oxidize in presence of air and hydrolyze under the effect of moisture. Therefore their derivatives are applied; the methods of obtaining them are given below [38].

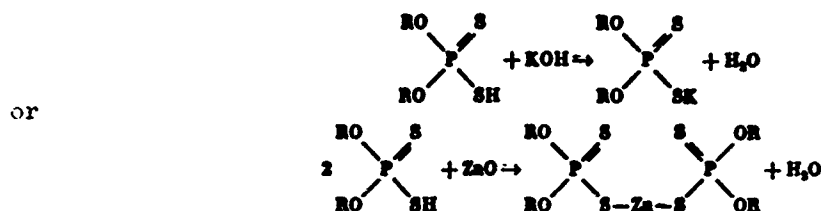
1. Neutralization of acid esters by organic bases. Such diesters of dithiophosphoric acids are sometimes used as inhibitors of oxidation or corrosion, but they are also effective as antiwear components to strong antiburr additives, since they lower surface wear at low loads; among such compounds are the additives VNIINP-353 and [LZ-30] (ЛЗ-30) obtained by reactions of alkylphends with phosphorus pentasulfide.

with phosphorus pentasulfide.

2. Oxidation of acid esters of dithiophosphoric acid in disulfides



3. Transformation of esters of dithiophosphoric acid into salts by reaction with metallic bases or with metallic oxides, e.g.,

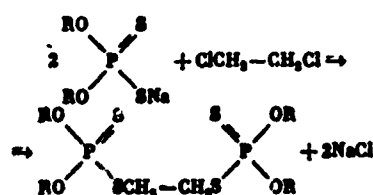


The latter, i.e., dialkyl or diarilditiofosfaty diarylditheophosphate of zink or barium, have obtained application as inhibitors of corrosion and oxidation, washing and antiwear additives to motoral oils; the additives [DF-1] (ДФ-1), DF-11 VNIINP-354, [V-501] (B-501), LZ-317, and others are of this type..

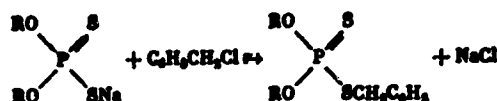
Now it is known that zink diatkyldithiophosphates are also very effective antiwear additives to oils for automobile hypoid transmissions. These compounds are added to the basic antiburr component of the additive [39]. Lowering surface wear at moderate and high loads, zinc dithiophosphates also increase load of jamming of surfaces and are activators of the antiburr components. The most favorable zink dialkyldithiophosphate with 4 to 8 carbon atoms in the alkyl radicals, namely dialkyldithiophosphate, is obtained from mixture of C_4-C_8 alcohols [40].

4. By the reaction of alkaline salts $(RO)_2 PSSK$ with halogen derivatives $ROCl$, $(RO)_2PSCl$, PCl_5 , or PCl_3 dialkyldithiophosphates such as $(RO)_2PSSR$, $(RO)_2PS-S-PS(RO)_2$, $[(RO)_2PSS]_3P$, $[(RO)_2PSS]_5P$ and others are obtained [25].

I. D. Afanas'yev and others [42] used the reaction of alkaline salts of dialkyldithiophosphoric acids with dichlorethane or with benzyl chloride to obtain effective antiwear additives, constituting esters of dialkyldithiophosphoric acids. For instance,



or



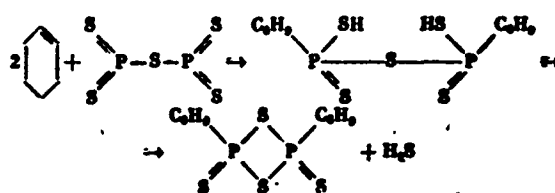
Thus antiwear additive LZ-306 was obtained, a benzyl ester of dibutyldithiophosphoric acid.

The reaction of P_2S_5 with unsaturated hydrocarbons [41]

Patent literature mentions obtaining additives which lower wear by means of the reaction of P_2S_5 with such unsaturated compounds as turpentine, polymers of cycloidiene, copolymers of isobutylene and styrene, diapentene, olefins of cracking, olefins with long chains, different polymers of olefins, acetylene hydrocarbons, [25].

The unsaturated products react with phosphorus sulfide exothermically forming acid organic compounds containing sulfur and phosphorus [43].

According to Fey [43] the reaction of cyclohexene with P_2S_5 flows in the following manner:



The phosphorus atom joins not at the double bond, but replaces hydrogen at the carbon atom neighboring it. A crystal product, Δ^2 -cyclohexene of dithiophosphoric acid, is obtained.

During the reaction of P_2S_5 with terpenes very little hydrogen sulfide

is given off and, as showed research, two or three double bonds react from 1 molar phosphorus sulfide. Although the chemical composition of the reaction products has not been investigated, from their physical state (viscous or amorphous solid matters) it is possible to assume that they contain polymers with repeating C-S-P and C-P-S bonds, poorly soluble in mineral oils. According to A. M. Ravikovich and I. V. Ladyzhenskaya [44] the reaction passes better in the presence of aluminum chloride, which allows lowering the formation of high-polymer insoluble substances. In this case sulfuric acid can also be applied as a catalyst.

However, the solubility of these products in oil is nevertheless insufficient.

In the United States as antiwear additives salts obtained by neutralizing the reaction products of terpenes with phosphorus pentasulfide by metallic bases are patented [45].

The reaction of P_2S_5 with oxygen-containing products [46]

Among oxygen-containing products the most commonly used are high-molecular esters (natural or synthetic), ketones and aldehydes, oxidized paraffins, etc.

The reaction of high-molecular esters of fatty acids, e.g., lard, sperm oil, cetyl palmitate, wool fat, etc., with phosphorus pentasulfide leads to the formation of surface-active phosphorus and sulfur-containing substances of more or less acid character depending upon the conditions of the reaction and the initial products. As the reaction temperature increases acidity, and also phosphorus and sulfur content in the final products are lowered due to hydrogen sulfide being given off and loss of phosphorus oxide in deposit [47].

Such products simultaneously possess antiwear and antifriction properties and are valuable additives to oils for worm transmissions.

There is a Soviet additive of this type, [EZ-2] (ЭЗ-2), constituting dehydrogenated castor oil, treated with P_2S_5 . It is added in quantity of 5% in oil, (GOST 3823-54), applied for worm transmissions of rear axles of trolley busses.

Phosphorus and sulfur-containing compounds may also be obtained by means of the reaction of PCl_3 , $POCl_3$ and $PSCl_3$ with alcohols and mercaptans.

During the reaction of phosphorus trichloride and oxychloride with alcohols the corresponding phosphites and phosphates are obtained, which, as noted above, in certain cases are satisfactory antiwear and anticorrosion additions to oils.

By the interaction of phosphorus thiochloride with alcohols, phenols and mercaptans esters of thiophosphoric acid are obtained, and the reaction of phosphorus trichloride with mercaptans produces thiophosphites.

The research of P. T. Sanin, Ye. S. Shepleva and others [28] showed that in lowering wear during friction in conditions of moderate loads in presence of oils with additives of thiophosphoric and thiophosphorous acid esters the decisive role belongs not to sulfur, but to phosphorus. Also, the presence of sulfur in the molecule gives an antiburr effect, causing lowering of wear and friction in the process of jamming. The most effective additives are the lower trialkyltrithiophosphites, containing from 3 to 5 carbon atoms in their molecule. However such low-molecular compounds are poorly soluble in petroleum oils.

C. Antiburr Additives

Antiburr additions intended to guarantee the work of friction surfaces without jamming or to soften the process of jamming, as a rule, do not lower wear at moderate loads as compared to wear of metal on pure oil. Conversely, due to the corrosional-chemical nature of their action on metal wear of friction surfaces at moderate loads can even be increased.

In connection with this to guarantee the antiwear properties of oils at moderate loads antiburr additives were recently applied in combination with the antiwear component.

1. Sulfur-Containing Antiburr Additives

Among the sulfur-containing antiburr additives are sulphurized mineral oils, containing partially free or colloidal sulfur, sulphurized fats (e.g., sulphurized sperm oil), sulphurized olefin hydrocarbons (e.g., sulphurized cracking-distillates, containing hydrocarbons with ethylene bonds);

sulphurized terpenes, xanthates, xanthogenates and thiocarbonates, alkyl and aryl disulfide and polysulfide.

Some of these compounds possessing moderate antiburr properties are simultaneously being inhibitors of corrosion and antiwear additives, are described above.

The simplest sulfur-containing antiburr additives of known structure are disulfides and polysulfides.

In combination with the chlorine component in foreign lands dibenzyl disulfide is widely used. With the chlorine component lacking in the concentration ensuring sufficient antiburr properties, this additive is poorly soluble in oils (4-5%).

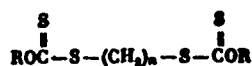
Antiburr additives, constituting alkylated cyclical compounds with lateral chains containing sulfur in the form of mercaptan, sulfide, polysulfide, thiocyanate, thiodetone, thioaldehyde, thiocarboxyl and thio-ether groups are also patented [48].

Polysulfides which are active antiburr additions can be synthesized from halide alkyls and polysulfides of alkaline metals [49]:



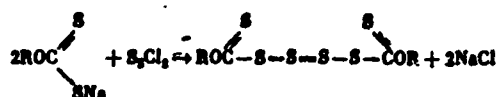
Alkylxanthogenates of alkaline metals are widely applied as flotation agents at ore concentration of nonferrous metals due to their high affinity to metals, thanks to which they also possess high antiburr properties. However, they cannot be applied as antiburr additives, since they are not dissolved in oils and are aggressive with respect to metal.

The compounds obtained from alkylxanthogenates of metals with the general formula

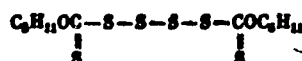


(where $n \geq 0$) easily soluble in oils and not provoking corrosion of metal, allowed creating effective antiburr additives to oils [24, 50].

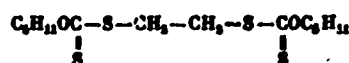
The interaction of potassium (or sodium) alkylxanthogenate with sulfur monochloride



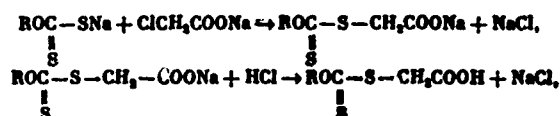
produces compounds [24, 42] with high antiburr properties, soluble in oil and applied during the Second World War in Germany under the name Mezulfol-I:



However, this additive turned out to be too aggressive; therefore, it was replaced by Mezulfol-II:

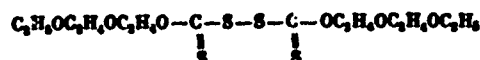


A French patent [50] suggests using an analogous type compound with a free carboxyl group as an additive. This product is simultaneously an antiburr and anticorrosion additive to oils and in contrast to many sulfur-containing additives does not increase the inclination of oil to form an emulsion with water. This substance is obtained by interaction of sodium xanthogenate sodium monochloracetate and hydrogen chloride by the following diagram:



where R is the $\text{C}_4 - \text{C}_{20}$ alkyl.

In recent years the Khyul'z factories patented a new product of this type, - diethyldiglycolxanthate [24].



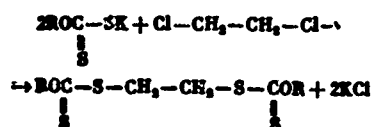
The Soviet additives LZ-6/9 (ethylene dibutylxanthate), LZ-24 (ethylene diethylxanthate), LZ-23 (ethylene diisopropylxanthate) and LZ-19 (ethylene diisoamylxanthate) can be liquid or crystal. The latter are individual compounds, are not having so sharp an odor as the liquid products.

Below are described the consecutive stages of the synthesis of ethylene dialkylxanthates [42]:

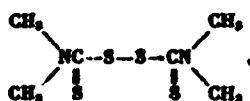
obtaining potassium (or sodium) alkylxanthogenate by the reaction of alcohol, carbon bisulfide and caustic alkali



interaction of potassium alkylxanthogenate with dichlorenthane to obtain ethylene dialkylxanthate



Disulfides and xanthogenic compounds not only give oil high antiburr properties but also act as inhibitors of oxidation. In this respect tetramethylthiuram disulfide (Thiuran E)



which, however, has limited solubility in mineral oil.

Figures 11 and 12 give graphs of the dependence of ball wear spots on load when testing oils with sulfur-containing additives on a four-ball machine per GOST 9490-60. The curves are constructed on a logarithmic grid.

Antiwear additives (Fig. 11): Diphenoldisulfide (2); MDS, described on page 44 (3), sulphurized octol, constituting sulphurized copolymers of amylenes and butylene (4), and, finally, xanthols, amylxanthol LZ-20 (6) and butylxanthol LZ-21 (5), increase the load of jamming little as compared to the pure base oil, [TS-14.5] (TC-14.5) (1). At the approach of jamming of surfaces a great jump of ball wear spots is observed, which indicates the ineffectiveness of these additives as antiburr additives.

In Fig 12 the results of tests on TS-14.5 oil with additives of xanthogenates, disulfide and sulphurized terpenes are compared with antiburr properties of oil for hypoid automobile transmissions (GOST 4001-53), constituting

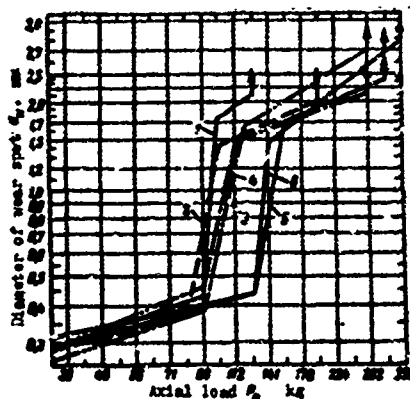


Fig. 11. Results of tests on TS-14.5 oil with sulfur-containing antiwear additives (10% in oil).

Curve	Additive	Antiburr Properties		
		OPI	P _K , kg	P _C , kg
1	Without additive;.....	36	89	126
2	Dsphenoldisulfide;*.....	42	79	200
3	*EDS;.....	48	89	282
4	Sulphurized Octol;.....	48	89	282
5	LZ-21;.....	62	126	316
6	LZ-20;.....	64	126	355

*Content in oil, 5%

sulphurized extracts obtained during nitrobenzene purification of oils, containing 1.5% sulfur. This oil causes high load of transition to jamming (first break of curve), but low load of welding of balls (end of curve).

[BEK] (BEK), bisethylxanthogenate ($C_2H_5OCS - S - S - CSOC_2H_5$), effectively increases the antiburr properties of oil, but evokes corrosion and heightened wear at loads lower than the load of jamming (6).

For ethylene alkylxanthates (additives LZ-6/9, LZ-19 and LZ-23) high load of transition to jamming (7, 8 and 9) and also absence of aggressiveness with respect to metal are, as a rule, characteristic.

Sulphurized terpenes yield in antiburr properties to all the remaining additives; the test results are shown in Fig. 12. However, sulfurized terpenes also possess anticorrosion properties and the ability to inhibit oxidation of oils.

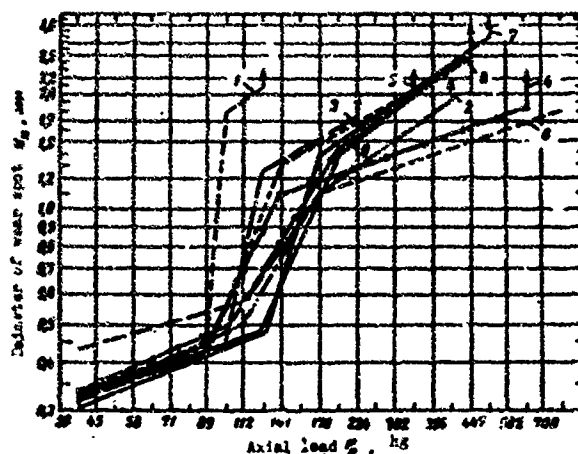


Fig. 12. Results of tests on TS-14.5 oil with sulfur-containing antiburr additives (5% in oil).

Curve	Additive	Antiburr Properties		
		OPI	P _K , kg	P _C , kg
1	Without additive;.....	36	89	126
2	Hypoid oil (sulphurized);.....	85	112	398
3	Sulphurized terpenes;.....	51	100	224
4	Dibenzylidisdulfide;.....	77	89	631
5	Thiuram E;.....	80	100	316
6	BEK;.....	83	112	774
7	LZ-6/9;.....	81	126	501
8	LZ-19;.....	76	126	447
9	LZ-23;.....	72.5	100	447

As a result of the reaction of sulfur with olefins at temperatures from 140 to 300°C heterocyclic compounds can be obtained containing 3 sulfur atoms in the molecule:

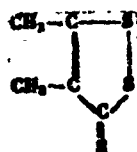


where R and R' can be hydrogen, alkyls or aryls.

Under the general name of "trithions" such products have a series of useful properties including the ability to increase a antiburr and anticorrosion properties of mineral oils and their resistance to oxidation [51].

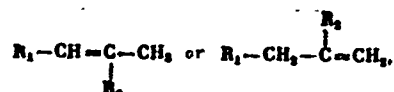
From this nomenclature of cycle the generic name of this compound is

1,2-dithio-4-cyclopentene-3-thion and, in particular, if R and R' are methyl radicals



the name is 4,5-dimethyl-1,2-dithio-4-cyclopentene-3-thion.

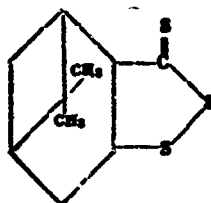
The reaction of trithionization consists of connecting three atoms of sulfur with H_2S given off. Olefins containing allyl and propenyl groups more or less easily enter into this reaction



where R_1 and R_2 can be the most diverse substitutes. Olefins with two substitutes

at one carbon atom with a double bond ($\begin{matrix} R_2 \\ \diagup \\ C \\ \diagdown \\ R_1 \end{matrix} = CH-CH_3$) do not give trithions.

Among trithions the most expressed antiburr properties evidently belong to 4,5-dimethyl-3-thion, isobutylene trithions, and, finally, trithion α -pinene, having the formula



Under the direct influence of sulfur on olefins the yield of trithions is very small (from 2 to 10%), especially in the case of aliphatic olefins. A higher yield is obtained during simultaneous influence of S and P_2S_5 on olefins, applying CS_2 as a solvent and conducting reaction under pressure

[52, 53, 54].

2. Chlorine-Containing Antiburr Additives

Organic compounds of chlorine are active antiburr additives to oils: They increase payload capacity of friction pairs and soften the process of jamming. However, at moderate loads chlorine-containing compounds do not improve the conditions of friction and they increase surface wear faster.

In antiburr properties chlorine derivatives, as a rule, yield to sulfur-containing additives, which are significantly more effective in preventing damage to surfaces during jamming.

The lower chlorinated hydrocarbons, such as carbon tetrachloride, trichloroethylene, hexachlorethane, tetrachlorethane and chlorinated butadiene, are very active antiburr additives; however, their great volatility, sharp narcotic odor and toxicity prevent wide use of these compounds for this goal. Nevertheless, in separate cases carbon tetrachloride, hexachlorethane (entering, e.g., as component in Soviet antiburr additive ZE-5) and hexachlorbutadiene (tripene) giving fire resistance to hydroliquids, are used as antiburr additives [55].

Chlorinated paraffin, containing from 30 to 50% chlorine, is widely used in foreign lands as an antiburr additive, in spite of its serious inherent deficiencies. It is known that these compounds can separate free HCl during heating and when water gets in them.

Chlorinated paraffins are produced in foreign lands under various names: alpha-chlorine-33 (additive of "Carlisle" with chlorine content of 33%), chlorafin-40 (chlorinated paraffins with chlorine content of 40%), anglamol-40 (by the firm, "Lubrizol"), tsereklor-42 (firm "ISI"), anglamol-50 (paraffins with content 50% chlorine and more), cerechlor-P50, P-60 and P-70. These products are also applied as additives to lubricating-liquid coolants during treatment of metals by cutting.

We also produce chlorinated paraffin with chlorine content of about 40%, constituting a product from yellow to brown, with high viscosity and no odor during good removal of free chlorine. As an antiburr additive chlorinated paraffin with chlorine content of 40% was offered for oils for lubricating

gears of main transmissions of automobiles under name of additive NAMI-T-12.

To prevent the possible corrosion under the action of HCl chlorinated paraffins are applied in combination with anticorrosive additives of the type of amines, phenolates, sulfonates and others. Thus, angl. 01-40 contains an anticorrosive component - hydroxypropylphenal [56], and addition VNIINP-402, besides the basic component - commercial chlorinated paraffin contains an inhibitor of corrosion - barium salt of the condensation product of alkylphenal with formaldehyde (additive VNIINP-371).

As a rule, the inhibitors of corrosion in this case somewhat lower the antiburr properties of the chlorine additives. In this respect sulfonates act especially negatively.

Inhibitors of the type VNIINP-371 and zinc dithiophosphates in this respect are an exception and do not lower the antiburr properties of chlorine-containing additives.

As an antiburr additive to mineral and ester oils polyvinyl chloride of low degree of polymerization is offered (molecular weight from 300 to 500), e.g. polyvinyl chloride with molecular weight of 310, containing 56.5% Cl [57].

Among ester oils an effective antiburr additis is ester $\alpha, \alpha', \beta, \beta'$ -tetrachloradipine or tetrachlorosebacic acids, and also pentachlorobutyric acid or its esters $\text{CCl}_3\text{CHClCHCCOOR}$ (R is equal to H, CH_3 or C_2H_5) [58].

The effectiveness of chlorinated aliphatic hydrocarbons as antiburr additives is higher than chlorinated aromatic compounds [59], such as polychlorodiphenyl (e.g., chlorinated biphenyl, a mixture of tetra and pentachlorodiphenyl), chlorinated benzene, chlorinated naphthalene, chlorinated phenol and others. Completely chlorine-substituted, five-member, unsaturated acyclic compounds, such as hexachlorocyclopentadiene or octachlorocyclopentene, significantly surpass in antiburr properties chlorinated aliphatic compounds, chloroparaffin and hexachlorethane, but alkylated aromatic compounds, containing chlorine not only in the ring but also in the chain, are equivalent to chlorinated aliphatic hydrocarbons at identical chlorine content in the molecule. This is illustrated in Fig. 13 which gives the antiburr property of TS-14.5 oil with different chlorine-containing additives according to tests on a four-ball machine (per GOST 9490-60).

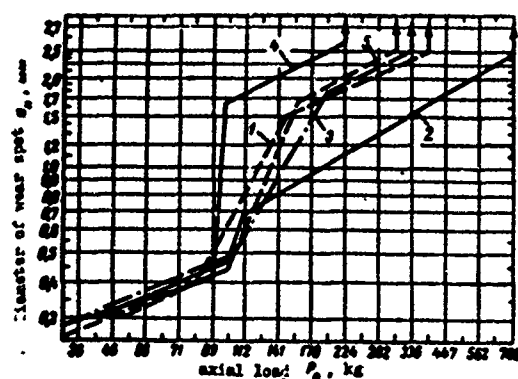
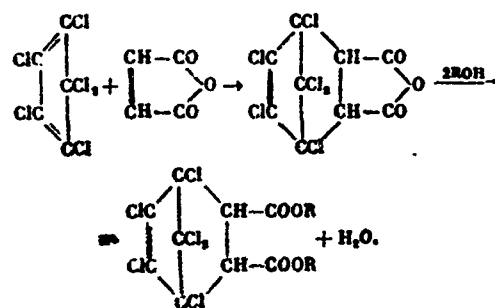


Fig. 13. Antiburr properties of TS-14.5 oil with Chlorine-containing additives (5% in oil).

Curve	Additive	Antiburr Properties		
		OPI	P _K , kg	P _c , kg
1	VD-2;.....	61	79	398
2	Octachlorocyclopentene;..	85	100	708
3	Hexachlorethane;.....	60	100	355
4	Chlorinated biphenyl:...	41	89	224
5	Chloroparaffin;.....	58	100	316

As a result of condensation of hexachlorocyclopentadiene and maleic anhydride with subsequent esterification by alcohol the ester of chlorendic acid is obtained,



where R is an alkyl with from 4 to 8 carbon atoms [60].

Some very effective antiburr agents are aromatic hydrocarbons, containing, besides chlorine, also oxygen or nitro group, in their cycle, for instance chloronitrophenol and chloronitrobenzene, chlorinated amines and salts of

amines [61].

As antiburr additives are offered also chlorinated oil products, not being individual compounds, but constituting a mixture of different chlorine derivatives, e.g., chlorinated mineral oils, chlorinated extracts from selective purification of oils, chlorinated naphthalene and coke squeezing (e.g., additive [AZNII-9] (азнии-9) containing 35-45% chlorine), chlorinated kerosene and kerosene fractions [62].

However, the application of these cheap and very accessible products is hampered due to their corrosional aggressiveness, due to which the selection of specially effective anticorrosive additives is required. Furthermore, the uncertainty of chemical composition of initial raw material leads to inconstancy in the properties of different batches of the product.

It has been established that not only chlorine, which is the most widespread component of antiburr additives, but also all the remaining halides, being introduced into lubricating oils, give them the ability to improve the conditions of friction and prevent jamming of surfaces [63].

The research on compounds of chlorine, bromine and iodine as additives to lubricating oils, conducted Davey [63], showed that the best antiburr properties belong to compounds of bromine. However, practical application of bromide compounds as additives to lubricating oils is limited by their high cost and toxicity.

Iodine compounds are the weakest antiburr agents and are not of practical value.

D. Multifunctional Antiburr and Antiwear Additives Containing Several Active Elements

The most effective, and therefore and the most wide-spread antiburr additives to oils for heavily loaded gear transmissions are substances containing several active elements. Are the most effective in antiburr properties and at the same time the most aggressive are compounds simultaneously containing sulfur and chlorine, and least effective in antiburr properties are additives containing sulfur and phosphorus. The latter, as was shown above basically possess antiwear and anticorrosion properties.

To improve the other operational properties of oils, as a rule besides antiburr additives inhibitors of corrosion, rusting, oxidation and so forth are added.

The first sulfochlorine-containing antiburr additives, appearing during Second World War, were combinations of dibenzylsulfide (30%) and chlorinated paraffin (70%). Such was the composition of Santopoid, added in quantity of 10% to oils for hypoid automobile transmissions. Subsequently during synthesis of additives other products were used; chlorinated naphtha in combination with thiocarbonate or alkylthiocyanate.

In the commercial assortment of Soviet additives there is a two-component sulfur-chlorine additive EZ-5, consisting of sulphurized terpene (3.5%) and hexachlorethane (1.5%) and possessing comparatively high antiburr properties.

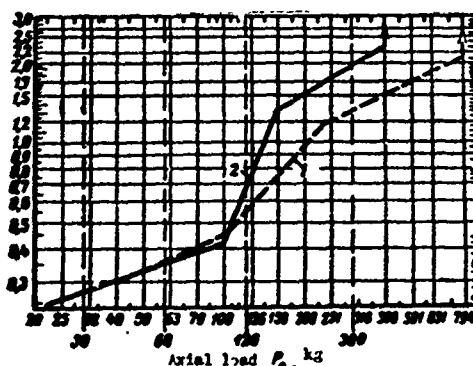


Fig. 14. Antiburr properties of TC-14.5 oil with additives consisting of compositions of sulfur-containing and chlorine-containing compounds. Test on four-ball machine.

Curve	Additive		Antiburr Properties		
	Designation	α in oil	OPI	P_K , kg	P_C , kg
1	Chloroparaffin + Dibenzyldisulfide (type Santopoid A)	7	96	100	794
2	Sulfurized Terpenes + Hexachlorethane (Additive EZ-5)	3			
		3.5	75	100	398
		1.5			

Figure 14 gives the antiburr properties of two sulfochlorine-containing additives according to the results of tests on a four-ball machine. Additive EZ-5 contains 36.8% S and 27% Cl, and the additive based on Santopoid A contains

Table 1. Characteristics of Soviet and Foreign Additives

Additive	Area of Application	Content of active elements in additive %				Concentration of additive in oil %	Source
		S	Cl	P	Zn		
Soviet Additives							
EZ-2	Worm Transmissions	2.6	--	1.2	--	5-10	GOST 3823-54
EZ-5	Gear transmission (with the exception of hypoid)	17.5	27	--	--	5	GOST 8412-57
CT-1	The same	18	3.2	--	--	5	TUTNZ 115-62
LZ-6/9	"	39-40	traces	--	--	5	GOST 9973-62
Sulfoil	"	8	55.8	--	--	4	GOST 72, 79
LZ-309	"	19.6	9.36	10.5	--	5	42
Chloreth	Hypoid transmission	--	34	10	--	2	72, 79
Sulfur and	"	8.66	31.8	1.9	2.27	7	72
DF-1 ¹	Different assignments including hydraulic system and hydrodynamic transmissions	5.55	--	4.5	5.28	0.5-3.0	40
	The same	3.4	--	1.63	--	3.5	40
Foreign Additives							
Firm "Lubrizol"	Worm transmissions	1.7	15.0	1.2	--	2	[12, 64]
Anglanol-48	Hypoid transmission	4.9	21.7	0.33	--	9	[12, 64]
Anglanol-70	CS-2758	16-17.5	16	2.9-3.3	3.1-3.6	10	[12, 64]
Anglanol-71 or	The same	10.5	2.8	0.3	--	10	[12, 64]
Anglanol-91	MIL-L2105	5.25	21.6	0.33	--	8-9	[12, 64]
Anglanol-82	The same	6.7	19.0	0.2	--	8.75	[12, 64]
Anglanol-83	"	4.8	20.0	0.3	--	9	[12, 64]
Anglanol-85	Oil of series GL-4 for hypoid transmissions MIL-L-002105A	16.0	16.5	3.0	3.0	9.5	[12, 64]
Anglanol-88	Gear transmission and lubricating-liquid coolant for treatment of metal	--	49	--	--	2-7	[12, 64]
Anglanol-93	The same	--	40	--	--	10	[12, 64]
Anglanol-50	"	42.5	0.2	--	--	0.3-3	[12, 64]
Anglanol-40							
Anglanol-31							

Table 1. (Cont.)

Additive	Area of Application	Content of active elements in additive %				Concentration of additive in oil %	Source
		S	Cl	P	Zn		
Anglanol-35	The same	13	23	--	--	1-12	[12, 64]
Anglanol-36	"	18	22.5	--	--	1-10	[12, 64]
Anglanol-32	"	46	--	--	--	0.5-5	[12, 64]
Lubrizol-1060	Motor and transmission oil	16.5	--	8.0	8.3	0.6-2.5% av	[12, 13]
Lubrizol-1360	The same	16.75	--	8.0	8.85	0.6-4.24% av	[12, 13]
Lubrizol-880	Turbine and hydraulic oils	0.58	13.3	--	--	2.5	[12]
Lubrizol-234 ²	Hydrotransmission, liquid of type A, suffix A	3.5	--	1.65	1.90	5	[12]
Lubrizol-243	Hydraulic oils	9.25	--	--	--	2.9-7.0	[12]
Lubrizol-245	Industrial oils	10.0	--	--	--	1-3	[12]
Firm "Mon-santo"							
Santopoid-22							
RI	Gear transmissions including hypoid	12	16.5	3.3	3.5	6.5-15	[13, 64]
Santopoid-23							
RI	The same	13.3	14.0	4.1	3.7	10-15	[13, 14, 39]
Santopoid-32	"	8.2	26.0	0.56	--	6.5	[80, 64]
Santopoid-33	"	8.5	26.0	0.55	--	6.75	[80, 64]
Santopoid-44	"	12.1	27.5	1.5	1.6	10	[80, 64]
Motor gear	"	4.0	30.2	1.8	2.0	5.5-15	[80, 64]
Firm "Enjay Company"							
Parapoid OC	Gear transmission	5.8	29.4	--	--	7-10	[64]
Parapoid-109	Industrial oils	7.0	0.3	0.2	--	--	[64]
Firm "Elco Labrikent"							
CL-concentrate	Hypoid transmission	4.7	4.3	75% PbO	--	--	[64]
Firm "Carlisle"							
Alpha-chlor-33	Gear transmission	--	33	--	--	10	[64]
Firm "Badische anilin und sodafabrik"							
Bayer I-G-L ³	The same	--	18	8.5	--	0.1-1	[75]
Bayer IYe	The same	--	18	9.1	--	0.1-15	[75]

¹Barium content 4.20%²Barium content 14%³Nitrogen content 0.5%

7.8% S and 28% Cl. The more stable bond of sulfur and the smaller chlorine content in addition EZ-5 are the cause of its somewhat decreased activity as compared to the addition of type of Santopoid.

Among the sulfochlorine additives released for heavy-loaded gear transmissions are a number of the additives represented in Table 2.

Sulfochlorine-containing antiburr additives can be obtained: 1) synthesis of compounds containing sulfur and chlorine in one molecule; and 2) introduction of separate sulfur- and chlorine-containing components of the additive to oil.

The following routes of synthesis of sulfochlorine-containing compounds are possible:

- 1) Reaction of sulfur-chloride and monochloride with compounds, having double ethylene bonds;
- 2) Reaction of halogenated hydrocarbons with organic sulfide or with sulfide of alkali metals and zanthogenates;
- 3) Chlorination of sulfur-containing organic compounds;
- 4) Sulfurization of chlorine-containing organic compounds

Products obtained by reaction of sulfur
chlorine with compounds having double bonds

This way of obtaining sulfochlorine-containing additives is the simplest; for synthesis it is possible to use various products.

Ethylene reacts with sulfur monochloride with the formation of $\beta\beta'$ -dichlorethylsulfide (yperite);



In this reaction along with sulfides are formed polysulfides $(\text{ClCH}_2\text{CH}_2)_2\text{S}_n$; lowering the reaction temperature promotes an increase in the quantity of polysulfides.

Patent literature mentions additives obtained by reaction of sulfur chloride with olefins, polymers of olefins, unsaturated fatty acids and their esters [65].

Among the additives released by foreign firms by the above described method, are Anchor, prepared by "Anchor Chemical" and constituting fatty oils

treated with sulfur chloride and recommended for application in oils for heavily loaded gear transmissions and treatment of metals, and also addition of firms "Pet Oil" ("Saxon basis"), "Carlisle" (sulchlor-55 and sulhlor-66) and "Chemical Works" (obtained by treating lard and sperm oil with sulfur chloride).

The Soviet additive OT-1, is obtained by treating a grade two turpentine with sulfur monochloride and contains 18-22% sulfur and 3-4% chlorine. By treating terpenes with sulfur chloride and monochloride a sulphochlorinated basis of certain multicomponent additives of Santopoid is obtained by the firm "Monsanto".

In patent literature [65] are meet methods of synthesizing sulfur-containing aromatic compounds by reaction of sulfur monochloride with cyclical hydrocarbons, and also additives obtained by treating polyisobutylene, alkyleneoxides and glycols with sulfur chloride.

Products obtained by reaction of chlorine-containing compounds with sulfides of alkaline metals, xanthogenates and organic sulfides

By treating chlorine-containing aliphatic compounds with sulfides of alkaline metals, as was shown previously, sulfur-containing derivatives of aliphatic hydrocarbons can be obtained by means of substituting sulfur for chlorine. However, if we do not bring the reaction of substituting sulfur for chlorine to its conclusion, then sulfochlorine-containing products are obtained [66].

R. G. Petrova and R. Kh. Freydina [67] described the reaction of formation di-(5,5,5-trichloropentyl) disulfide by heating 1,1,1,5-tetrachloropentane with Na_2S and elementary sulfur:



The yield of ready product is 90%.

Similarly by the reaction of tetrachloropentane with sodium sulfide R. G. Petrova synthesized di-(trichloropentyl) sulfide, which by Ye. S. Shepeleva as the antiburr additive "sulphol" to lubricated oil [68]. The initial product for synthesis of sulphol, tetrachloropentane, is a byproduct of the production of synthetic fiber enanth, whose process of production was developed

by R. Kh. Freydlina and Sh. A. Karapetyan [68]. Tetrachloralkane is obtained by telomerization of ethylene and carbon tetrachloride. In the production of enanth fiber tetrachloralkanes are used which contain 7, 9 and 11 carbon atoms, and tetrachloropentane is a byproduct used for obtaining sulfol, di-(trichloropentyl) sulfide:



or thiodivaleric acid $[\text{HOOC}(\text{CH}_2)_4]_2\text{S}$ by subsequent hydrolysis of sulfol. The yield of sulfol is 70%.

The additive contains 55.8% chlorine and 8% sulfur and is introduced in oil in quantity of 4%. However, without an anticorrosion component the additive is corrosionally aggressive (Fig. 15) and gives heightened wear of surfaces (Fig. 16). These negative phenomena are eliminated upon adding a second

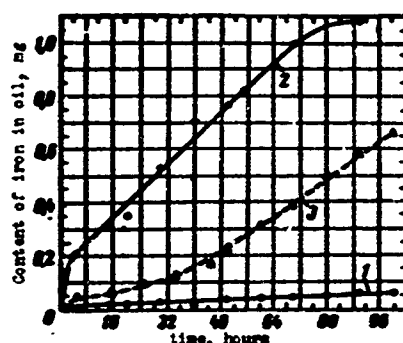


Fig. 15. Corrosion of steel at 200°C under the action of oils with sulfochlorine-containing additives. Established by the method of radioactive isotopes (Yu. S. Zaslavskiy, G. O. Shor and R. N. Shneyerova) 1) mineral oil TS-14.5; 2) TS-14.5 with 4% sulfol; 3) TS-14.5 with 4% sulfol and 3% DF-11.

component, — zink dialkyldithiophosphate (DF-11), which simultaneously lowers surface wear, increases antiburr properties (Fig. 17), acts as an inhibitor of corrosion and improves the thermal stability of oil.

The interaction of alkyl- and arylchlorine derivatives with xanthogenates of alkali metals or with thiocarbonic acids produces a large quantity of contemporary additives. For instance, to obtain a sulfochlorine-containing

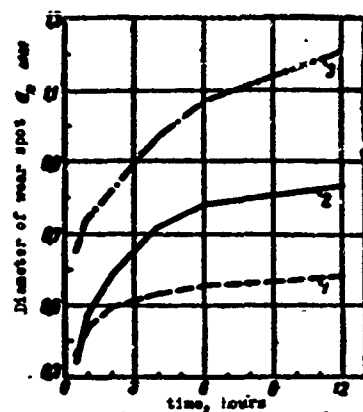


Fig. 16. Effect of sulphol and DF-11 on ball wear during tests on a four-ball machine. Load on upper ball, 10 kg.
1) TS-14.5 + 4% sulphola + 3% DF-11; 2) TS-14.5; 3) TS-14.5 + 4% sulphola.

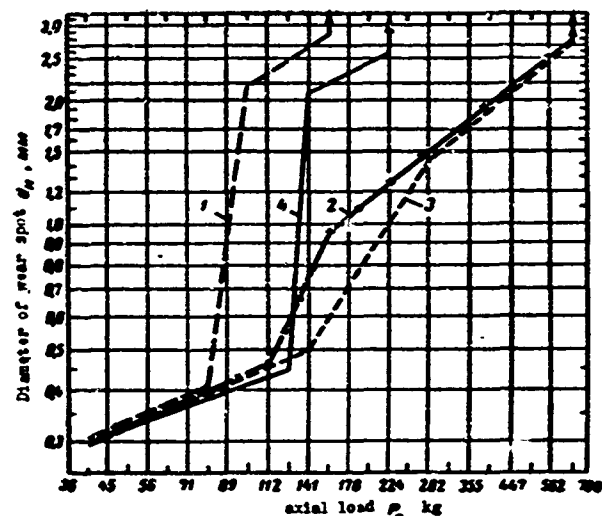
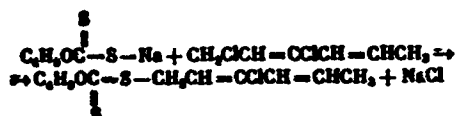


Fig. 17. Effect of zink dialkyldithiophosphate (DF-11) on antiburr properties of TS-14.5 oil.

Curve	Additive		Antiburr Properties		
	Name	% in oil	OPI	P _K , kg	P _S , kg
1	None.....	--	36	79	158
2	Sulfol.....	4	84	112	631
3	Sulfol + DF-11.....	3	95	141	631
4	DF-11.....	3	55	120	224

antiburr additive "Monsanto" [65] uses the reaction the product of chlorinated ligroin, containing 54% chlorine, with potassium isopropylxanthogenate. In an analogous way these additives produced: chlorohenzylalkylxanthate, chloronaphthaxanthate and polychloroligroin xanthate, chlorohylxanthate (e.g., $\text{C}_5\text{H}_{11}\text{OC}(=\text{S})-\text{S}-\text{C}_{12}\text{H}_{21}\text{Cl}_4$) containing from 10 to 15% sulfur and from 30 to 35% chlorine, and also products of reaction of sodium xanthogenate with chlorine-derivatives of ethylene hydrocarbons [69], for instance



To obtain sulfochlorine-containing compounds I. D. Afanasev and T. A. Rogachevskaya used the reaction of sodium salt of mercaptobenzothiazola with 1,3-dichlorobutene-2 (additive LZ-311); the obtained product contains 24% sulfur and 12% chlorine.

Products obtained by chlorination of sulfur organic compounds

Sulfochlorine-containing additives can be obtained by chlorination of organic compounds of sulfur. Thus, e.g., are these additives obtained: perchloromethylmercaptan, tetrachlorodiphenylsulfide, dichlorophenylmethylpolysulfide, dichloronaphthylmethylpolysulfide and others [70].

The products, according to patent data possessing good antiburr properties [70], can be synthesized by heating styrene with sulfur for 6 hours at 225-230°C with a reflex condenser, as a result of which a mixture of 2,5- and 2,4-diphenylthiophene is produced. By recrystallizing the mixture from butanol a purer crystal product consisting mainly of 2,5-diphenylthiophene is obtained. After passing gaseous chlorine through this compound a final product containing 35% chlorine is obtained.

2,2, 3,4, 5,5-hexachloro-3-thiophene is synthesized by chlorination of thiophene with gaseous chlorine. This product possesses good antiburr ability and is stable to 225°C. Higher than this temperature this product decomposes [70].

In an analogous way chlorinated alkylsulfides and polysulfides, and also chlorodibenzyl disulfides are obtained [70].

Products obtained by sulfurization of haloid-containing compounds

This method of obtaining sulfochlorine-containing additives is not widely applied. The patent literature mentions products obtained by sulfurization of perchloromethylmercaptan, and also sulphurized chloronaphthalene and sulphurized chlorinated naphtha with an anticorrosion additive [71].

At present as antiburr additives not only compounds, in which chlorine and sulfur simultaneously enter, but also a mixture of substances containing these elements separately are used.

The activity of such two-component mixtures to a significant degree depends on the ratio of chlorine-containing and sulfur-containing components in oil at their constant total percent of the concentration [72].

Figure 18 gives the dependence of the index of antiburr properties of [OPI] (OIV), calculated per GOST-9400-60, on the concentration of sulfur and chlorine additives in TS-14.5 oil. In the left part of the diagram the antiburr properties are increased as the concentration of chlorine component in oil increases (from 0 to 10%), and in the right part they increase with increase (from right to left) of concentration of sulfur-containing additive (also from 0 to 10%). In the middle part of the diagram the total concentration of additive remains constant (10% in oil). The content of sulfur and chlorine components changes so that with decrease of one the quantity of other component increases correspondingly.

From the diagram it follows that upon introduction of sulfur and chlorine components into the oil adding a small quantity of sulfur additive to the chlorine component sharply increases the antiburr properties of oil (middle part of the diagram of Fig. 18). The maximum effect is attained approximately at a ratio of 70% chlorine component and 30% sulfur and, evidently, almost does not depend on concentration of sulfur in the sulfur component of the additive (see curves 7 and 8 in Fig. 18).

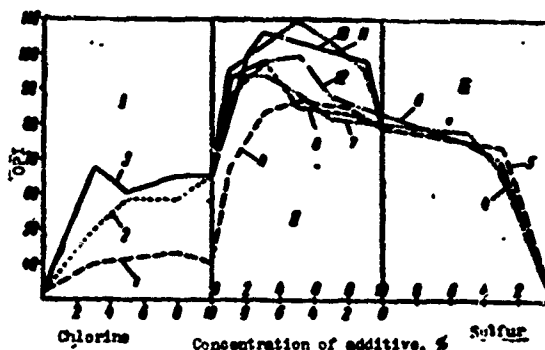


Fig. 18. The effect of concentration of sulfur and chlorine components on antiburr properties of TS-14.5 oil. I) Chlorine-containing additive; II) Sulfochlorine-containing additive; III) Sulfur-containing additive. 1) chlorinated biphenyl (40% chlorine); 2) chlorinated paraffin (40% chlorine); 3) hexachlorethane (90% chlorine); 4) dibenzyl-disulfide (26% sulfur); 5) LZ-6/9 (39% sulfur); 6) sulphurized terpenes (25% sulfur); 7) dibenzyl-disulfide + chlorinated paraffin; 8) LZ-6/9 + chlorinated paraffin; 9) LZ-6/9 chlorinated biphenyl; 10) LZ-6/9 + hexachlorethane; 11) hexachlorethane + sulphurized terpenes; 12) chlorinated paraffin + sulfurized terpenes.

Figure 19 gives the curves of dependence of wear on load when testing TS-15.4 oil with two-component additives on a four-ball machine (GOST 9490-60). From the figure it can be concluded, that the antiburr properties of oil with identical concentration of sulfur and chlorine components strongly depends on the activity of the chlorine component of the additive, which is determined to a large degree by the structure of the compound and to a lesser degree by the quantity of chlorine in the molecule.

Vog found that certain compounds of antimony and bismuth are activators of antiburr properties of sulfur and chlorine additives [73]. Among such compounds are anilylates and ethylates of antimony and bismuth, triphenylbismuthine and antimony oleate [23].

Extraordinarily active as antiburr additives are chlorophosphorus-containing compounds.

At present there are both Soviet and foreign chlorophosphorous-containing antiburr additives, e.g., the Soviet additive chloreth-40 (2% in oil), additives of the firm "Bayer-Leverkuzen," chlorophenylphosphate and Bayer-LE (from 0.1 to 1.5% in oil).

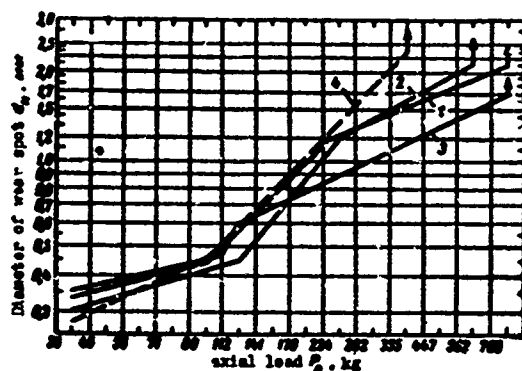


Fig. 19. Antiburr properties of TS-14.5 oil with two-component additives.

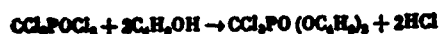
Curve	Additive		Antiburr Properties		
	Name	% in oil	OPI	P _K , kg	P _C , kg
1	Chloroparaffin + Dibenzyldisulfide	7 3	96	100	794
2	Chloroparaffin + 12-6/9	7 3	95	126	631
3	Hexachlorethane + sulfurized terpenes (7+3).....	7	109	112	794
4	Chlorinated biphenyl + 12-6/9.....	7 3	84	100	398

P. I. Sanin and Ye. S. Shipeleva synthesized and investigated a number of chlorophosphorus-containing compounds of the type of esters of chloralkylphosphinic acids. It was found that especially highly active esters of chloralkylphosphinic acids contain the CCl_3 group [28]. It should also be noted that at identical content of chlorine in molecule the chloralkyl esters of phosphorous acids, containing CCl_3 groups, e.g., tri-(trichlorethyl)- or (trichlor-tert-butyl)-phosphites, do not yield in activity to esters of trichloralkylphosphinic acids, however the first of these are corrosionally aggressive.

Esters of chloralkylphosphinic acids can be obtained by interaction to carbon tetrachloride with esters of phosphorous acid [74]:



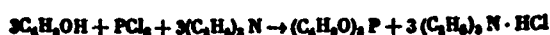
A compound of a similar type - dibutyl ester of trichloromethylphosphinic acid (additive chloreth-40) was obtained by Ye. S. Shipeleva also by the reaction of acid chlorides of trichloromethylphosphinic acid and butyl alcohol by the equation



The reaction occurs in the presence of triethylamine, which bonds with the hydrogen chloride that is given off.

Authors recommend for industrial production of chloreth-40 to use simpler way and to conduct the process in two stages.

The first stage is obtaining tributylphosphite from butyl alcohol and phosphorus trichloride in a solution of benzene and in the presence of triethylamine:



The second stage is the synthesis of dibutyl ester of trichloromethylphosphinic acid from tributylphosphite and carbon tetrachloride:

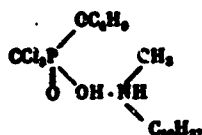


As the authors show, side reactions leading to the formation of acid chloride of dibutylphosphoric acid can also occur; in presence of moisture this acid chloride can form acid esters of phosphoric acid and hydrochloric acid, which can easily corrode metals. Furthermore, when the initial products of synthesis of first stage (butyl alcohol, triethylamine and benzene) contain moisture, this also leads to the formation of a byproduct, the incomplete ester of phosphorous acid, dibutylphosphite, having an acid character. Evidently, this explains the sometimes observed corrosion of metal details when testing oils with additives of esters of chloralkylphosphinic acids. Obviously, at the high temperature developing during friction this type of additive decomposes and, in the presence of moisture, as was shown above, forms corrosionally aggressive compounds.

The production of esters of chlorophosphinic acids is described in a number of patents [75]. In foreign lands additives of chlorophosphinic acids

and their esters are applied mainly in liquids for treatment of metals by cutting; in oils for heavily loaded gear transmission more frequently are applied the stabler salts of amines and chlorophosphinic acids.

B. V. Kleymenov synthesized a substance constituting a salt hydroxybutyl trichloromethylphosphinic acid and methyl octadecylamine, "chlorethamine":



The initial products for synthesis of chlorethamine are dibutyl ester of trichloromethylphosphinic acid (chloreth) and methyl octadecylamine. Synthesis is conducted during boiling of chloreth with methyloctadecylamine (140-160°C). Butylene separates and must be condensed during strong cooling. The termination of the reaction is determined by the quantity of separating butylene. The yield of ready product is 60-70%. At the same time the methyloctadecylamine neutralizes the acid byproducts formed during the synthesis of chloreth.

As a test of a 2% solution of this compound in TS-14.5 oil showed, it is a fully stable product, does not evoke corrosion of metal in conditions of high loads and friction temperatures and yields little to chloreth-40 in antiburr properties.

Figure 20 gives the antiburr properties of TS-14.5 oil with 2% of additives of esters of chloromethylphosphinic acids and chlorethamine during tests on a four-ball machine (GOST 9490-60). The lowest antiburr properties belongs to oil with additive of butyl ester monochloromethylphosphinic acid (4); in this case during jamming a great jump of ball wear spot occurs. Chlorethamine significantly lowers wear during jamming (5). Technical chloreth-40 (3) is somewhat more effective in antiburr properties than the chemically pure product (2), since chloreth-40 contains an admixture of dialkylphosphite, which is especially active with respect to metal. This is confirmed by the fact that a mixture consisting of 2% chemically pure chloreth-40 and 0.2% dialkylphosphite (7) gives a significant increase of antiburr properties and at the same time is corrosively aggressive.

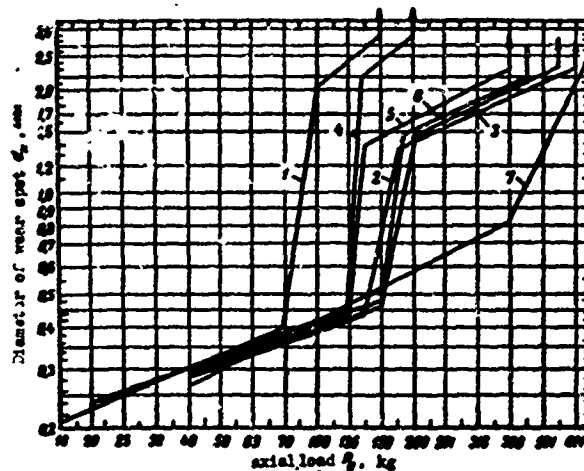


Fig. 20. Antiburr properties of TS-14.5 oil with additives of derivatives chlorophosphinic acids (2% in oil).

Curve	Additive	Antiburr Properties		
		OPI	P _K , kg	P _C , kg
1	Without additive.....	36	79	158
2	Chloreth-40 (chemically pure).....	86	141	631
3	Chloreth-40 (technical).....	88	153	562
4	Butyl ester of mono-chloromethylphosphinic acid	53	126	200
5	Chlorethamine.....	72	126	398
6	Amyl ester of tri-chloracetoxyposphinic acid.....	86	158	447
7	Chloreth-40 + dialkylphosphite ¹	128	224	708

¹0.2% dialkylphosphite in oil.

Curve 6 shows the dependence of wear spot of balls on axial load on the upper ball for TS-14.5 oil with additive of amyl ester of trichloracetoxyposphinic acid. In antiburr properties this substance is approximately equivalent to chloreth-40; however, it is less stable due to the presence of a carbonyl group in it.

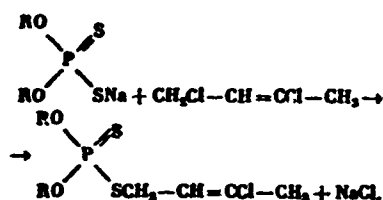
There patents [76] on the use as antiburr additives of alkyl- and arylchlorine-substituted esters of phosphoric acid, chlorous alkylphosphates obtained by the action of PCl_3 on a mixture of alcohol with thiophenol, products obtained from the reaction of acid halides with alkaline salts of

dialkyldithiophosphates and others.

Sulfophosphorus additives are basically anticorrosion and antiwear and, as a rule, do not possess high antiburr properties.

Contemporary antiburr additives applied in oils for hypoid transmissions of automobiles contain, as a rule, three active elements (sulfur, chlorine and phosphorus) combined in one molecule or, more frequently, introduced into the oil in the form of a composition of several substances. While sulfur and chlorine are the basic antiburr elements, phosphorus acts as an inhibitor of corrosion and an antiwear agent. In a number of cases the role of phosphorus can be fulfilled by a nitrogen compound. For instance, there are antiburr additives obtained by the reaction of chlorinated paraffin with alkyldithiocarbonic acid or arylthiourea [24], by the reaction of thiourea with alkylchloride [77] etc.

Among the Soviet additives containing three or more active elements, it is necessary to note the products synthesized by I. D. Afanasyev and T. A. Rogachevskaya from sodium dialkyldithiophosphate and 1,3-dichlorobutene according to the scheme [42]



Such an additive is LZ-309, in which R is the isopropyl radical. This additive is added to oil in quantity of 5%, which gives it not only high antiburr, but also good antiwear properties.

Metallic salts of acid esters of dialkyldithiophosphoric acids are multifunctional additions to oils. They possess washing, anticorrosion, antiwear and stabilizing properties, more or less strongly expressed depending upon the structure of these compounds [40].

Zinc dialkyldithiophosphates not only actually somewhat increase the antiburr properties of oils, but, when introduced into oil jointly with strong antiburr additives, act as activators of the basic antiburr components, compounds

containing sulfur and chlorine in active form. Along with this zinc dialkyldithiophosphates lower the chemical aggressiveness of sulfur and chlorine-containing compounds, i.e., they remove corrosion and decrease wear of metallic surfaces, observed in presence of such compounds.

These valuable properties of low-molecular zinc dialkyldithiophosphates are the reason that contemporary strong antiburr additives, applied in foreign lands in oils for hypoid transmissions of automobiles, contain zinc dialkyldithiophosphates as one of their components [39]. Such additives are Anglamol-91 and Anglamol-93, Santopoid 22RI and Santopoid 23RI and others, as this can be seen from Table 2.

We should also remember the already mentioned Soviet additive, Sulphol, applied in combination with DF-11, as a result of which the combined product contains sulfur chlorine, phosphorus and zinc.

Among Soviet zinc dialkyldithiophosphates in antiwear properties the most effective additive is DF-11, synthesized by reaction of a mixture of isobutyl and isooctyl alcohols with phosphorus pentasulfide and subsequent reaction of the complex acid ester of dialkyldithiophosphoric acid with zinc oxide [40]. Additive DF-11 contains 5.23% Zn, 4.5% P and 5.55% S. In oils for gear transmissions it is introduced in quantity of 3% in combination with the optimum quantity of the antiburr component.

However, good results in lowering surface wear is also given by application of zinc dithiophosphates synthesized on a base of cyclical alcohols, and also on alcohols obtained by oxysynthesis and constituting a mixture of normal and isoalcohols of different molecular weight. At present, besides DF-11, VNIINP-501, VNIINP-354 and LZ-317 are tested with positive results.

Among foreign additives Lubrizol-1060, Lubrizol-1360 Santolube-493 and others can be called analogous.

Bimetallic salts of esters of dithiophosphoric acids are recommended as additives to oils for hydrodynamic transmissions, since they well combine washing and stabilizing properties with antiwear [38]. Such, e.g., is Lubrizol-284 [12].

Different organic and inorganic compounds, containing metals

In compositions of antiburr additives all the more frequently are organic and inorganic compounds of metals being applied: lead, copper, potassium, sodium, aluminum, lithium, zinc, antimony, bismuth, molybdenum, tungsten, titanium, cobalt and even iron in a colloidal state. Organic compounds of metals do not have independent value as antiburr additives, since they insignificantly improve the antiburr properties of oils. However, being added in oil together with sulfur and chlorine components of the additive, they turn out to be very effective activators of the basic antiburr elements (sulfur and chlorine): besides, some of them can lower surface wear during moderate friction and are inhibitors of corrosion and oxidation.

Among the first antiburr additives developed for hypoid transmissions of automobiles were mixtures of lead soaps with sulphurized fats. Additives of naphthenates and oleates of lead in composition with sulfur chlorine, and sometimes with phosphorus-containing compounds are applied even now (e.g., Makom of the firm "Shell", the Czech oil YeRN, GDR oil for hypoid transmissions of automobiles and others). Such oils are especially favorable during work of gears on conditions of high speeds, characteristic for transmissions of passenger automobiles, and also for operation in the first period of work. Besides high antiburr properties, lead soaps in combination with sulfur possess two more positive properties, extraordinarily rarely combined and usually being antagonistic: the ability to act as a deemulsifier and at the same time to lower the corrosional aggressiveness of oils. However, as with most of the other compounds of heavy metals, lead soaps form insufficiently stable colloidal systems in oil.

We have already indicated the multifunctionalness of zinc salts of esters of dialkyldithiophosphoric acids and their ability to activate the antiburr component of the additive. An analogous ability is possessed by naphthenates and oleates of antimony and bismuth [78].

During the last few years natural molybdenum disulfide has attained propagation as an additive [31]. Molybdenum disulfide is released in the form of powders, pastes and suspensions, applied to the surface or introduced in lubricating material. The colloidal suspension of molybdenum disulfide in

oil is insufficiently stable and is inclined to separate during storage.

Molybdenum disulfide acts as an antiburr additive only in sufficiently high concentration (higher than 10%); however, it also possesses antifriction properties. Similar properties belong to tungsten disulfide.

Molybdenum disulfide is effective both at high (to 400°C) and at very low temperatures.

At temperatures higher than 400°C molybdenum disulfide starts to oxidize (it is assumed into MoO_3). Then the additive loses its lubricating properties, since MoO_3 acts as an abrasive. The efficiency of molybdenum disulfide is kept approximately to 500°C until all the MoS_2 is converted into MoO_3 .

Molybdenum disulfide can lower fretting corrosion and prevent fatigue painting of surfaces [17]. Therefore it is recommended to apply MoS_2 in nodes with reverse-vibrating movement with small shifts, where there is danger of fretting corrosion appearing.

Of significant interest are compounds of molybdenum which can form colloidal solutions in oil [82, 83]. Organic compounds of molybdenum blue, constituting complex oxygen compounds of molybdenum, derivatives of molybdenum phosphoric acid, organic molybdenum-nitrogen compounds, molybdates and oxalate molybdate organic amines, thiomolybdates of organic nitrous bases and molybdoalkoxyxanthogenates have been suggested [84].

With the exception of molybdenum xanthogenates and thiomolybdates, the remaining compounds of molybdenum, without the addition of a second component composed containing chlorine and sulfur, are slightly active antiburr additives.

II 2. Boundary Friction and Mechanism of Action of Oil Additives Improving the Conditions of Friction

At present it is considered that the terms "oiliness" and "durability of oily film", which previously were applied to characterize the ability of an oily film to be retained on the surfaces, lowering friction and wear, and also preventing jamming, are foggy and indefinite and absolutely do not reflect the essence of the phenomenon.

It is known that durability of threshold (monomolecular) layers of lubricant is essentially equivalent to durability of materials of the friction surfaces. The limit of efficiency of the oily film is by no means its "durability" property. The works of Blok [85], Beeck, Givens, Smith and Williams [26], Frewing [21], Bowden [86, 87], Khrushchev and Matveyevskiy [15] prove that the property determining efficiency or "payload capacity" of an oily film in conditions of threshold friction is its thermoresistance. Disturbance of an oily film occurs as a result of its desorption under influence of high temperatures of friction on micro-contacts. A measure against this can be the selection of those additives which, due to chemical reaction with metal under influence of high temperatures or adsorption on surface of metal, ensure lowering of friction and wear or preventing jamming of surfaces. This can occur due to high plasticity of surface layers, provoking chemical polishing of surfaces and promoting appearance of "quasihydrodynamic" friction [26], due to lowered durability (or heightened fragility) of surface layers forming under influence of chemically active elements in the lubricant, leading to light destruction of grasping points, and, finally, due to the formation of a cleaning effect as a result of molecules of the lubricant oriented on the surface [88].

Depending upon which principle underlies the additive's mechanism of action, improvement of conditions of friction can occur: 1) by lowering friction at normal threshold conditions (antifriction additives); 2) by lowering surface wear at moderate loads (antiwear additives); 3) preventing and easing the process of jamming (antiburr additives).

A. Antifriction Additives

Antifriction additives are those substances which are added in oil to stabilize friction or lower it during work of surfaces at normal threshold conditions without jamming.

Polar-active molecules of such substances fully cover the metal surface, placing their long axes perpendicular to it. The adsorptive layers of the lubricant act to lower friction by two means.

On the one hand, the molecules oriented in parallel are joined by active groups to the metal surface, simultaneously being attracted one to another by the forces of molecular attraction. When the molecules are quite long they can be inclined and bent under the action of tangents of forces and to slip one past the other, lowering the resistance to shift.

On the other hand, dense packing of such a "nap" prevents direct contact of surfaces or migration of atoms of metal under the effect of their mutual attraction.

Such an oriented structure of adsorptive layers not only can sustain very high loads, but it also can create a wedging pressure, shifting the threshold conditions of friction in semiliquidness, ("quasihydrodynamic"), characterized by easing the resistance to shift.

To explain the role of boundary films in lowering friction Bowden, Gregory and Tabor [89] offer the following expression for frictional force:

$$T = S_{\phi}(\alpha\tau_s + (1-\alpha)\tau),$$

where S_{ϕ} is the carrier surface; $\alpha = S_M/S_{\phi}$ is the part of this surface on which destruction of lubricating film occurred; τ_s is the metal's resistance to cutting; τ is the resistance to shift of the oily film.

For good threshold films existing on the whole carrier surface and possessing high polar activity $\alpha = 0$ and τ is sufficiently small, which ensures a low value of frictional force. However, if on part of the carrier surface there occurred disturbance of the oily film, the magnitude of frictional force will be determined mainly by the resistance to cutting τ_s of the metal or the product of reaction of metal with additive, having lowered resistance to cutting as compared to the initial metal and facilitating destruction of

grasping points on friction surfaces.

For the characteristics of interaction of surface-active and chemically effective oil additives at high temperatures Bowden [86] offers the diagram shown in Fig. 21. For mineral oil, paraffin base, the coefficient of friction is continuously increased as temperature rises in conditions of threshold friction (I); oil with polar active additive of fatty acid gives a sharp

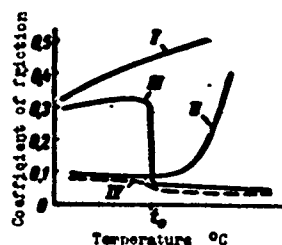


Fig. 21. Change of coefficient of friction depending upon temperature during operation with lubricants of different types. I) nonpolar paraffin; II) fatty acid; III) mineral oil with antiburr additive, reacting with surface at a temperature t_0 ; IV) oil containing a two-component additive consisting of an antiburr component and a fatty acid.

increase of the coefficient of friction at a definite temperature corresponding to the temperature of disorientation of molecules (II); for a lubricant containing a chemically effective antiburr additive, the start of its reaction with metal appears in a sharp drop of the coefficient of friction, which has a high value at room temperature (III). According to Bowden's assumption, the most successful combination is the joint application of a surface-active and a chemically effective substance; with this the coefficient of friction will have a low value both at room and at high temperatures (IV). However, with respect to antiburr properties this assumption is not justified, since adding an antifricition component to an antiburr, as a rule, lowers the antiburr properties of the additive.

B. Antiwear Additives

Friction is accompanied by wear, which leads to baring the surfaces and to the formation of free bonds in the crystal grid. The latter easily joins the free atoms of the neighboring surface or actively reacts with a chemical medium, which is the lubricant or the surrounding atmosphere.

In conditions of moderate loads and temperatures surface-active substances can serve as antiwear additives. However, friction leads to significant heating of surfaces, and increase of temperature leads to disorientation of molecular structure and to loss of the lubricant's adsorbability. Because of this polar-active substances cannot serve as stable antiwear agents. The latter

can be substances or compositions of compounds which in the presence of polar activities with increased temperatures can react with juvenile surfaces of metal to form films preventing surface grasping. Among such substances are certain sulfur-containing compounds with durably combined sulfur (in most cases they simultaneously possess anticorrosion properties), and also esters of phosphoric and phosphorous acids.

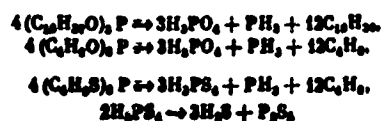
For sulfur-containing antiwear and anticorrosion additives the type of reaction occurring in the formation of complex of metal with molecule of organic compound not containing a replaced atom of hydrogen is characteristic [90]. However, this direction of reaction depends on specific conditions of the contact. In specially rigid temperature conditions the reaction can occur with detachment of sulfur and with subsequent formation of a sulfide.

The characteristic property of phosphorus-containing compounds is their ability to lower surface wear at moderate loads and to ensure high smoothness of friction surfaces.

According to the hypothesis of Beeck, Givens, Smith and Williams [26], under the effect of high contact temperatures of friction on surface eutectic alloys of iron are created with the phosphorus contained in the additive. Such a eutectic alloy has a lower temperature of fusion than steel and, because of this, possess high plasticity, causing, as it were, chemical polishing of surfaces.

It was established [28, 91] that during decomposition of phosphorus compounds under the influence of temperature on the order of 200°C phosphine (PH_3) will be formed, which enters into reaction with the metal. The reaction of phosphine with iron occurs significantly more rapidly than other active materials, which to a definite degree prevents the reaction with the metal of other elements, often causing the lowering of activity of the other antiburr components of the additive. Evidently, this partially explains the mechanism of anticorrosion action of phosphorus compounds.

P. I. Sanin and A. V. Ul'yanova [92] studied the process of thermal decomposition of esters of phosphorous acid. The disintegration of trioc'adecylphosphite, tributylphosphite and tributyltrithiophosphite maybe given by the following equations:



Trialkylphosphites decompose in the temperature range from 250 to 280°C. The phosphine thus obtained interacts with metals (and their oxides), forming phosphides. According to P. I. Sanin and A. V. Ul'yanova copper (but not iron) acts as a catalyst in the process of decomposition of phosphites, lowering temperature and accelerating the process of decomposition.

This whole picture is also reproduced in conditions of friction on metal surfaces, where in the case of tributyltrithiophosphite, besides phosphine hydrogen sulfide is also a product of the reaction, leading to the formation of a sulfide of metal of stabler than the phosphides.

It was established [28] that phosphine compounds containing hydrocarbon radicals directly combined with phosphorus, e.g., esters of alkylphosphinic acids $\text{RP}(\text{OR}_1)_2$, are significantly more active than compounds containing only the alkoxygroup (e.g., esters of phosphoric and phosphorous acids $(\text{RO})_3\text{P}$ and $(\text{RO})_3\text{P} = \text{O}$). Davey [93] found that phosphites are better antiwear additives than phosphates, but alkyl esters of phosphoric and phosphorous acids are better than their aryl esters.

As was established [94], the effect of organophosphorus compounds appears in the region of comparatively low temperatures and moderate conditions of friction, at which phosphorus additives ensure a substantial lowering of surface wear and a certain increase of load of jamming, combined with their chemical polishing effect.

Chemical polishing leads to a negative effect at high loads, when the actual area of contact increases so much that grasping focuses from separate points are distributed over the whole area of friction, causing instantaneous jamming. Because of this for additives containing only organic compounds of phosphorus a sharp process of jamming, developing violently, with large destruction of surface in depth is characteristic.

Due to this the application of single-component phosphorous additives is not an effective measure for preventing wear and jamming under heavy conditions of friction.

It is expedient to apply organophosphorus compounds in combination with other active elements with a complimentary functional demarcation of their action.

Certain phosphorous compounds can form stable anticorrosion films on metal surfaces. The first fixed layer of such a film will be formed as a result of the chemical reaction of metal with the phosphorus contained in the additive; subsequent layers are retained by adsorptive forces. However, the ability of phosphorous compounds to form protective films on surfaces, as noted, often lowers the activity of the other antiburr components.

C. Antiburr Additives

The action of antiburr additives consists in of entering into reaction with metal surfaces at high temperature of friction and forming compounds with metals, which possess the ability to prevent jamming of surfaces. Such compounds, sulfides, chlorides, etc., have lowered resistance to shift as compared to the initial metal, due to which the destruction of grasping points during friction is localized in surface layers.

If the medium is insufficiently active and cannot quickly react with fresh surfaces, and the site of contact flows, being subjected to plastic deformation, grasping increases to jamming of surfaces, obtaining an avalanche character.

Chemically active additives to oils not only increase the load of jamming, but also smooth the process of jamming, meanwhile lowering besides surface wear and coefficient of friction.

This process may be ensured by application of complexes containing sulfur and chlorine separately and in combinations among themselves in the basic compound as additives.

The problem of correct selection of antiburr additives is that they should become active only under the effect of contact temperatures of friction, entering in reaction on the areas of contact. At the same time the additive should not exhibit aggressiveness with respect to metal at moderate temperatures, i.e., should not evoke corrosion of surfaces.

The difficulty of selecting a good antiburr additive consists of just

this: the requirement of high antiburr properties and absence of corrosion contradict each other, since chemical activity causes the action of the additive.

According to research [95] the temperature of friction surfaces at normal threshold conditions without jamming should not exceed 250°C . Evidently, it is more favorable if the additive reacts with iron in the temperature range of $150\text{--}250^{\circ}\text{C}$, since 150°C is the maximum which can be attained in the oil in transmission crankcases. When the temperature of interaction of the additive with iron is lower than this maximum, the additive can react with all the details, located in the oil and evoke their undesirable corrosion. If the temperature of reaction of the additive with iron is higher than 150°C , this limits the action of the additive to the friction surfaces where actual temperatures of friction exceed 150°C .

To investigate the temperature-selective action of antiburr additives it is useful to use themographic analysis of substances in mixture with metallic powders; this allows us to judge about change in the aggregate state according to disturbance of smooth slope of curves of heating and cooling, appearing due to yield or absorption of heat in the process of the reaction [19, 95].

For research we used the photorecording pyrometer of N. S. Kurnakov with automatic recording of temperature as a function of time, allowing us to reveal weak thermal effects, appearing during change in the aggregate state of substance, by simultaneously recording two curves obtained from simple and differential thermocouples.

The connection of the thermocouples is shown in Figure 22.

In the absence of thermal effects the recording of the simple thermocouple is a slanted straight line; an endothermic effect is characterized by a collapse of the line, an exothermic effect by a jump.

The differential thermocouple serves to determine the difference of temperatures of standard and sample and, as it were, is two independent thermocouples, whose thermoelectric currents are mutually subtracted. A galvanometer, included in the circuit of the differential thermocouple, records the difference of two thermal electromotive forces.

The differential thermocouple is very sensitive, but gives only qualitative readings, which attain their full value only if it is applied in combination

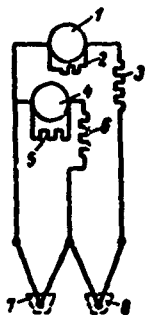


Fig. 22 Connection of the Kurnakov pyrometer.
1) galvanometer of the differential thermocouple;
2) shunt of the differential thermocouple;
3) rheostat of the differential thermocouple;
4) galvanometer of the simple thermocouple;
5) shunt of the simple thermocouple;
6) rheostat of simple thermocouple;
7) investigated substance;
8) substance-standard.

with a simple thermocouple.

Thermographic research of antiburr additives was conducted in conditions of slow heating to high temperatures in pure form and with additive of chemically pure metallic powder reduced by hydrogen, in a ratio ensuring surplus of metal [19].

As has been shown in the work of P. I. Sanin and others [28], the number of simple compounds interacting with metal in the process of additive decomposition during friction is evidently insignificant. For the majority of additives these can be phosphine, sulfur, hydrogen sulfide, chlorine, hydrogen chloride and others. In certain cases direct interaction of a substance with metal (e.g., additive of the type of carboxylic acid), and also the formation of intermediate compounds with metal, e.g., mercaptides can occur; these compounds are then subjected to decomposition at contact temperatures on friction surfaces [96].

A result of the reaction of active compounds with friction surfaces is the formation of metal oxides, chlorides, sulfides, phosphides, etc., possessing lowered resistance to shift.

1. Sulfur-Containing Compounds

A characteristic property of active sulfur-containing compounds is their ability not only to increase the load of jamming of surfaces, but also to strongly lower their wear and friction in process of jamming.

Influence of organic compounds of sulfur on surface starts from their adsorption at moderate temperatures. However, adsorption is not the decisive side of mechanism of action of sulfur-containing antiburr additives, but to a larger degree is peculiar to antifriction and antiwear additives containing stable combined sulfur.

Relative to the mechanism of action of sulfur-containing antiburr additives in conditions of high temperatures of friction on micro-contacts the most probable should be considered decomposition of organic compounds of sulfur

with yield of hydrogen sulfide and its subsequent reaction with surfaces with formation of a metal sulfide of metal. In certain cases the formation of a metal sulfide can occur as a result of light splitting off of sulfur.

Radiographic research of sulfide films [97] on irradiated gears, tested on a stand working in a closed cycle showed that the reaction speed of forming iron sulfide is increased as the temperature of friction increases. The thickness of sulfide films on steel increases as load increases and at constant conditions does not change. Also, the thickness of the film increases towards the head and leg of the gear tooth, i.e., in zones of the greatest slip, and consequently also the highest temperatures.

Sulfide films forming under the influence of compounds with various chemical activity can have different antiburr properties due to the following causes, the more active substances react at lower temperatures and the process of forming a sulfide is developed earlier and deeper. For instance, the temperature at which metal sulfides form in the process of sulfonation, conducted to increase the resistance to wear of machine parts, is not below 200°C and to the strongest degree depends on prescriptions of bath for sulfonation and on the brand of steel [98].

Thermographic analysis of dibutylxanthate ethylene (additive LZ-6/9 applied in Soviet transmissional oil) showed that its reaction with iron powder occurs in the temperature range of 192-197°C (Table 3).

The mechanical (durability) properties of sulfide layers change depending upon the rate of formation and the depth of their penetration, which in the first place is determined by the temperature factor. The character of the sulfide also changes depending upon temperature: while FeS appears at temperatures of 400-600°C and starts to form in small quantities at about 200°C the formation of FeS₂ is observed at significantly higher temperatures on the order of 1000°C [99].

Jointly with S. S. Kulagina [95] the author investigated structural transformations in friction surfaces of balls during tests on a four-ball machine with different types of additives in [TS-14.5] (TC-145) oil [TU 110-61] (TV-110-61)

Interpolating the dependence curve of microhardness of [ShKh-6] (ШХ-6) steel on temperature of tempering allowed us to approximate the temperature arising

Table 3. Results of Thermographic Analysis of Certain Compounds as Applied as Antiburr Additives to Oils

Compound	Temperature of reaction°, °C					
	Fusing		Boiling or disintegration		Interaction with iron	
	Without iron	With iron	Without iron	With iron	Start of process	Temperature jump
Sulphol [LI - (trishlerpentyl) - sulfide]	32 (-)	32 (-)	317 (-)	—	153 (+)	153—244
LZ-6/9 (ditutylxanthate ethylene)	—	—	243 (-)	—	185 (-)	Insignificant
Chlorinated paraffin	56 (-)	56 (-)	200 (-) 235 (+)	200 (-) 285 (+)	135 (+)	•
LZ-309 (ester obtained through interaction of sodium dialkylidithiophosphate with dichlorobutene)	—	—	178 (-) 253 (+)	173 (-) 272 (-)	184 (+)	184—230
Anglacol-70, multicomponent sulfachlorophosphorus-containing additive, type of compound unknown	—	—	198 (+) 280 (+)	—	230 (+)	Insignificant

• (+) — Exothermic reaction (-) — Endothermic reaction

under friction, from the microhardness of surface layers of the wear hole. It was found that during the test of oil with sulfur-containing additives on a

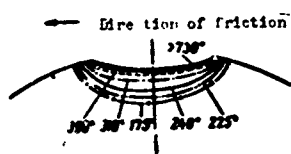


Fig. 23 Isotherms in surface layers of the wear hole of a ball after testing oil TS-14.5 without additive on a four-ball machine. Load preceding welding of spheres.

four-ball machine per GOST 9490-60 the temperature of friction surfaces was significantly lower than it was in the case of pure mineral oil and oil with chlorine-containing additives. Isotherms constructed on the basis of measuring the microhardness during gradual abrasion of wear holes on balls (Figures 23 - 24) show that the zone of secondary hardening appearing for given brand of steel at temperatures higher than 730°C is observed after test of balls in pure TS-14.5 oil (Figure

23) and in oil with chlorine-containing additives (Figure 24b), in particular with 10% chlorinated paraffin. In the test of oil with sulfur-containing additives [LZ-6/9] (LZ-6/9), dibenzylsulfide, etc.) tempering of surface layers of metal is typical (Figure 24a); in this the temperature does not exceed 450°C.

Research of oil with dibenzyldisulfide additive, conducted by G. V. Vinogradov and O. Ye. Morozova [100], showed that the zone of secondary hardening appearing in first moments of test disappears in process of friction due to high operating properties of sulfur-containing additives.

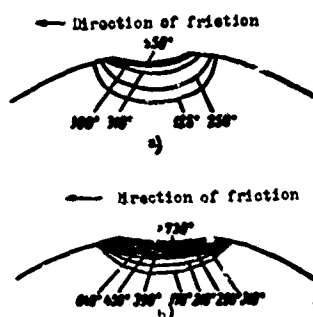


Fig. 24. Isotherms in surface layers of wear holes in balls after test of TS-14.5 oil with additives. a) 5% LZ-6/9; b) 10% chlorinated paraffin. Load preceding welding of spheres.

These phenomena are observed at regimes of jamming of surfaces and indicate that sulfur-containing additives significantly soften the process of jamming and act in this period as antifriction, additives, i.e., they lower the works of friction while chlorine-containing compounds (including chlorophosphorus derivatives) to a larger degree act in the direction of preventing welding of surfaces.

Other elements of group VI of the chemical table, in particular selenium, tellurium and oxygen, also possess antiburr properties [101, 102]. The intense flow of the oxidizing processes in regimes of jamming leads to softening of jamming, since molecular oxygen gives an antiburr effect. At threshold friction without jamming intense reacting of oxygen leads to increased friction and wear due to formation of oxides.

2. Chlorine-Containing Compounds

Chlorine-containing compounds applied as additives to oils are typically antiburr, but not antiwear agents.

It was determined that not only chlorine, the most wide-spread active element in antiburr additives, but also the other halides give oils the ability to improve the conditions of friction and prevent jamming of surfaces [63]. It is known that fluorinated hydrocarbons possess not only exceptional thermoresistance, but also heightened antiburr properties.

Of all the halides bromine compounds possess the best antiburr properties [63]; however, the practical use of these compounds in as additives to lubricating oils is limited by their high cost. In connection with this we will only consider chlorine-containing additives.

The mechanism of action of chlorine derivatives during friction consists of the formation of iron chloride films on metal. In the opinion of Prutton and others [103], the formation of iron chlorides during friction can occur in two ways:

- 1) direct reaction of chlorine derivatives with the metal;

2) decomposition of chlorine derivatives under the action of high temperature of friction with formation of hydrogen chloride and producing chlorides of the metal as a result of interaction of hydrogen chloride with the metal surfaces.

The action of ferrous chloride films of chlorous iron is maintained to comparatively low temperatures (on the order of 300°C) [104]. According to thermographic analysis the interaction of chlorinated paraffin with iron already occurs at 135°C , and decomposition of the reaction product of chlorinated paraffin with iron starts at 265°C . According to the results of metallographic research jamming develops at the temperature of the friction surface, approximately 370°C [95].

Chlorinated paraffin is inclined to evoke corrosion of surfaces during detachment of chlorine under the effect of high temperature or as a result of hydrolisis in the presence of moisture. During hydrolisis of active chlorine compounds replacement of the most mobile atoms of chlorine on hydroxyl groups leads to strong lowering of antiburr properties of oil.

As in case of the previously considered sulfur-containing additives, the effectiveness of chlorine derivatives depends on their stability in conditions of friction; this is combined with the chemical structure of substances: chlorine derivatives of the paraffin series with long chains are less effective than acid chlorides with long chains [83]. In first case the compounds are more stable at high temperatures than in the second. The high stability and weak reactivity of chlorine derivatives of aromatic hydrocarbons containing chlorine at the carbon of the ring were also noted.

Corrosion of surfaces under the effect of the forming hydrogen chloride can be eliminated with the help of anticorrosion additives of the alkaline type, surface-active materials, enveloping the surface (ioneks [ionex] etc.), and neutralizing amines.

3. Sulfophosphorus-Containing Compounds

The mechanism of action of thiophosphoric additives to oils was investigated by G. V. Vinogradov, M. D. Rezbord'ko, Yu. S. Zaslavskiy, P. I. Sanin and others [91, 94].

Their research showed the high reactivity thiophosphororganic additives the effectiveness of these compounds is especially high in the presence of functional differentiation of the action of sulfur and phosphorus compounds.

According to the opinion of P. I. Sanin and A. V. Ul'yanova [92], during decomposition of thiophosphororganic compounds in conditions of high temperatures of friction the most reactive product of decomposition, phosphine, reacts with the metal first; hydrogen sulfide reacts at the highest temperatures. This explains the fact that at moderate conditions of friction phosphorus compounds in thiophosphoric additives have an advantageous effect characterized by low wear of surfaces. Under conditions of jamming at high temperatures on micro-contacts the action of sulfur starts to appear; this is expressed in softening the process of jamming, decreasing the destruction of surfaces and guaranteeing their operation.

G. V. Vinogradov with co-authors found that the biggest effect from application of thiophosphoric compounds is obtained in the presence of relatively lowly mobile phosphorus and highly mobile sulfur. The latter can be ensured, if sulfur is in the β - or γ -position relative to the oxygen ester bond [94, 104]. At the same time the presence of too active sulfur can increase surface wear at moderate conditions and, in the opinion of certain researchers, lead to lowering of the load of jamming [91].

It was also revealed that increasing the hydrocarbon chain of thiophosphoric compounds lowers the load of jamming, and thus, the activity of thiophosphoric compounds from this point of view is opposite of that characteristic for surface-active substances during adsorption of films [28, 91].

On the basis of all this one should conclude that during synthesis of thiophosphoric antiburr additives it is necessary to go along the line of selecting compounds with more or less short hydrocarbon chains, in which phosphorus has low mobility in the presence of comparatively mobile sulfur. The mobility of sulfur is ensured by proximity of double bonds in hydrocarbon chain, or the oxygen ester bond.

4. Chlorophosphorus-Containing Compounds

The essential distinction between thiophosphorus and chlorophosphorus-containing additives is that when phosphorus is combined with chlorine in organic compounds, where both element are distinguished by sufficiently high mobility, the determining role is evidently played by chlorine and not by phosphorus [28].

It was found that among the chlorophosphorus-containing additives the most effective antiburr properties are possessed by esters of chloroalkylphosphinic acids and chloroalkyl esters of phosphorous acids containing the CCl_3 group [28, 79].

This is explained by the great mobility of chlorine in the trichloromethyl group, which can bond directly with metal to a chloride of the metal.

The high reactivity of the CCl_3 group appears during thermographic analysis of compounds of this type in presence of iron powder in the form of a strong exothermic effect in range from 96 to 200°C depending upon the character of compounds and the presence of impurities in them; e.g., acid alkylphosphites (compare points 1, 2 and 3 of Table 4). The latter strongly lower the reaction temperatures of esters of chloroalkylphosphinic acids with metal and can cause a corrosional effect similar to that of oil additives on the metal surface, and also promote the increase of antiburr properties of oil (Figure 20, Curves 2 and 7).

Thermograms of a number of derivatives of chloroalkylphosphinic acids are shown in Figures 25-28.

Chemically pure butyl ester of trichloromethylphosphinic acid (Chloreth-40) in absence of iron is stable to 225°C , at which it gives effect with absorption of heat: at 240°C it gives effect with liberation of heat (Figure 25). With iron powder Chloreth-40 reacts stormily with liberation of heat at 135°C . In practice during work in friction node this reaction also has a very stormy character and when it is caused by heating of oil in total, it leads to corrosion of surfaces of steel details.

The reaction temperature of Chloreth-40 with iron is still lowered acid dialkylphosphite is an impurity in the product. This is particularly indicated by the thermogram of Chloreth-40 with impurity of dibutylphosphite (Figure 26).

Table 4. Results of Thermographic Analysis of Certain Derivatives of Chlorophosphinic

Additive	Temperature		
	Endothermic		Exothermic interaction with iron (start of process and temperature jump)
	Boiling with decomposition without iron*	Decomposition without iron*	
1. Chloreth-40 (butyl ester of trichloromethylphosphinic acid) chemically pure	225	240	135-275
2. Chloreth-40, technical	232	208	96-230
3. Chloreth-40, chemically pure, +10% dialkylphosphite	220	203	98-220
4. Butyl ester monochloromethylphosphinic acid	259	None	200-266
5. Chlorethamine (salt hydroxybutyltrichloromethylphosphinic acid and methyl octadecylamine)**	None	232	178-234
6. Amyl ester of trichloroacetoxyphosphinic acid	"	175	110-250

*In presence of iron decomposition is lacking.

** Temperature of endothermic process of fusion (with and without iron) 45°C.

At full similarity of the character of curves in Figures 25 and 26 the temperature of decomposition of Chloreth-40 with impurity of dibutylphosphite is lowered to 208°C, and its reaction with iron occurs at 96°C.

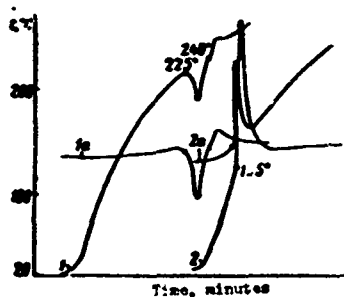


Fig. 25. Thermogram of butyl ester of trichloromethylphosphinic acid (Chloreth-40) 1) simple thermocouple, substance without iron powder; 1a) the same, differential thermocouple; 2) simple thermocouple, recording in the presence of iron powder; 2a) the same, differential thermocouple.

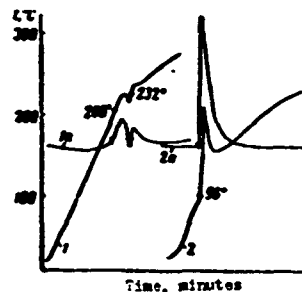


Fig. 26. Thermogram of Chlorethamine. For conditional designations see Fig. 25.

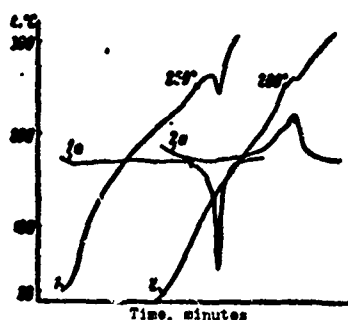


Fig. 27. Thermogram of butyl ester of monochloromethylphosphinic acid. For conditional designations see Fig. 25.

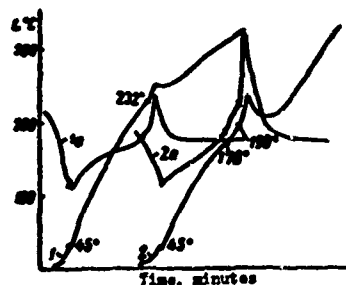
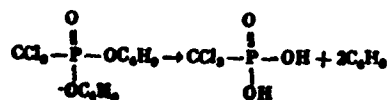


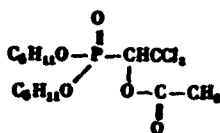
Fig. 28. Thermogram of Chlorethamine. For conditional designations see Fig. 25.

According to the existing method of obtaining trichloromethylphosphinic acids by pyrolysis of esters [75], the decomposition of esters of trichloromethylphosphinic acids starts at 150°C with separation of unsaturated hydrocarbons and with formation of trichloromethylphosphinic acid.



In thermography for chemically pure butyl ester of trichloromethylphosphinic acid this process is observed at a higher temperature (225°C). The first effect is revealed by absorption of heat and intense bubbling. Evidently, the second effect with liberation of heat at 240°C is combined with further process of decomposition, which, possible, includes the separation of the trichloromethyl group.

Even less stable is amyl ester of trichlorethylaceoxyphosphinic acid:



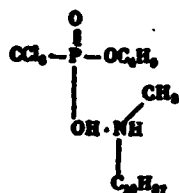
Its disintegration starts at 175°C. The reaction temperature of this ester with iron is lower than that of Chloreth-40 (110°C), although it gives off heat less intensely.

Butyl ester of monochloromethylphosphinic acid



is a comparatively stable and slightly reactive substance (Figure 27). It boils giving off butylene at 259°C and reacts with iron at 260°C with small liberation of heat. Its antiburr properties are comparatively low (curve 4 in Figure 20).

Heightened stability and good antiburr properties (curve 5 in Figure 20) belong to the salt of monobutyl ester of trichloromethylphosphinic acid and methyloctadecylamine, chlorethamine, synthesized by B. V. Kelymenov:



The thermogram of this substance is shown in Figure 28. At 45°C heating is accompanied by intense absorption of heat due to fusion of chlorethamine. In the absence of iron powder the differential curve gives a jump at 232°C, indicating that reaction with liberation of heat occurs there (evidently, decomposition of the substance). In presence of iron powder the reaction of chlorethamine starts at 178°C, i.e., higher than for the previously considered esters of trichlorophosphinic acids.

These data agree with practice: the stability of salts of amines with chloralkylphosphinic acids is the reason for their application as antiburr additives.

5. Compounds Containing Sulfur and Chlorine Simultaneously

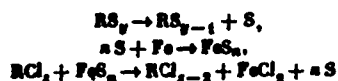
A very effective antiburr composition is a mixture of sulfur and chlorine compounds; however, in an overwhelming majority of cases it leads to corrosion of steel during rigid operating conditions, thus determining high contact temperatures.

It has been established [103] that the presence of active sulfur in an additive, consisting of a mixture of sulfur and chlorine compounds, accelerates the formation of iron chlorides, but the formation of iron sulfides in presence of chlorine components decreases. The presence of sulfur-containing compounds does not affect the production of hydrogen chloride, whereas the production of hydrogen sulfide is increased in presence of chlorine component.

The catalytic effect of sulfur compounds on the formation of chlorides is approximately proportionally to their activity during formation of sulfides; therefore, slightly active organic sulfides weakly assist the formation of chlorides.

The essence of the catalytical action of sulfur-containing compounds is that the iron sulfides forming under the influence of the temperature of friction then quickly react with chlorine, whereas the reaction of formation of iron chlorides by direct influence of chlorine on the surface of iron occurs significantly more slowly.

According to source material [103] this reaction can be depicted by the following equations:



Thus, according to these equations the sulfur-containing compounds quickly reacts with metal either directly, or being decomposed with yield of sulfur. The sulfides react with the chlorine-containing compound, forming chlorides and sulfur, which again gives FeS or FeS_n .

Analysis of electron diffraction of a copper plate subjected to the influence of oil with a sulfochloride-containing additive, carried out by K. V. Shishokina, revealed lines belonging to Cu , $CuCl_2 \cdot 2H_2O$, $CuCl_2$ and weak lines of CuS . After scratching the surface of the sample the lines of CuS are strengthened on the electron-diffraction pattern, and the lines of $CuCl_2 \cdot 2H_2O$ and $CuCl_2$ are significantly weakened. This indicates that the sulfide layers of metal appearing under the influence of sulfochlorine-containing compounds are stabler, penetrate deeper into the metal and, evidently, serve as substances which further react with chlorine compounds. This does not exclude the independent role of sulfur-containing compounds in preventing of grasping of surfaces.

Organic compounds containing chlorine and selenium also act this way; on the friction surfaces chlorides of metal are revealed, whereas selenium plays the role of a catalyst in forming chlorides [104].

The mechanism of catalytical action of sulfur in conditions of friction was also confirmed by Davey on a number of organic compounds containing, besides sulfur, also chlorine, iodine or bromine [63].

Jointly with Ye. I. Petyakina and others the author showed that the catalytical action of sulfur is indicated sufficiently by adding a small quantity of sulfur-containing additive to the chlorine component to sharply increase the antiburr properties of this composition in oil. This is illustrated by the diagram in Figure 18 (middle part). The maximum effect is attained at a ratio of approximately 70% of the chlorine component and 30% of the sulfur component. This effect almost does not depend on the sulfur concentration in the sulfur component of the additive, but to the strongest degree depends on the activity of the chlorine component, determined both by the structure of the compound and also by the quantity of chlorine in the molecule [72].

A very active sulfochlorine-containing additive is DI-(trichloropentyl)-sulfide, or Sulphol (see p. 57).

The activity of this compound is determined by the presence of the trichloromethyl group and the ratio of the quantities of chlorine and sulfur in the molecule. The trichloromethyl group causes the exothermic jump characteristic for compounds of this type at 153°C in the presence of iron powder indicating the intense reaction of Sulphol with iron (see Table 3).

6. Compounds Containing Sulfur, Chlorine and Phosphorus Simultaneously

Additives containing three active elements, sulfur, chlorine and phosphorus, possess great universality and, as a rule, act satisfactorily both at high loads and also at high speeds and low loads. Phosphorus promotes lowering of wear and smoothing of surfaces; sulfur lowers friction and is the catalyst of the antiburr effect ensured by chlorine.

Research in electron diffraction of steel surfaces subjected to the influence of oil containing an additive . . . three active elements, conducted on the request of the author by K. V. Shishokina, showed the chlorides concentrate on the surfaces and that the sulfides penetrate into the depths.

Through the radioactive isotope method it was shown [91] that the formation of metal sulfides on surfaces decreases in presence of phosphorus and chlorine.

The stability and ability to interact with metallic surfaces depends mainly on the character of the compound containing the three active elements (sulfur, chlorine and phosphorus). The Soviet additive LZ-309, obtained by the reaction of sodiumdialkyldithiophosphate with 1,3-dichlorbutene-2, disintegrates at 253°C (see Table 3). Interacting with iron powder, LZ-309 is effective in comparatively low concentrations, 5% whereas the foreign additive, Anglamol-70, containing dibenzylidysulfide as the sulfur-containing and being a composition of several compounds, is effective only in concentration of 9%. Thermographic analysis of Anglamol-70 (see Table 3) indicates its high stability; decomposition occurs at 289°C, and the reaction with iron powder occurs at 230°C with small liberation of heat.

7. Compounds Containing Metals

Lead soaps in combination with sulfur and chlorine compounds are good operating substances.

The mechanism of action of additives containing lead soaps and sulfur was studied [105] by the method of electron diffraction. Films forming at 150°C on steel under the influence of oil containing these additives were investigated.

It was determined that if the oil contained lead naphthenate and sulphurized fats, during a brief effect of temperature on steel films of lead sulfate (PbSO_4) formed, and during long or more intensive effect of temperature lead sulfide (PbS) formed. Upon heating in oil with only lead naphthenate the latter is evidently adsorbed on surfaces, which is revealed by diffraction pattern, similar to the diffraction of lead. During subsequent heating of these films in sulphurized oil the diffraction pattern changes, passing into rings characteristic for lead sulfate.

Thus, in the opinion of Simard and co-authors, the interaction of additives containing lead soaps and active sulfur with steel surfaces flows according to the following mechanism: first the lead soaps are adsorbed on the friction surfaces; then the lead soap film reacts with the sulfur with participation

of oxygen leading to the formation of lead sulfate; and, finally, lead sulfide is subsequently formed.

The mentioned authors consider that there can be two causes of lowering friction in presence of additives containing lead soaps and active sulfur:

1) lowering the resistance to shift of the formed lead sulfide films as compared to the resistance to shift of the initial metal (steel); 2) the formation a eutectic alloy, FeS-PbS , with a lowered point of fusion (970°C), which during friction transforms into a plastic state.

Contrast to this, Davey [9] assumes that lead sulfide will be formed independently of lead sulfate; in the process of reaction of iron with lead soaps, iron soaps and free lead appear; the free lead then reacts with sulfur to form lead sulfide.

An absolutely different, purely physical mechanism of action is ascribed to natural molybdenum disulfide (or tungsten disulfide). It is assumed that it is analogous to the mechanism of action of graphite. Slippery scales of these substances easily shift one along another under the effect of tangents of forces like a deck of cards.

The ability of the MoS_2 grid to shift is determined by the fact that the strongly polarized cations of molybdenum are combined with easily polarized anions of sulfur and thus the bond between Mo and S turns out to be significantly more durable than the bond between two atoms of sulfur, which ensures an easy shift in this plane [81].

Evidently the oxidized compounds and xanthogenates of molybdenum act otherwise, although, in the opinion of Hugel [83], the mechanism of action of molybdenum blue in combination with sulfur additives is analogous to the action of MoS_2 suspensions: under the effect of temperatures appearing during friction the complex compound of molybdenum blue decomposes and MoS_2 will be formed on the surfaces. During decomposition of molybdenum xanthogenates a film of molybdenum hydroxysulfide appears on the friction surfaces.

It seems to us that to explain the mechanism of action of molybdenum blue in combination with sulfur compounds there is no need to assume the formation of molybdenum disulfide with a flaky structure.

Jointly with Ye. I. Pyatyakina the author conducted research allowing the assumption of another mechanism.

In Figure 29 it is clear that Mo blue (2) in the absence of a sulfur component increases the antiburr properties of TS-14.5 oil (1), although to a lesser degree than in combination with the sulfur-containing additive, LZ-6/9 (3). This is full, naturally, since Mo blue is an oxygen rich compound. Meanwhile oxygen, just as sulfur, is a representative of group VI of the periodic table and, as proven by G. V. Vinogradov [106], easily interacts with metal surfaces, giving a strong antiburr effect.

Regarding molybdenum disulfide, as follows from the data of Figure 29, even a 10% concentration of it in oil does not give an effect equivalent to that which appears upon adding 1.5% Mo blue to oil (curves 7 and 2). The combination of Mo blue with chlorinated paraffin gives oil even higher antiburr properties (see curve 4).

The results of electron diffraction research of films forming on steel surfaces under the effect of molybdenum additives are given in Table 5.

Steel plates (steel 45) were heated in oil with the additives enumerated in the table at the shown temperatures for 1 hour. After that the plates were washed in hot benzene, then in ethyl alcohol and their surfaces were investigated.

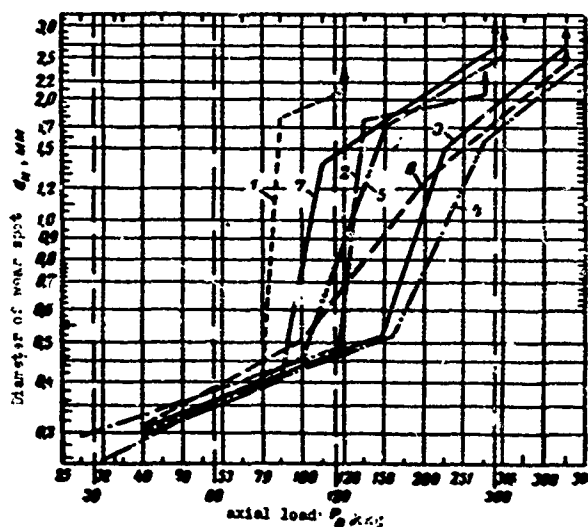


Fig. 29. Antiburr property of oil TS-14.5 with additives of molybdenum compounds.

Curve	Additive	Antiburr Properties			
	Designation	% in oil	OPI	P _k , kg	P _c , kg
1	Without additive...	-	37	79	126
2	Mo blue.....	1,5	56	126	282
3	Mo blue and LZ-6/9.....	1,5	89	158	447
4	Mo blue and chloroparaffin.....	3,0			
5	Chloroparaffin.....	1,5	97	163	501
6	LZ-6/9.....	5,0	58	100	280
7	Molybdenum disulfide	3,0	74	100	447
		10	52	89	316

Tabl. 5. Electron Diffraction Research of Films Forming on Steel Surfaces Under the Effect of TC-14.5 Oil with Additives of Molybdenum Compounds (According to K. I. Shishokina)

Indices	Additive				
	Mo S ₂		Mo Blue + LZ-6/9		Mo blue
Concentration of the additive	10		1,5+3		1,5
Temperature of experiment °C	150	250	150	250	150
Compounds revealed on surface	MoS ₂	MoS ₂	α-Fe α-Fe ₂ O ₃ *	γ-Fe ₂ O ₃ *	γ-Fe ₂ O ₃ *

*MoS₂ is observed.

As can be seen from the table, molybdenum disulfide was observed by diffractional lines only after heating the plate in oil with molybdenum disulfide, but not in oil with additive of molybdenum blue or with the sulfur additive LZ-6/9.

All this indicates that adding Mo blue in combination with a sulfur component will not form MoS₂ on the friction surfaces and practical calculation of the sulfur component by the stoichiometric formula on MoS₂ is groundless.

The presence of higher oxidized compounds of molybdenum on the surfaces after the test for friction is revealed by the qualitative electrographic method. Oxidized compounds of molybdenum pass to gelatinized paper impregnated with the electrolyte (potassium chloride) during transmission of a 30 ma current for one minute; after that they appear at first in a solution of tin chloride, and then potassium thiocyanate. In presence of potassium thiocyanate the MoC(SCN)₆ ion will be formed, coloring the paper a pink-raspberry color.

It is possible to assume that molybdenum blue, which is complex oxidized form of molybdenum with a variable valence, possesses high surface activity and reactivity with active element of the second component of the additive. Mo blue activates chlorine and sulfur evidently by forming of very different in character compounds of molybdenum with sulfur and chlorine, including oxysulfides and oxychlorides of molybdenum. With this the antiburr effect characteristic for compounds of sulfur and chlorine is combined with high surface activity of molybdenum blue which, in particular, affects the exclusively high value of the critical load P_k for compositions of additives containing Mo blue.

An analogous effect could evidently be obtained with other elements giving complex compounds due to their variable valence.

II. 3. Recommendations for Selecting Oil Additives

Selection of oil additives is determined by the operating conditions of the lubricating substances in friction nodes and the specific requirements of the machine or mechanism.

A. Automobiles

Here we will not consider additives used in oils for internal combustion engines in detail; this question exceeds the bounds of this work. As a rule, in this case washing, antioxidant and anticorrosion additives, also possessing antiwear properties are used.

In selecting additives to oils for automobile transmissions the following considerations hold.

The highest and impact loads are carried by the main transmission of the rear axle. When the main transmission has hypoid gears, the high speeds of relative slip of teeth cause intense heat emission, which leads to jamming of surfaces; to prevent this a strong antiburr additive is unconditionally required.

Gears and bearings of transmission boxes usually do not carry specially high loads, and therefore, as a rule, application of antiburr additives in oils lubricating the mechanisms of automobile transmission boxes is not necessary,

Table 6. Additions to Oils for Friction Nodes of Automobiles

Lubricated nodes	Addition	
	Recommended type	Approximate composition
Transmission Box	No additive or an anti-wear additive is recommended	Sulfur and phosphorus-containing products; chlorine-containing additives are not recommended
Rear axel with spiral-conical transmission	Antiburr additive of average activity	Chlorine-containing additives, most often chloroparaffin; sulfur-containing additives or sulfur and chlorine-containing additives
	For longer wear special long-wear additives ¹	Most frequently additives containing sulfur and lead soaps
Rear axel with hypoid transmission	Strong antiburr additives;	Sulfochlorine-containing component and zinc dithiophosphate. Additives containing S, Cl and P. Sulfochlorine-containing additives with an anticorrosion component.
	Long-wear additives for factory filling	Sulphurized fats and lead naphthenate or a component containing sulfur and chlorine and lead naphthenate, or a chlorine-containing component and zinc dithiophosphate, or a sulfochlorine-containing additive with an anticorrosion component
Steering control	Antiwear additives (the same as in oils for transmission boxes;)	Sulfur or sulfophosphorus-containing products
	Long-wear additives ¹	Sulphurized fats and lead soaps
Cardan joints	No additive or an additive against fretting corrosion	Colloidal suspensions of graphite or molybdenum disulfide

¹The desirable properties of these additives in the first period of operation theoretically should, that as a result of heightened wear of surfaces, ensure their intense extra operation and smoothing, evoking, on the one hand, lowering of local loads, and on the other, a shift to more perfect "quasihydrodynamic" conditions of friction.

Table 6. (Cont.)

Lubricated nodes	Addition	
	Recommended type	Approximate Composition
Combined transmissions having toothed engagement and hydrodynamic transmission and serviced by one lubricating system	Antiburr additives of average activity, inhibitors of corrosion and oxidation	Additives containing sulfur, chlorine and phosphorus and anti-corrosive component of alkaline type. Dialkyldithiophosphates of metals
Rear axel and differential having friction clutches of limited slippings, serviced by oil from one lubricating system.	Strong antiburr additives containing a friction stabilizing component.	Sulfochlorine derivatives, zinc dialkyldithiophosphates and sulphurized fatty oils.

and sometimes can be harmful, since it can evoke heightened wear of the working surfaces and corrosion of details. In most cases in transmission boxes it is expedient to use oils with antiwear additives. For new constructions of heavy trucks it frequently appears necessity to use oils with antiburr additives in transmission boxes.

The character of additives to oils applied in different nodes of automobiles is given in Table 6 [107, 108].

B. Turbines

Besides lubricating transmission gears from the turbine to the screw propeller, turbine oils should also fulfill the function of a lubricant of the slip bearings of liquid friction and roller bearings, and also the function of a cooling oil in the case of a steam turbine and working fluid in the case of a hydroconverter. Therefore additives to turbine oils should not only improve the antiwear properties, but also should not allow corrosion of colored and black alloys, should not worsen the deemulsifying ability of turbine oils and should ensure their high stability and absence of sedimentation [109, 110, 111]. Furthermore, in steam turbines, where cases of moisture getting into the lubricating system are observed, the additive should not evoke rusting of metal or be subjected to hydrolisis. Additives for oils servicing hydrotransformers should not negatively affect the linings. The types of applied additives are

given in table 7.

Table 7. Additives to Turbine Oils Servicing Gear Transmissions, Hydroconverters and Bearings.

Recommended Type	Approximate Composition
Antiburr additives of average activity	Sulfur-containing additives with anticorrosion component or sulfochlorophosphorus-containing additives.
Inhibitors of oxidation, corrosion and rusting.	Ionol, zinc dithiophosphates, amines, derivatives of maleic anhydrides, alkylsalicylates of calcium.

C. Rolling Equipment

Gear transmissions of rolling mills are subjected to high impact loads. Therefore, cases of jamming of toothed wheels are common, although basic type of damage remains fatigue pitting of surfaces; this cannot be prevented with antiburr additives. Most subjected to jamming are the teeth surfaces of roller gears directly adjoining to roll stands of rolling mills. Water, passed under high pressure to the rolled metal for sintering, gets into the lubricating system of roller gears (and if the lubricating system is a general circulatory one, then it gets into the general lubricating system). The presence of water in the lubricating systems reducers and roller gears of rolling mills extraordinarily complicates the selection of antiburr additives. They should be required not to evoke corrosion and rusting of metal in presence of water, not to hy ~~size~~ and not to worsen the demulsifying ability of the oil. These requirements are met by antiburr additives of average activities, being compositions of lead and sulphurized fats.

D. Metal-Cutting Machines

Friction nodes of metal-cutting machines, as a rule, do not need antiburr or antiwear additives, since wear of gears, especially guides, has an abrasive character. It is expedient to use antifriction (for worm transmissions) and

friction stabilizing (for guides) additives given in Table 8. Abroad, as friction stabilizing additives are applied saturated fatty acids in foreign lands (for instance, stearic), and we have developed additive [V-401] (B-401).

Table 8. Additives to Oils for Metal-Cutting Machines

Lubricated nodes	Recommended type	Approximate composition
Feed guides	Additive; friction stabilizing	Saturated fatty acids and their salts (e.g., aluminum stearate)
Worm transmissions	Additive, lowering friction and increasing efficiency.	Sulphurized, unsulphurized, or phosphorus pentasulfide treated animals fats.

For heavily loaded worm transmissions compounds of mineral oils with animal or vegetable fats are recommended. In USSR for this purpose the additive, [EZ-2] (33-2), constituting etherified castor oil treated with phosphorus pentasulfide has been developed.

For high-speed worm transmissions in foreign lands they use a synthetic oil, constituting a mixture ethylene and propyleneoxides. From the available information this oil lowers loss of power in worm engagement noticeably more than petroleum oils [112, 113].

E. Textile Machines

The most important question in textile machines is lowering losses from friction, inasmuch as expenditure of power on direct fulfillment of technological operations is minute (2-5% of total power consumption), and the number of friction nodes and loss of power overcoming friction are great (95-98%). Because of this in oils for textile machines, especially in oils for lubricating spindles, it is expedient to apply antifriction additives.

Oils for spindles of spinning machines and runner ring of ring-spinning machines also needs antiwear and antiburr additives [7] due to spot wear of spindle and jamming of runner, leading to frequent breaking of thread.

Table 9 gives the approximate types of additives used for this goal [114].

Table 9. Additions to Oils for Textile Machines

Lubricated nodes	Recommended type	Approximate composition
Step bearings of spindles	Antifriction and anti-wear	Esters (e.g., glycerine monooleate)
	Anticorrosion and stabilizing	Alkaline sulfonates, alkylphenolates
Runners of ring-spinning machines	Antifriction and antiburr	Esters, sulphurized terpenes
	Anticorrosion and stabilizing	Sulfonates of calcium or sodium, alkylphenolates.

Additives increasing the stability of oil are also very important in this case, since this allows lowering the accumulation of deposits in spindles meshes, increasing interoverhaul periods and lowering losses on friction in step bearings.

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