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CHEMISTRY

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ADSORPTION

UDC 543.544

ADSORPTION OF NITROGENOUS BASES TO NITRILE-SILICONE KhE-60 AND AT SUPPORT-GAS INTERFACE

Kiev TEORETICHESKAYA I EKSPERIMENTAL'NAYA KHIMIYA in Russian Vol 20, No 6, Nov-Dec 84 (manuscript received 11 Jul 83; in final form 23 Jul 84)
pp 751-754

MANDROV, G. A. and PENKE, I. Kh., Industrial Pharmaceutical Chemistry
"Olaynfarm" Association, Olayne

[Abstract] Determinations were made of the adsorption coefficients and thermodynamics of the adsorption of various nitrogenous bases (pyridines and pyrazines) to nitrile-silicone KhE-60 (3-8% cyanoethylpolysiloxane KhE-60 on chromaton-N-super) at 413-453°K. Under conditions typical of gas chromatography under hydrogen gas flow data were obtained which were summarized in tabular form, demonstrating, for example, that at 433°K approximately 70% of a given base is retained within the immobile base, and that the coefficient of adsorption for that phase increases insignificantly with an increase in the number of C atoms. For pyrazines the negative heats of reaction ranged from 35.9 to 41.0 kJ/moles, and for the pyridines from 46.8 to 59.8 kJ/mole. The relatively high heats of adsorption indicated the presence of specific intermolecular interactions predetermined by the electronic structure of the amines. The high positive values for the free energies of adsorption at the KhE-60-support interface reflected the mechanistic difficulties of interphase adsorption. References 8 (Russian). [146-12172]

ALKALOIDS

UDC 547.944/945

ALKALOIDS OF LINDELOFIA MACROSTYLA (BUNGE) M. POP.

Dushanbe DOKLADY AKADEMII NAUK TADZHIKSKOY SSR in Russian Vol 27, No 10,
Oct 84 (manuscript received 27 Jun 84) pp 577-581

SADYKOV, Yu. D. and KHODZHIMATOV, M., Institute of Chemistry
imeni V. I. Nikitin, TaSSR Academy of Sciences

[Abstract] The alkaloids viridiflorin, lindelofin, echinatin and their
corresponding N-oxides were extracted from lindelofia macrostyla (Bunge).
Pharmacological tests of some salts of these alkaloids on cats showed that
lindelofin chlorohydrate has hypotensive and spasmolytic properties.

References 7 (Russian).

[194-12765]

ANALYTICAL CHEMISTRY

UDC 545.83

SIMULTANEOUS DETERMINATION OF CARBON, HYDROGEN AND PHOSPHORUS IN
ORGANOSELENIUM COMPOUNDS. PART 2.

Alma-Ata IZVESTIYA AKADEMII NAUK KAZAKHSKOY SSR: SERIYA KHIMICHESKAYA
in Russian No 6, Nov-Dec 84 (manuscript received 3 Mar 83) pp 1-2

BAZALITSKAYA, V. S., LELYUKH, M. I., ALEKSEYEVA, N. N. and SAYDAKOVA, M. S.,
Order of the Red Banner of Labor Institute of Chemical Sciences,
Kazakh SSR Academy of Sciences

[Abstract] Description is provided for the simultaneous combustion analysis of carbon, hydrogen and phosphorus in 15 organoselenium compounds. A quartz vessel filled 2/3rds with quartz and 4-6 mg of the sample, received a quartz tube filled with nickel oxide, and was subsequently heated to 900°C with a 25 ml/min oxygen flow. After 40 min of combustion, carbon, hydrogen and phosphorus were determined by standard analytical methods, with the results uncomplicated by the volatility of selenium dioxide, which was absorbed by the nickel oxide. The error in the determination of carbon, phosphorus and hydrogen was ± 0.3 abs.%. References 6 (Russian).
[129-12172]

UDC 543.4:546.791

EFFECTS OF ACIDITY ON KINETICS OF ARSENAZO III-URANYL ION COMPLEX FORMATION

Kiev TEORETICHESKAYA I EKSPERIMENTAL'NAYA KHIMIYA in Russian Vol 20, No 6,
Nov-Dec 84 (manuscript received 31 Oct 83) pp 749-751

POGONIN, V. I., LIKHONINA, Ye. A. and CHIBISOV, A. K., Institute of
Geochemistry and Analytical Chemistry imeni V. I. Vernadskiy, USSR Academy
of Sciences, Moscow

[Abstract] Spectrophotometry was employed in obtaining pH profiles of complex formation between arsenazo III and the uranyl ion over a wide pH range (0.5-7.0) at 298°K. Complexing is reflected in the disappearance of the absorption at 450 nm (due to the reagent) and the appearance of absorption at 590-700 nm. With an increase in the pH to 6-7 the effective rate constant for complexing decreases, due to hydrolysis of the uranyl ion and the low reactivity of $UO_2(OH)^+$ in complexing with arsenazo III. Figures 4; references 6: 4 Russian, 2 Western.
[146-12172]

BIOCHEMISTRY

UDC 543.5:546.3

DETERMINATION OF PHYSIOLOGICALLY ACTIVE METALS IN BIOLOGICAL SAMPLES BY
KINETIC METHODS

Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA: KIMIYA in Russian Vol 25, No 6,
Nov-Dec 84 (manuscript received 29 Jun 83) pp 559-562

USHAKOVA, N. M. and DOLMANOVA, I. F., Chair of Analytical Chemistry

[Abstract] An analytical method has been developed for the determination of Co(II) levels in human urine samples which depends on the catalytic activity of the metal in diphenylcarbazone. A 5 ml sample was subjected to dry ashing, and the ash used as a catalyst in the oxidation of diphenylcarbazone by hydrogen peroxide, with the construction of standard linear plots. The lower limits for the determination of Co(II) were on the order of 2×10^{-4} $\mu\text{g/ml}$. Normal levels of Co(II) in human urine were found to fall in the range of $(2-8) \times 10^{-3}$ $\mu\text{g/ml}$. Figures 1; references 11: 6 Russian, 5 Western. [135-12172]

UDC 542.0

REDUCTION OF SODIUM NITROPRUSSIDE WITH SUBSEQUENT ELIMINATION OF NITROGEN
OXIDES IN ANIMAL BODIES

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 59, No 2, Feb 85
(manuscript received 20 Dec 83) pp 462-467

KLESHCHEV, A. L., MORDVINTSEV, P. I., SHABARCHINA, M. M. and VANIN, A. F.,
Institute of Chemical Physics, USSR Academy of Sciences, Moscow

[Abstract] White mice were given abdominal injections of sodium diethyldithiocarbamide to form mononitrosyl iron complexes in organ tissues, followed by injections of nitroprusside ions. They were then sacrificed and blood and organ tissue samples taken for electron paramagnetic resonance (EPR) analysis at 77°K and at 290°K. Analogous experiments were conducted on an Ehrlich strain of bladder cancer incubated in the mice. At the lower temperature, liver cells perfused with the nitroprusside showed an asymmetric

singlet EPR signal with a weakly-expressed component ascribed to a reduced form of the nitroprusside, stable in polar organic solvents. Detailed EPR analysis of organ tissues and cancer cells indicated that the nitroprusside broke down into free Fe-NO groups. In living tissue, this apparently led to the activation of cellular enzymes by nitrogen oxide. Equivalent concentrations in various organs indicated the actual breakdown occurred in the blood or on the surface of the cancer cells. Figures 4; references 17: 6 Russian, 11 Western.
[209-12672]

UDC 547.833.1:547.833.3

ISOQUINOLINE DERIVATIVES. 23 COMMUNICATION. SYNTHESIS AND BIOLOGICAL PROPERTIES OF 1-ARYLALKENYL-6,7-DIMETHOXY-4-SPIROSUBSTITUTED HYDROGENATED DERIVATIVES OF ISOQUINOLINE AND THEIR NONCYCLIC ANALOGUES

Yerevan ARMYANSKIY KHIMICHESKIY ZHURNAL in Russian Vol 37, No 11, Nov 84 (manuscript received 14 Nov 83) pp 707-712

AYRAPETYAN, G. K., ARUSTAMYAN, Zh. S., PARTEV, D. Z., SARKISYAN, L. M. and MARKARYAN, E. A., Institute of Fine Organic Chemistry imeni A. L. Mnzhoyan, ArmSSR Academy of Sciences, Yerevan

[Abstract] In earlier studies, 1-arylalkenyl- and 4-spirosubstituted derivatives of isoquinolines were synthesized. In the present work, isoquinoline derivatives were synthesized with both of these fragments in one molecule in order to study the relationship between their biological activity and the arylalkenyl double bond combined with spirocycloalkane substituent. To obtain these compounds, a selective reduction with LiAlH_4 and aluminum hydride of the amide and imine groups conjugated with the carbon-carbon double bond was carried out. These compounds showed only weak spasmolytic or coronarodilating activity and weak activity towards the CNS. Anti-convulsive properties were also very limited. References 6 (Russian).
[205-7813]

CATALYSIS

UDC 541.128.13

HALOGEN ION-MEDIATED OXIDATION OF ARSINE BY HETEROPOLY ACIDS

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 58, No 12, Dec 84
(manuscript received 21 Mar 83) pp 2975-2979

DORFMAN, Ya. A., ALESHKOVA, M. M., DOROSHKEVICH, D. M. and KEL'MAN, I. V.,
Institute of Organic Catalysis and Electrochemistry, Kazakh SSR Academy of
Sciences, Alma-Ata

[Abstract] Thermodynamic and kinetic studies were conducted on the oxidation of arsine by heteropolyacids catalyzed by halogen ions. Analysis of the kinetic data indicated that in a system employing P-Mo-V heteropoly acid the rate-limiting step appears to be intraspheric oxidation of arsine in the intermediate complex formed by V(V) with AsH_3 and the halogen ion. The conclusion was also supported by quantum mechanical calculations of the electron structure of the intermediate complex. The energies of activation with I^- , Br^- and Cl^- were calculated as 47.8, 48.8 and 61.4 kJ/mole, respectively. Figures 2; references 11: 9 Russian, 2 Western.
[122-12172]

UDC 541.128+546.57

ACTIVE CENTER FORMATION IN Ag/SiO_2 CATALYSTS

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 58, No 12, Dec 84
(manuscript received 30 Sep 83) pp 2980-2983

VOROB'YEV, V. N., KORONTSEVICH, A. Yu. and RAZIKOV, K. Kh., All-Union
Scientific Research Chemical Engineering Institute of the Medical Industry,
Tashkent

[Abstract] Electron spectroscopy and other techniques were used to follow the structural transformations in Ag/SiO_2 catalysts (1-35 wt% Ag) over the 20-1100°C temperature range. The catalysts were formed by impregnation of silica gel with $AgNO_3$ solutions, drying, and heat treatment for 5 h at temperature of 300 to 1100°C. Analysis of the electronic spectra demonstrated that in addition to decomposition of $AgNO_3$ to metallic Ag there

was also intensive oxidation of Ag and Ag^+ to Ag^{++} and Ag^{+++} , as well as migration of the Ag ions into support matrix. The Ag^{++} and Ag^{+++} were stable at 1100°C , and remained refractory to reduction by hydrogen at temperatures approaching 1000°C . Since the Ag/SiO_2 catalysts are employed under oxygen or air at temperatures exceeding 600°C , they undergo gradual oxidation to the ionic forms of Ag that are irreversibly lost by migration into the support, and thereby lead to gradual loss of catalytic activity. Figures 4; references 7 (Russian).
[122-12172]

UDC 541.128

CATALYTIC TRANSFORMATION OF 1,1-DIMETHYLHYDRAZINE BY $\text{Ir}/\text{Al}_2\text{O}_3$

Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA: KHIMIYA in Russian Vol 25, No 6, Nov-Dec 84 (manuscript received 21 Jul 83) pp 545-547

RAZUMAYEVA, A. Ye., YEMEL'YANOVA, G. I. and STRAKHOV, B. V., Chair of Physical Chemistry

[Abstract] An impulse microcatalytic method was employed for the transformation of 1,1-dimethylhydrazine (DMH) by $\text{Ir}/\text{Al}_2\text{O}_3$ (30 wt%), with the products separated chromatographically. At 100°C the transformation involved breakage of the N-N bond and the formation of dimethylamine (DMA, 65%) and ammonia (22%) as the major products, as well as the formation of N_2 (10%) and CH_4 (3%). At 250°C , breakage of the N-N bond is a less dominant reaction with the formation of greater quantities of N_2 (19%) and CH_4 (16%), while DMA (49%) and ammonia (16%) are formed in lesser quantities. The rate constants at 100°C and 200°C for the transformation of DMH were, respectively, 1.2 and $3.2 \mu\text{moles/g}\cdot\text{atm}\cdot\text{sec}$. Loss of catalytic activity was observed with repeated use of $\text{Ir}/\text{Al}_2\text{O}_3$, apparently due to large granule formation and loss of surface area. Figures 2; references 7: 5 Russian, 2 Western.
[135-12172]

UDC 541.183.03

AGING AND STRUCTURE OF SPONGY RHODIUM, RUTHENIUM AND RHODIUM/RUTHENIUM CATALYSTS

Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA: KHIMIYA in Russian Vol 25, No 6, Nov-Dec 84 (manuscript received 16 May 83) pp 575-578

GRISHINA, T. M., NESTERENKO, L. N. and VOVCHENKO, G. D. (deceased), Chair of General Chemistry

[Abstract] A variety of physical and chemical methods, including electron microscopy, were used in studies on the phase structure of aging spongy Rh, Ru and Rh/Rh catalytic systems. Phase composition was found not to be

affected by aging, and neither were the lattice parameters. However, aging was accompanied by a decrease in the particle size, each consisting of 2-3 blocks. A genetic relationship was found to exist between the starting melts and the final spongy products. Figures 1; references 8 (Russian).
[135-12172]

UDC 547.362+66.095.253.7

ALKYLATION OF 1,3,3-TRIPHENYLPROPYNE BY INTERPHASE CATALYSIS

Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA: KHIMIYA in Russian Vol 25, No 6, Nov-Dec 84 (manuscript received 7 Jul 83) pp 588-591

DEM'YANOV, P. I., MALO NYANGA and PETROSYAN, V. S., Chair of Organic Chemistry

[Abstract] Interphase catalysis was employed for the alkylation of 1,3,3-triphenylpropyne in benzene, THF, dimethyl sulfoxide, or acetonitrile, employing iodoethane or bromoethane as the alkylating agents in the presence of bases (KOH, NaOH, KF, Bu_4NF), and 18-crown-6 ether, tetrabutylammonium fluoride, or benzyltriethylammonium chloride as the catalyst. Alkylation of 1,3,3-triphenylpropyne yielded the formation of 1,3,3-triphenyl-3-ethylpropyne in low yields in mixtures with 1,3,3-triphenyl-1-ethylallene. Under the conditions employed, alkylation of 1,3,3-triphenylpropyne was complicated by its isomerization into triphenylallene in the presence of the bases, and the subsequent dimerization of the triphenylallene. References 12: 3 Russian, 9 Western.
[135-12172]

UDC 541.128:542.941

HYDROGENATION OF GLUCOSE IN AQUEOUS AND WATER-ALCOHOL SOLUTIONS ON IMMOBILIZED CATALYST. PART 1. HYDROGENATION ON Ni/Ti CATALYST

Alma-Ata IZVESTIYA AKADEMII NAUK KAZAKHSKOY SSR: SERIYA KHIMICHESKAYA in Russian No 6, Nov-Dec 84 (manuscript received 16 Jun 83) pp 27-31

SHUMATEVA, N. F., BIZHANOV, F. B. and PRNAZAROV, Zh., Institute of Organic Catalysis and Electrochemistry, Kazakh SSR Academy of Sciences, Alma-Ata

[Abstract] Hydrogenation of glucose in aqueous and isopropanol solutions was carried out in an autoclave over an immobilized Ni-(3%)Ti-(50%)Al catalyst, under hydrogen pressures of 3.9-11.8 MPa and a temperature range of 393 to 433°C. The hydrogenation reaction was first order with respect to glucose and hydrogen, and enhanced by the presence of the alcohol. Maximum sorbitol yield (88.4%) was obtained at 393°C, 7.8 MPa hydrogen, 15% glucose concentration, and an isopropanol: water ratio of 4:1. Figures 4; references 6 (Russian).
[129-12172]

UDC 541.128

INVESTIGATION OF INFLUENCE OF CdSO_4 ON PROPERTIES OF CATALYST Pt/SiO_2
USING METHOD OF DETERMINING 'SOLUBLE' FORM OF PLATINUM

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 59, No 2, Feb 85
(manuscript received 5 May 83) pp 346-348

SHEKHOBALOVA, V. I. and MOCHALOVA, T. I., Chemistry Faculty, Moscow State University imeni M. V. Lomonosov

[Abstract] Silica gel with a relative surface of 136 m^2 was used to prepare catalysts with 0.86 to 3.8 wt.% Pt. These were exposed to CdSO_4 solutions for 48 h and the amount of adsorbed salt measured. This remained fairly constant regardless of the amount of Pt on the silica gel, a not unexpected result due to the relatively low levels of Pt. The adsorbed salt reached a concentration 20-30 times the Pt surface concentration, but was apparently all adsorbed directly on the silica gel surface and did not significantly affect the catalytic activity in the reduction of hydrogen peroxide. The content of CdSO_4 did not appear to affect the quantity of the soluble form $[\text{Pt}^{+4}]$ of Pt on the working surfaces. A determination of various kinetic properties of the catalysts confirmed the lack of poisoning effect of CdSO_4 on these Pt-silica gel catalysts used for dissociating hydrogen peroxide. Figures 4; references 4 (Russian).
[209-12672]

UDC 541.135+183:546

INFLUENCE OF TEMPERATURE ON RATE OF ELECTROREDUCTION OF NITROETHANE ON
ELECTRODEPOSITED PALLADIUM-RHODIUM CATALYSTS

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 59, No 2, Feb 85
(manuscript received 1 Mar 83) pp 477-479

GRISHINA, T. M., Chemistry Faculty, Moscow State University imeni imeni M. V. Lomonosov

[Abstract] Pd-Rh catalysts with 0, 18, 31, 44, 75, 88, and 100 atom % Rd were used for electrochemical reduction of 0.2 M solutions of nitroethane in 1 N sulfuric acid over the range 10-40°C. In all cases, the reaction rate increased with temperature, with the effect more strongly expressed at higher anode voltages. Reaction rates were highest with alloys having high Pd content; these corresponded to the lowest effective energies of activation. Apparently, surface poisoning also affected the reaction rate and was more pronounced for alloys with higher Rd content. Figures 1; references 5 (Russian).
[209-12672]

UDC 541.15:541.183.03+543.42

ADSORPTION PROPERTIES OF γ -IRRADIATED ALUMINOPLATINUM CATALYST

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 59, No 2, Feb 85
(manuscript received 22 Jun 83) pp 496-498

KUZEMBAYEV, K. K., KUANYSHEV, A. Sh., and KRYLOVA, L. P., Institute of Organic Catalysis and Electrochemistry, KaSSR Academy of Sciences, Alma-Ata

[Abstract] The adsorption of purified CO on a catalyst of 5% Pt/ γ -Al₂O₃ was studied by infrared spectrometry before and after gamma irradiation using catalysts in the form of pressed plates and as a suspension in vaseline on glass. Irradiation in oxygen, hydrogen, or helium decreased the intensity of the CO adsorption band. Irradiation apparently reduced the chemisorption capacity of the catalyst for CO by injecting electrons from the metal into the carrier. Annealing in a hydrogen stream at temperatures up to 500°C removed radiation defects which had tended to increase the catalytic activity. Under these conditions, infrared spectroscopy indicated the presence of Pt hydride, apparently formed where radiation defects were removed by the annealing. The hydride reaction appeared to be independent of the reduction of CO oxidation products which had formed on the surface at room temperature chemisorption. Figures 2; references 8: 7 Russian, 1 Western.
[209-12672]

UDC 665.656.2:54-44:661.183.6

PHYSICOCHEMICAL AND CATALYTIC PROPERTIES OF METAL-ZEOLITE CATALYSTS FOR ISOMERIZATION OF n-ALKANES PROMOTED BY HYDROGEN SULFIDE

Moscow NEFTEKHIMIYA in Russian Vol 25, No 1, Jan-Feb 85
(manuscript received 4 Jan 84) pp 8-16

TOPCHIEVA, K. V. (deceased), DOROGOCHINSKAYA, V. A., BASINA, B. V., KUBASOV, A. A. and IVANOVA, T. M., Groznenskiy Petroleum Scientific Research Institute; Moscow State University imeni M. V. Lomonosov; Scientific Research Institute for Organic Semimanufactured Products and Dyes

[Abstract] Processing with various promoters, such as CO₂, H₂O, H₂S or thiophene has been used effectively to increase the activity of metallic catalysts of n-alkane isomerization. The last two promoters, H₂S and thiophene, have given ambiguous results, and the present article seeks to clarify these contradictions by comparing catalytic surfaces, structures, acidic and electronic properties of initial and hydrogen-sulfide processed Pd-containing zeolite catalysts. Palladium was introduced by ion transfer; hydrogen-sulfide processing was conducted at 120°C, while air at 450°C and hydrogen at 350°C were also brought into contact with the catalyst. Subsequent analysis showed infrared spectral bands that confirmed the presence of sulfur and the resultant increase in durability. Thiophene also had beneficial effects on the Pd-zeolite catalyst. Proton acidity was

higher for the sulfur-treated catalyst; this was related to decomposition of hydrogen sulfide and thiophene and was accompanied by proton formation. X-ray photoelectronic spectroscopy and X-ray phase analysis showed that Pd particles on the zeolite surfaces were reduced in size when treated with sulfur compounds. The processing regimen of H_2S at 120° , air at 450° and hydrogen at $350^\circ C$ was recommended for treating the catalyst. Figures 6; references 18: 12 Russian, 6 Western.
[206-12131]

UDC 665.652.2:661.183.6.004.14

ISOMERIZATION OF m-XYLENE AND ETHYLBENZENE ON CATALYSTS THAT CONTAIN HIGH SILICA ZEOLITE

Moscow NEFTEKHIMIYA in Russian Vol 25, No 1, Jan-Feb 85
(manuscript received 11 Mar 83) pp 17-21

ANOKHINA, T. A., KHADZHIYEV, S. N., BAYBURSKIY, V. L. and
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[Abstract] Modern petroleum processing uses zeolite catalysts with high ratios of $SiO_2:Al_2O_3$. Recent Soviet research has developed ultra-high-silica (UHS) zeolites of the ZSM family. The present article reports on details of the reaction of xylene isomerization on such catalysts. The hydrogen form of the UHS zeolite with a molecular ratio of SiO_2/Al_2O_3 of 36.0 was enhanced with 2.0% Pd by weight. After further processing, a hydrocarbon mixture with 77% m-xylene and 23% ethylbenzene was passed over the catalyst in a reaction chamber. Subsequent gas-liquid chromatography results showed that isomerate yield depended on catalyst composition and the conditions under which the experiment was conducted. Increasing temperature from 350 to $450^\circ C$, for example, increased the amount of whole p- and o-xylenes in the isomerate, although with increased UHS-zeolite content (from 5 to 50% by weight), the temperature factor became less important. Active phase content was also important in determining p- and o-xylene fractions. By-products such as benzene, toluene and trimethylbenzenes were regarded to be products of ethylbenzene transformation. Very little disproportionation and hydrodealkylation took place. The basic source of hydromethylation of products of xylenes was p-xylene. Figures 1, references 11: 9 Russian (of which 5 are reports on US patents), 2 Western.
[206-12131]

UDC 547.214:542.952.1:541.128:661.183.6

TRANSFORMATION OF n-BUTANE IN C₄-C₅ ISOPARAFFINS ON MORDENITE CATALYSTS

Moscow NEFTEKHIMIYA in Russian Vol 25, No 1, Jan-Feb 85
(manuscript received 9 Nov 83 pp 22-27)

KRUPINA, N. N. and DOROGOCHINSKIY, A. Z., Groznenskiy Petroleum Institute

[Abstract] Isobutane and isopentane produced in isomerization of normal C₄ and C₅ hydrocarbons are used in alkylation processes to make motor fuels, synthetic rubbers and other chemical products. The present article reports on study of popular mordenite catalysts and conditions for conducting reactions to determine intensity and selectivity in forming C₄-C₅ isoparaaffins from n-butane. The SiO₂:Al₂O₃ ratio of the zeolite tested was 11.0; the zeolite was granulated with a 20% Al₂O₃ binder. Tests were then conducted at 200-400°C in a constant feed chamber at pressure of 0.1-2.5 mPa, with varying feed speeds, molecular ratios and overall duration of testing. General catalyst activity was measured on the basis of n-butane transformation, while activity in forming C₄-C₅ isoparaaffins was determined on the basis of yield comparing input and output materials. The search for optimum conditions included varying SiO₂:Al₂O₃ ratios to 19, with 0.5% platinum by weight. Results showed that increased pressure brought a decrease in n-butane conversion from 56.0 to 40.0%, while isoparaaffin yield also fell from 42.7 to 34.4% (both by weight). Optimum conditions of 250°C, 1.5 mPa pressure and other parameters gave 46.5% n-butane conversion and 39.2% yield of isoparaaffins. Figures 3; references 7: 3 Russian (1 US patent), 4 Western.
[206-12131]

UDC 547.313.2:661.183.6.004

TRANSFORMING ETHYLENE ON HIGH SILICA ZEOLITES

Moscow NEFTEKHIMIYA in Russian Vol 25, No 1, Jan-Feb 85
(manuscript received 20 Feb 84) pp 28-31

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[Abstract] Recently synthesized nitrogen-containing ultra-high-silica (UHS) zeolites are of great interest as catalysts and adsorbents. The present article reports on study of the effects of chemical composition and experimental conditions on the product of ethylene conversion. Molecular ratios of SiO₂/Al₂O₃ of 26, 64 and 80 were tested in decationed forms. Ethylene fed at 150 hour⁻¹ at 573 K produced basic products in the C₃-C₆ range, with a predominance of isoparaaffins. The UHS zeolite retained high catalytic activity throughout the tests, but as test duration increased, there was a

shift in conversion products resulting in less C_3-C_4 and more C_5-C_6 hydrocarbons. At elevated temperatures the UHS-26 zeolite showed reduced weight of converted products. Results differed markedly for the control UHS-91 zeolite, which had maximum yields of all fractions at the highest test temperature, 573 K. Figures 1; references 6: 4 Russian, 2 Western.
[206-12131]

UDC 547.535.1:665.2:661.183.6

CONVERSION OF PSEUDOCUMENE ON HIGH SILICA ZEOLITES

Moscow NEFTEKHIMIYA in Russian Vol 25, No 1, Jan-Feb 85
(manuscript received 10 Mar 83) pp 32-35

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[Abstract] In the last decade much has been published about use of ZSM zeolites for alkylation, trans-alkylation, disproportionation and isomerization of aromatic hydrocarbons. The present article reports on Soviet TsVK-XI-4 and TsVM zeolites in the isomerization of pseudocumene, in comparison with mordenite, dealuminized mordenite, NU zeolite and amorphous aluminosilicate. Catalyst crystallization was 95 and 100%, and the molecular ratios of SiO_2/Al_2O_3 60 and 30. Catalytic conversion of pseudocumene was studied at atmospheric temperature in a continuous flow laboratory device. Although the SVK zeolites were less active than amorphous aluminosilicate, mordenite or U zeolite, their catalytic selectivity was markedly higher and avoided production of tetramethylbenzenes. Results showed that in the presence of NTsVK and NTsVM catalysts, pseudocumene at 500°C forms 40-50% isomers yielding about 22% mesitylene, and no tetramethylbenzenes. Amorphous aluminosilicate, NU zeolite and dealuminated mordenite worked as catalysts at lower temperatures, but produced side reactions of disproportionation and dealkylation. References 13: 8 Russian, 5 Western.
[206-12131]

UDC 541.128:54-44:[546.719+546.92]542.941.8:547.592.1

EFFECT OF OXIDES OF ALKALINE EARTH ELEMENTS ON PROPERTIES OF Pt+Re gamma- Al_2O_3 CATALYSTS IN DEHYDRATION OF CYCLOHEXANE

Moscow NEFTEKHIMIYA in Russian Vol 25, No 1, Jan-Feb 85
(manuscript received 28 Dec 83) pp 36-40

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[Abstract] In recent years wide application has been made of rhenium in preparing alumoplatinum reforming catalysts. The present article reports

on study of such catalysts with third components of iridium, germanium, cobalt, tin and other alkaline earth elements to determine activity and thermal stability during dehydration of cyclohexane. Catalysts were prepared with 0.4% platinum or 0.2% rhenium (by weight). Then tests were made in a continuous flow catalytic device at 573 K with volume feed of cyclohexane at 1.0 hour⁻¹. Before dehydration, the catalysts were reduced in electrolytically pure hydrogen at 773 K for 2 hours. Results indicated that oxides of alkaline earth elements (AEE) had little impact on benzene yield for samples hardened at 813 and 873 K, but those hardened at 973 and 1073 K were more active than the control catalysts. For samples containing Ca and Ba and hardened at the higher temperatures, the highest benzene yield was with atomic ratios of Me:Pt at 3:1-7:1. Introduction of AEE oxides into Al-Pt-Rh catalysts brought stabilization of the metal phase of the catalyst, and retarded roasting of narrow pores in the presence of either air or hydrogen. Dispersion of platinum and catalyst activity grew in the order of Mg→Ca→Ba with roasting at 973 K and above. Figures 2; references 15: 9 Russian, 6 Western.
[206-12131]

UDC 547.592.2:542.973:542.943.4

LIQUID PHASE OXIDATION OF CYCLOHEXENE-CYCLOHEXANOL IN PRESENCE OF
HETEROGENIZED METAL COMPLEXES

Moscow NEFTEKHIMIYA in Russian Vol 25, No 1, Jan-Feb 85
(manuscript received 13 Jun 83) pp 68-71

BERENTSVEYG, V. V., CHAN BIK NGA, BARINOVA, T. V., SHUBINA, M. D. and
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[Abstract] Use of metal-complex catalysts on polymer bases has become common in liquid phase oxidation of hydrocarbons, but oxidation of the catalysts themselves remains a problem. The present article reports on study of metal complexes bonded to thermally and chemically durable mineral bases, using as examples iminodiacetate complexes of Co, Mn and Cr attached to the silica "Silokhrom S-120". After oxidation in a static chamber, chromatographic analysis indicated the occurrence of induction periods during introduction of metal complexes into the inhibitor-ionol system, suggesting a mixed radical-chain process during heterogenization of the metal complexes, without the participation of the heterogenic catalyst. Products of reactions were a hydroperoxide of cyclohexene, cyclohexenol, cyclohexenone and cyclohexanon. The heterogenic metal complexes participated in the reaction at the stages of initiation and chain breakdown. Figures 3; references 10:
7 Russian, 3 Western.
[206-12131]

UDC 547.535:542.943.7:541.128.1:546.562

OXIDATION OF CUMENE IN CUMYL HYDROPEROXIDE ON ETCHED COPPER CATALYSTS

Moscow NEFTEKHIMIYA in Russian Vol 25, No 1, Jan-Feb 85
(manuscript received 5 May 84) pp 72-74

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[Abstract] The cumene method of obtaining phenol involves oxidation of cumene in hydroperoxide, thereby achieving simultaneous synthesis of both phenol and acetone for industrial uses. This has been done at 110-120°C with metals of varying valence as catalysts. The present article reports on study of the means of producing etched copper catalysts and the nature of its active surface on the oxidation of cumene in cumyl hydroperoxide. Catalysts were prepared either by impregnation using a copper chloride solvent, or by chemical bonding to a silica base modified with lithium. Further processing resulted in a 2% (by weight) concentration of copper on the substrate. Oxidation was conducted in the liquid phase in a pure cumene medium in a temperature range of 75-120°C with oxygen pressure of 0.1 mPa. Results indicated that insufficient dispersion of the metal on the carrier was achieved by reduction in the 200-350°C temperature range. The catalyst not only eliminated the induction period needed in radical-chain processes, but also gave markedly higher conversion of cumene. At the upper reaction temperature (120°C), hydroperoxide decomposed and cut the efficiency of the basic process. Catalysts produced by chemical reduction were more active than those produced by impregnation, until higher temperatures reduced the activity of the former. Figure 1; references 3 (Russian).
[206-12131]

UDC 547.534.2:542.943.7:546.141'73

OXIDATION OF XYLENES IN ACETIC ACID SOLVENT WITH COBALT BROMIDE CATALYST

Moscow NEFTEKHIMIYA in Russian Vol 25, No 1, Jan-Feb 85
(manuscript received 27 May 83) pp 75-77

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[Abstract] Despite much study of the oxidation of methylbenzene in the presence of metal-bromide catalysts under mild conditions, little attention has been paid to valence factors, resulting in ambiguous notions about the mechanism involved. The present article reports on study of o- and p-xylenes oxidized under replicable conditions to achieve deep conversion of the initial hydrocarbon. The reactions were conducted in an acetic acid solvent in the presence of a cobalt-bromide catalyst, at 60°C, with various

molecular ratios. Kinetic curves of xylene and Br^- ion consumption, as well as the accumulation of toluic acid and Co^{3+} ions confirmed the autoacceleration of the reaction. The active form of the catalysts was determined to be $[\text{Co}^{3+} \dots \text{Br}^-]$, which limited the rate of the process in reactions with hydrocarbons. Figures 2; references 4 (Russian).
[206-12131]

CHEMICAL INDUSTRY

EFFECT OF INNOVATIONS

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 17 Jan 85 p 2

[Article by V. Surman, deputy head of Department of Chemical Industry, Central Committee, Belorussia Communist Party, Minsk]

[Text] Labor Productivity is a Key Indicator. In 4 years, labor productivity in the Belorussian chemical industry has increased by more than 20 percent. Because of this, most enterprises have increased output by more than 90 percent. Labor collectives have successfully fulfilled the additional obligation of production beyond the plan by one percent.

Doing the maximum, not the minimum, overfulfilling assignments, constantly increasing output--this is the spirit in which Belorussian chemists are working today. Where are they finding the reserves? Almost half of the increase in productivity comes from new equipment and advanced technology. Both party committees and industry leaders are increasing their attention to these factors. This is understandable. Retooling has become complicated and requires that the approaches used be carefully analyzed, taking into account the latest scientific achievements.

As early as the beginning of the 1950's, the collective of the S.O. Pritytskiy Production Association "Azot" in Grodno took an initiative approved by the Central Committee of the Belorussian Communist Party: they fulfilled the plan for producing and supplying mineral fertilizers ahead of schedule. Moreover, the capacities of the enterprises were being developed and used to the maximum. Under these conditions, the only right approach was to rely on modernization and rebuilding equipment. First, this had to be done quickly. Second, it had to be done so that rebuilt departments would match the best Soviet and foreign analogs in terms of tooling used in the production process.

To manage this assignment, the enterprise established its own scientific research center, the first in the industry. Agreements were concluded on creative cooperation with 30 scientific and planning organizations. All this made it possible to realize a set of measures to increase capacity by introducing innovations, most of which are on the level of the best achievements worldwide. In only 4 years, more than 40 inventions have been introduced. Thirty of these were developed on-site. The number of manual laborers has been halved. Loading/unloading operations are 96 percent mechanized. By

September "Azot" had fulfilled its four-year plan for producing nitrogen fertilizers.

The enterprise's party committee is constantly seeking new forms and methods of party action to improve the work of the research base and expand contacts with scientists. Every year it analyzes and approves an integrated re-equipment plan and periodically reviews problems of creative cooperation with institutes. A specially created commission monitors progress in completing the plan.

We might say, "So 'Azot' is a huge enterprise." But how could it be small if engineers are scarce and there is barely enough money for science? Of course, small enterprises do not have such capabilities. But that is why they have to be used, as we say, to the hilt. A good example in this respect is the Minsk Chemical Plant. In scale, it compares to a shop at "Azot." However, small scale does not get in the way of large accomplishments. The Minsk chemists have the highest labor productivity in the industry--three times that of the industry average. How did they do it? Science became their assistant. The plant now cooperates with more than 10 institutes. For this reason, it is discovering nontraditional technical approaches and is the first in the industry to introduce effective innovations.

Research organizations and the collective of the Novopolotsk Production Association "Polimir" have energetically joined together finding reserves. Here introduction of the latest scientific and technical achievements is unique: a wide range of people study innovations. This requires the so-called Novopolotsk Method. Creatively building on the Shchekinskiy experience, the chemists at Novopolotsk have adapted an integrated method of equipment maintenance. The production process is carried out by the collective, each member of which knows all the assemblies and equipment in the stream. This requires that worker qualifications be raised and work become more varied and interesting. Technical and organizational improvement of production encourages increased output and, at the same time, reduces the size of the work force. In 4 years, the work force has been decreased by 200 people.

By the way, the Novopolotsk Method is being partially or completely used by all the republic's chemical enterprises.

The responsibilities of chemical enterprises include increasing labor productivity by at least 1.1 percent against the plan. There is room to do this. Several plants are not using full capacity because of lack of raw material. Somewhere plans for new equipment are not being met, and the efficiency with which advances in science and technology are being implemented remains low. For example, each ruble invested in new equipment returns 2 r 10 k at "Azot," but only 9 k at the "Khimvolokno" enterprise in Grodnen. A Bureau of the Central Committee of the Belorussian Communist Party oversees the efforts of this enterprise's party committee and management. To be just, we must say that there are objective causes for this. However, it is bad that the collective is a captive of these causes, has decreased its creative activity, and slackened the search for internal reserves.

But here is what is disturbing. In the past 5 years, all enterprises maintained by the trust implemented new capacity. Growth of fixed capital is causing an increase in the amount of capital repairs. However, the trust itself is not growing. It does not have enough high-capacity cranes; its machinery base, where instruments and tools are produced, is weak. In other words, the rate at which the trusts' fixed capital is growing today is far slower than is the rate of growth of repair work to be done.

Does the Ministry for Production of Mineral Fertilizers know this? It does, but is not hurrying to correct the situation. Will this slowness mean irrecoverable losses? This is the question being discussed by responsible agencies in the Ministry.

Poorly equipped shops and departments in chemical enterprises intended to produce consumer goods is disquieting. Output per worker here is much lower than in main shops. As a result, labor productivity for the enterprise as a whole decreases. The reason is simple: the equipment now in use at Novopolotsk consists of obsolete machinery and assemblies.

Output of consumer goods is a national problem which has never been emphasized in party documents. If it is to be successfully solved, the Ministries for the Chemical Industry, the Petrochemical Industry, and other ministries of the USSR must provide high-capacity equipment to all the enterprises which they oversee.

12809

CSO: 1841/138

ACTIVE REAGENTS USED IN MINERAL EXTRACTION

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 19 Jan 85 p 2

[Article by V. Noskov, correspondent, Dzerzhinsk, Gor'kiy Oblast]

[Text] Construction of a large department to produce chemical reagents has begun at the Dzerzhinsk Production Association "Orgsteklo." This specific product [sic] has broad application. Reagents are beginning to be used in the coal, gas, and oil industries. As additives, they are being used in solutions during drilling of super-deep oil and gas wells which pass through permafrost and aggressive saline media. In this respect, the reagents have a critical role--to protect the drilling tool and, at the same time, reinforce well walls. Use of these reagents speeds drilling work and improves well operating reliability.

12809

CSO: 1841/138

MODERN CHEMISTRY AND WAR

Moscow KHIMIYA I ZHIZN' in Russian No 2, Feb 85 pp 24-26

[From a report to the All-Union Chemical Society imeni D. I. Mendeleeva, October, 1942, by S. I. Vol'fkovich*, corresponding member, USSR Academy of Sciences]

[Text] A nation's chemical warfare potential is determined not only by the level of development of its whole national economy and the power of its chemical and raw materials base, but also by its timely storage of scarce raw materials and finished products, its production base, and the creativity of its workforce.

It is obvious that we would not find information about the production volume of chemical warfare materials either in a foreign country's press or in other official sources. Before the war only a little information was published about the extraction and production of petroleum, synthetic rubber, mineral raw materials, and a few chemical products. At the beginning of the Second World War in Europe, publication of even this information was either curtailed or it was fragmented, for the most part from non-belligerent nations. It makes sense that the newest militarily significant chemical technology would be held in the highest secrecy...

The enormous significance of raw material resources for war was graphically expressed by the former French minister Clemenceau, who said that in the next war petroleum and synthetic rubber will play no less of a role than that of human blood. The English minister Lord Kerson, speaking of the 1914-18 War, said, "The allies floated to victory on waves of petroleum."

In 1940, world petroleum production was about 300,000,000 tones...The USSR has the largest petroleum reserves in the world. Each year, new oil deposits are discovered in various regions of the USSR. The most important of these regions are the area between the Volga and the Urals (the Second Baku), and also parts of Siberia, the Far East, and Central Asia...

The USSR has made a great leap from the old, puny, semi-manual, chemical factories of czarist Russia to a new, powerful chemical industry featuring leading technology and hundreds of new products. Many industrial giants have been built in the eastern parts of the USSR in compliance with the tasks

*Editor's note: The renowned Soviet chemist S. I. Vol'fkovich (1896-1980) was elected to full membership in the USSR Academy of Sciences in 1946.

set forward by the 16th VKP(B) Congress. A series of duplicate plants have been built far from the border. These enterprises furnish their products to our Red Army and Fleet,...

Today the Soviet Union leads the world in reserves of petroleum, peat, iron ore, phosphates, potassium, sodium, magnesium, manganese, and several other raw materials. But the USSR's reserves of hard coal are only in second place, comprising one-fifth of the world's reserves.

Our country is also in second place in reserves of tin, nickel, and several other raw materials.

...At present the world chemical industry's capacity is at least three and one-half times that of the pre-WWI period, and in some countries such as Japan, it is five to six times greater.

The industry in the USSR has grown even more. The organic chemistry industry in the USA has increased six to seven times. The chemical warfare potential of the belligerent nations has grown immensely. Therefore, the operational tactics and initiative of the belligerent nations takes on greater significance in the areas of the more accessible raw material resources, perfection of new technologies, new chemical production, the various types of notably scarce materials and so on. A great deal depends on the ingenuity of the chemists, on their initiative, and their ability to move rapidly from word to action.

In the USSR the mobilization of science to defense needs proceeds on a wide scale. Thousands of laboratories, scientific research institutes, plants, and educational institutions are dedicated to it. A powerful network of All-Union, Ukrainian, Belorussian, and Georgian institutes of the Academies of Sciences and also scientific research institutes and laboratories of the "narkomats" together with scores of lower chemical schools through their personnel and equipment insure our capacity to resolve any scientific or technical tasks...

During this Great Patriotic War, Soviet chemists have substantially broadened and deepened their work on the study of raw material resources, using all possible means to put into production local types of raw materials, using of scrap, and also developing of notably scarce materials and food sources. They have carried on this great work through increasing the productivity of existing enterprises, without large capital expenditures, by intensification of production processes. A number of new types of the armaments have been developed as have been methods to increase the effectiveness of munitions, chemical defense equipment, decontamination, therapeutic and nutritional resources which are very important under wartime conditions.

We will cite a few examples from the large number of finished and perfected scientific research work:

The raw materials base for explosives production has been greatly increased.

Production and use of various plastics, has based on scientific work, grown a great deal.

Production has started on a large number of scarce metals, and also on super-hard, heat-resistant, high-resistance and other special steels and metal alloys which are essential in the production of various types of armaments. There has been great success in the production of a number of acids, salts and important organic compounds.

Much valuable work has been done in the production of high quality motor fuels, and also in increasing the effectiveness of combustion and economy of motor fuels.

Technology has been developed for new types of synthetic rubber.

Methods have been developed for synthesis of new military medical and therapeutic resources--antiseptics, antiparasitics, sedatives, and respiratory stimulants, which take away fatigue and sleepiness. A new antiseptic balm-impregnated bandage which speeds wound healing has been produced, as has a new type of plaster cast which makes first aid treatment of broken bones easier. Many problems have been solved in production of new vitamins, including the blood-clotting vitamin. A new easy method for storing blood and several food products has been developed.

Chemical heaters have been developed for industry, transportation, and medical needs.

Several simple methods for making clothing and wood fire-resistant were developed.

Chemical methods for packing earth and making it water repellant have been developed.

A great deal of research has improved modern methods for chemical defense.

Methods for speeding up and simplifying detection and rapid analysis of chemical warfare agents have been developed.

The raw material base had been broadened, and new formulations for illuminants have been developed.

Extremely effective organic adhesives have been put into production.

Obviously, enumeration of these achievements is only a small number of examples of the subjects on which Soviet chemists have now successfully worked.

...A further area of the use of chemistry is explosives production, which presently is growing very rapidly. Due to the fine creative work of chemists in the last two or three decades, the raw material base for gunpowder and explosives has grown rapidly. There has been a substantial increase in the

level of production of toluene from coking coal and petroleum products. It is used in one of the most widely used explosives--TNT (trinitrotoluene). Together with toluene, other less scarce aromatic compounds have gained wide use, and in recent years use of a number of aliphatic-series petroleum hydrocarbons has begun.

Production of another explosive, nitroglycerine, has taken on a broader raw material base with synthesized glycerine. In the USA, glycerine has been obtained from petroleum. Cotton, which is essential for the production of nitrocellulose, has begun to be replaced by wood cellulose. In almost all countries, nitric acid is no longer manufactured from natural sodium nitrate, but from the synthesis of ammonia.

We have recently begun to produce, on an industrial scale, solid and liquid explosives, synthesized from plentiful types of mineral and synthetic materials in many new facilities, for use in agriculture and mining as well as in artillery shells, bombs, and naval mines.

To increase the shattering effect of high-explosive bombs, mines, and other shells, the chemists have continuously worked to increase the capabilities of explosive substances, synthesizing on industrial scales many new products. Various combinations of explosive with toxic or smoke-forming properties have been developed.

Chemical substances have also been perfected in the technology of shell explosions, for example chemical delayed-action detonators with a delay action from a few minutes to several hours in duration. For the metallic coatings for shells, there have been introduced new alloying additives, which strengthen or weaken the durability of the coatings, protect them from corrosion, and so on.

Both solid and liquid incendiary substances (ZV) have attained wide use in modern warfare. Besides the known thermites, electronic, alkali-metal combined with gutta-percha sheets and so on, modern warfare has gone to the use of grenades, bottles, and mines which are filled with fuels and self-igniting substances containing phosphorus, metal-organic and other substances. These substances play a large role not only at the front, but in the guerilla war with the German occupation forces.

Signal and illuminating rockets, which help fliers get oriented, have, as a result of successful work by chemists, have now attained tremendous illuminating power of several thousand candlepower and more.

Protective paints, obscurant mists of various colors, and horizontal and vertical smoke screens, which allow the obscuring of airfields, dumps, planes in the air and ships at sea are constantly being updated and are being produced on industrial scales.

The basic toxic (OV) agents in the 1914-18 war were choking agents, which were produced at a level of 123,000 tons, blister agents--12,000 tons, sternutatives--7,000 tons, tear agents--6,000 tons. Largest production was

that of phosgene, diphosgene, and chlorine. There was less production of yperite [mustard gas], and then chloropicrin, diphenylchloroarsine, ethyl-dichloroarsine, "vensenite" (a CW agent based on prussic acid), and other toxic agents in varying amounts.

The effectiveness of toxic agents is demonstrated by the following statistical data, pertaining to 1914-1918: for each casualty inflicted there were expended 5,000 machine gun or rifle rounds, or 45 chemical rounds (22.5 round for yperite). An average of 225 kilograms of explosives or only 86 kilograms of toxic gas, excluding cladding (for yperite - 27 kilograms) was expended per casualty. By the end of the 1914-18 war about 50 percent of the German artillery shells contained toxic gas, and in preparation for the majority of attack operations on the western front in 1917-19 they used toxic gas. The number of casualties to toxic gas in all cases during the First World War was about 1,300,000 persons. Of these, 90,000 were killed. In all there were 60,000,000 chemical rounds used.

Secret instructions of the German High Command concerning chemical warfare which were published in our press in July, 1941 underline the necessity of surprise and massiveness of chemical attacks. In the instructions it is stated that "elements of surprise are each change of the character of the chemical warfare agent and the methods of its use...Simultaneously there must be prepared other measures, for example, bombardment with high-explosive or smoke shells."

...Only exact and concrete knowledge by the entire army and populace of the properties of CW agents and measures for defense against them will yield the capability for successful struggle with this danger, and attentiveness, high qualifications, and initiative of military chemists is essential for quick neutralization of a surprise attack and successful struggle against new means of attack.

This inarguable proposition of the unique role of knowledge and science in chemical war bears repetition, because success at the front often leads to complacency and undervaluing new means and methods of warfare.

A well-organized intelligence service, a surveillance and warning system of a threatening danger insures timely warning of an attack. Again and again it is necessary to check readiness of all gas shelters, and there where the simplest covering is still not installed, to finish this work as quickly as possible. Degasification chambers and stations everywhere must be brought to complete readiness, and there where they are still not finished, it is essential to prepare them immediately, and to put into wide use all capabilities to obtain steam, hot water, and solvents, chemicals, and so on.

It is necessary to learn to work in gas masks for as long as possible, since without training a person quickly tires, and the attacking side can count not only on the asphyxiation, but also on the exhaustion of the enemy, both of which may render him incapable for battle.

Carelessness manifests itself in practice such that personnel stop carrying gas masks, stop checking their fit and quality, and do not pay attention to the condition of protective clothing (gas shelters, degasifiers).

Hitler's command has so far not decided to use chemical weapons--probably because it fears the retaliatory attack from the allied antifascist nations who are chemical powers.

It is essential to disseminate widely that the danger of chemical warfare has not decreased, but grown. In the warm time of year, the use of toxic agents is much easier. In winter the persistence of toxic vapors decreases, and several of them solidify, which makes them less active in the cold. Nevertheless the possibility of winter use of toxic agents as one of the final and threatening means of war cannot be excluded...

There must be all-out mobilization of local forces and resources for strengthening the reserve and there must be improvised means for chemical defense and degasification.

To solve the problems which can suddenly arise in chemical warfare with speed and initiative, all-out stimulation of the initiative work of our scientific research cadres is essential... There is no doubt that after the upcoming victory of all living, progressive forces of human society over death-dealing Fascism - Hitlerism, chemistry will not only heal wounds which were inflicted by the enemy, but will gain raise the well-being and culture of the freedom-loving nations.

From "Vestnik Akademii Nauk SSSR", 1943, Nr. 1-2

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COAL GASIFICATION .

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OPTIMUM CONDITIONS FOR THERMAL DISSOLUTION OF FAN-YAGNOBSKIY COALS IN AUTOCLAVE

Dushanbe DOKLADY AKADEMII NAUK TADZHIKSKOY SSR in Russian Vol 27, No 10,
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[Abstract] Preliminary autoclave studies showed that Tajik coal from the Fan-Yagnobskiy deposit lends itself well to thermal dissolution (about 66%) with low gas evolution. However, solid nodules are formed during the process which tend to shut down a continuous process of coal liquefaction. In the present work optimum conditions for conducting the process were found to be: 420°-425°C at 60 minutes residence time, 1.0:1.8 ratio of coal to solvent which contains 50% tetralin, and 10 and 0.42% kerogen and aniline, respectively. References 5 (Russian).
[194-12765]

COMBUSTION

COMBUSTION: HISTORY OF PROGRESS, PROSPECTS FOR FUTURE

Moscow PRIRODA in Russian No 2, Feb 85 pp 30-43

[Article by Ya. B. Zel'dovich, V. B. Librovich, and A. G. Merzhanov: "Combustion: A Modern Look at an Ancient Process"]

[Text] In learning how to use the process of combustion, humanity made a great stride in its development; not for nothing does the ancient epic literature tell about the act of Prometheus, who gave man fire.

Modern civilization could not be imagined without steam boilers and internal combustion engines. Firearms making use of the propelling action of gunpowder and the use of explosive (detonating, destructive) blasting substances have transformed military technology. Explosive substances have also found extensive worldwide application, for example in the mining industry. Likewise, the mastery of space is based on burning rocket fuels.

How Combustion Occurs

We know that combustion is a chemical reaction between fuel and oxygen which is accompanied by the release of energy, or more precisely, the conversion of chemical energy into thermal and other forms of energy. Using this definition one may say that life is combustion, since animals eat food which can be combined with oxygen from the air to provide for the energy requirements of the body. But this is a very specific means of burning fuel; it is carried out at the body temperature of the animal using biocatalysts--enzymes.

How does the "usual" chemical reaction proceed? It occurs with the collision of molecules. This means that the greater the concentration of oxygen molecules (its partial pressure), the greater the reaction rate. We may expect that the rate is proportionate to the product of concentrations of reacting substances.

Experience shows that the combustion reaction is characterized by the existence of limits--that is, the reaction rate is an uneven jump-type function of the conditions--pressure and temperature. Initially there is no reaction, or a slow reaction "below the limit," then a rapid reaction, an explosion with bright luminescence (sometimes even destruction of the apparatus) "above the limit." The first to observe this sharp transition were Yu. B. Khariton and Z. I. Val'ta in 1925. The detailed theory of chain reactions and thermal

explosion, which made it possible to explain the similar behavior of fuel mixtures, brought world renown (and the Nobel Prize in 1956) to N. N. Semenov. Today mathematicians are creating an overall theory of phenomena (known as catastrophe theory) which is characterized by great, fundamental restructuring of the process with a small change in the parameters which determine it.¹

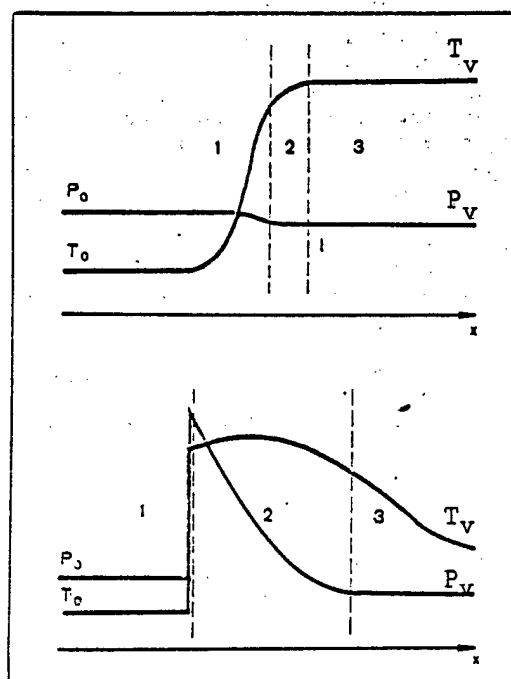


Fig. 1. Distribution of temperature, T , and pressure, P , in a wave of deflagration (above) and a wave of detonation (below). 1, 2, and 3 are the zones of original fuel mixture, the chemical reaction, and the products of combustion. In the wave of deflagration, the pressure from initial P_0 to final P_v changes insignificantly; in zone 1 the original substance is heated by molecular heat conductivity without marked chemical conversion; the reaction is concentrated in the relatively narrow region 2, at a temperature near maximum --the combustion temperature, T_v . In the detonation wave, the advance shock wave abruptly (with a leap) raises the pressure and temperature and initiates a chemical reaction whose occurrence is accompanied by a change in temperature and pressure.

In an inert medium, movement of the substance equalizes pressure, heat conductivity equalizes temperature, and diffusion equalizes concentration. At a glance one can see that the chemical reaction must accelerate equalization of concentration: after all, where there is more fuel it is expended more rapidly. In actuality, the combustion reaction, on the contrary, creates great differentials of concentration, temperature, and sometimes even pressure in space.

We ignite an explosive mixture--that is, cause a chemical reaction--in a certain place. The spread of the flame (wave of deflagration), or detonation, begins.² A flame is a thin layer separating the area where the reaction is completed from the area where the reaction has not yet begun. The reaction occurs only in this layer. The release of heat and (or) the increase of pressure in this layer affect the neighboring layer, which ignites the following one. In the language of modern science it is customary to say that in the thermodynamics of a nonequilibrium system there arises a definite geometricity and spatial structure. The study of such structures has now become a specialized sector of science called synergetics.³ Phenomena of the spreading of flames are now regarded more precisely as particular cases of autowave processes.

The authors, who have spent a combined total of nearly 100 years studying combustion, now feel like Moliere's philistine, who wanted to learn the manners of the gentry. As he touchingly says to his teacher: "Honestly, I never suspected that for 40 years now I have been speaking in prose." Thus, too, until recently, we did not suspect that we were dealing with catastrophe theory and synergetics. However, to some extent we guessed--it was well known that situations analogous to explosion or the spread of flames are also encountered in problems which are remote from combustion, for example in the deformation of polymers.

Combustion in Nature

Let us begin with unflattering words directed at humanity. Like a prodigal living high on his parents' fortune, humanity is living on the solar energy which has fallen on earth for billions of years in the form of coal, oil, gas shale, and peat, and is burning it up with such extravagance that these reserves may be completely exhausted within a few hundred years.

Nature has laid in a stock of all that is necessary for combustion: combustible material and the ignition device--lightning. Fires starting in nature stop only when all the combustible material burns up or almost all the oxygen in the air is used up.

A fire is a splendid experiment in gas dynamics: in the earth's field of gravity, release of heat in the atmosphere leads to convection--that is, the conversion of thermal energy into mechanical energy. The powerful current of combustion products and hot gases rising from the place of combustion forms a thermal "column" which rises to a great height. Pulling into movement adjoining layers of cold gas, the current gives rise to circular eddies, and carries ashes, soot, and tiny particles of unburned solid fuel to the upper layers of the atmosphere. The disturbances from the fire in the upper layers of stratified atmosphere (that is, having varying density) can give rise to what are known as internal waves, able to spread great distances without dying down, which bend around the entire globe. The effect of major fires, like volcanic eruptions, is so great that the weather in whole regions of the earth is changed, and winds carry the products of the fire many kilometers; then these products fall along with precipitation in regions of the planet which are distant from the site of the fire. There is no question that fires would intensify the global lethal effect of nuclear war.

Still more impressive are fires which give off coiling currents--cyclones. Possessing a great reserve of kinetic energy in rotation and a great internal stability, eddies with combustion (small combustible components drawn into the eddy will burn) move great distances and cause serious damages. The twisting of eddies and their intensification occurs under the action of Coriolis forces in the earth's rotation.

Recently, important strides have been made in the mathematical modeling of natural fires both at the initial stage of formation of a convection movement in the atmosphere and development of vortex structures, and also at the stage where a heat column has formed, and its evolution in terms of the rise of hot gas and interaction with wind. But much still remains unclear, especially since scheduled fire observations are costly. It was no accident that when a major hydrogen leak occurred on an American rocket base and a powerful fire started, maximum efforts were undertaken so that scientists could make use of this situation, making measures of radiation, velocity field, temperature, and also other important characteristics of the fire.

Understanding the mechanism of development of a fire helps to organize fire-fighting measures, especially at the initial stages of a fire: to limit it and stop its spread. As for assessing the situation as a whole, fires in nature continue to cause terrible natural disasters.

Ecological and Power Engineering Problems of Combustion

Humankind is situated in a narrow film of the atmosphere enveloping the earth; in thickness, it is approximately one-hundredth of the earth's diameter; in terms of the mass it includes, it is one millionth part of the planet's mass. We have already observed that natural fires affect the state of the atmosphere. But today, the purposeful actions of people are having a greater effect on the atmosphere. The steady growth of energy capacities, the wider and wider spread of domesticated fire--in furnaces and boilers of thermal electric stations, factories, and plants, the boiler houses of cities and villages, internal combustion engines and diesel motors, in rocket and aviation motors--this is leading to a situation in which the heat released becomes comparable in amount to the components of thermal balance of the atmosphere.

In addition, the output of microscopic condensation particles into the atmosphere is increasing--soot, ashes, crushed fuel, and condensation products of combustion; they change the optical properties of the atmosphere, in particular the ratio between absorbed and reflected solar energy, and they increase the "greenhouse effect," which involves an increased concentration of carbon dioxide over the course of a prolonged time span. Incidentally, unidentified flying objects ("flying saucers") have been explained by science as turbulent fields in the atmosphere with high concentrations of small condensation particles which, as good reflectors of light, create the impression of a solid shining body.

The intensive energy activities of mankind have given rise to the danger of harmful effects on the flora and fauna by toxic combustion products; oxides of sulfur, nitrogen, and metals, carbon monoxide, and carcinogenic substances--products of incomplete pyrolysis of organic fuels.

Of all the types of natural fuels widely used in modern power engineering, the first prize, from the point of view of ecological purity, must unquestionably go to natural gas--almost pure methane. With appropriate regulation of combustion installations working with lean fuel mixtures (having a large excess of air) it is possible to completely avoid the formation of condensation particles of ashes; sulfur is also absent in the combustion products. It is possible to achieve a small output of nitrogen oxides, produced from oxidation of nitrogen in the air, and a small release of carbon monoxide. The carbon dioxide formed in combustion is assimilated by plants and processed into oxygen; in contrast to carbon monoxide, and oxides of nitrogen and sulfur, it is not toxic; the normal atmosphere always contains 0.3 percent carbon dioxide, while its concentration in the human lungs reaches several percent. So, to refer to carbon dioxide in the same breath as other, toxic oxides, as is sometimes done, is inaccurate from the ecological point of view.

The formation of nitrogen oxides and carbon monoxide strongly depends on the conditions of combustion. Hence the preference for lean fuel mixtures, with a great excess of air, whose combustion temperature is relatively low. But these mixtures are difficult to burn. So, recently combustion devices have been developed which have "heat recycling": part of the heat from combustion products is given back to the original fuel mixture, facilitating its combustion. In such devices it is possible to burn mixtures which previously did not burn at all, and, in addition, to raise the productivity of the process by dozens of times. Precombustion chamber burning has also begun to be used; in a small incineration chamber--the precombustion chamber--the well-heated enriched mixture is burned, then the reacting gas is "spilled" into the main combustion chamber; as a result, the great mass of the fuel gas burns rapidly and completely.

The transition of major cities and industrial centers to gas supply is largely leading to purification of the air basin. It is still important to convert internal combustion engines of motor transport to liquefied gas. As for ash, it is formed in the pyrolysis of complex hydrocarbon fuels which occurs in areas where there is insufficient oxygen. The ash formed is then difficult to convert into a gaseous state. But in natural gas, the main components are methane and carbon monoxide, which do not form ashes during combustion.

There is no question that the purest fuel is hydrogen. The product of its combustion--water--moves in a natural fashion into the cycling of substances in nature. The only danger which remains even in the combustion of hydrogen is the formation of oxides of nitrogen from the air.

In nature the reserves of unbound hydrogen are small; it must be obtained with great energy expenses, for example by breaking down water. (Compare: the simplest means of obtaining hydrogen--electrolysis--requires a 100 percent outlay of electricity, while its coefficient of useful action in engines and energy facilities is no higher than 30 percent). So until quite recently, the wide use of hydrogen in power engineering (except for rocket technology) was out of the question. But the rapid development of atomic energy makes it possible to regard the production of hydrogen in large quantities as fully possible. But many problems still remain unclear: how to ensure safe work

with hydrogen (it is an easily ignited gas), how to transport and store it, and what alterations will be required to the existing combustion chambers and burners in converting them to operation on hydrogen fuel mixtures. In addition, the ecologically pure product--water--possesses a substantial corrosive action and may disable certain units. In other words, the hydrogen question is a question for the future.

So, despite the allure of using gas fuels, combustion of an ancient form of fuel--coal--for energy purposes will continue to be practiced for a long time. Coal resources on earth are greater than the resources of other natural fuels. The Soviet Union has major coal deposits: Ekibastuz, Kansk-Achin, and others with an exposed position of the coal reserves, so that extracting them is surprising inexpensive. Naturally, it is a sin not to take advantage of such an opportunity, recalling prophetic words of the great D. I. Mendeleev that it is not very sensible to burn up money (Mendeleev meant oil and gas, excellent raw materials for the chemical industry).

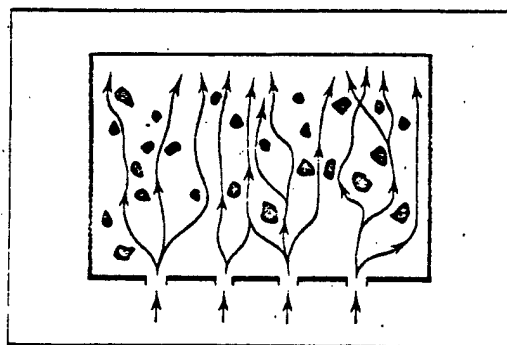


Figure 2. Layout for burning coal in a fluidized layer. The color components show the hot lumps of coal, the black show the pieces of dolomite. The arrows are the lines of flow of the gas.

The quality of coal in an exposed position, however, is not high: it is cinder coal, with high concentrations of water, sulfur impurities, and many non-combustible components. The inert material in it reaches 40-45 percent, so burning this coal is not easy. (This observation, moreover, applies to all coal reserves, since with time the quality of coal declines). Certain new ways of organizing the work process in coal furnaces are now being considered, for example burning the coal in a fluidized bed. Under the action of an ascending current, the filled layer of fuel coal begins to hover freely, it mixes well with the oxidizing agent, and ensures intensive heat removal of the heat generated into the walls and cooling elements of the furnace. This layout makes it possible to use low-quality grades of coarse-ground coal and effectively bind the sulfur oxides which form in combustion--to do this, the inexpensive natural mineral dolomite is introduced into the fluidized layer. But a substantial shortcoming of this layout is the intensive formation of small, poorly burning particles of coal under mechanical friction; these particles are carried out by the air flow; thus, the fluidized layer must be combined with a subsequent afterburning of the small fractions of coal by the old direct-spray formulas.

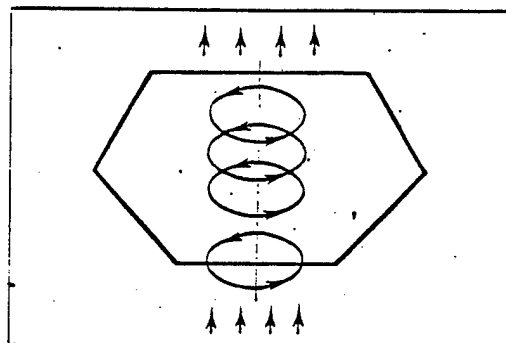


Fig. 3. Layout of a cyclone furnace. Symbols are the same as for the preceding figure.

Another promising method of burning coal is the cyclone furnace; in it the combustion of coal particles occurs in a coiled gas flow. Centrifugal forces arising from the rotation separate particles and impurities according to size, further crush them, and facilitate the removal of liquid slag. In addition, it is possible to regulate the gas atmosphere in these chambers, for example introducing ammonia, which can act on the kinetics of formation of nitrogen oxides from the nitrogen contained in the fuel itself. In burning coal, these nitrogen oxides appear in approximately the same quantity as in oxidation of nitrogen in the air. Sometimes coal contains rare-earth metals, in small quantities, it is true, but their oxides--tiny, submicron particles--are very poisonous and difficult to catch.

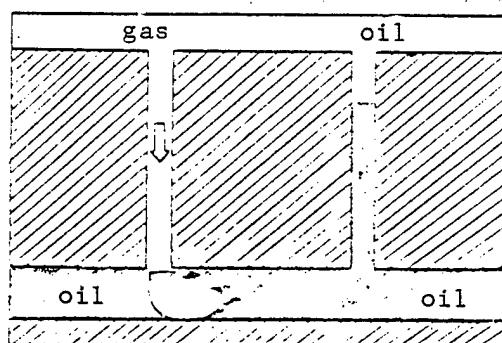


Fig. 4. Layout of intrastratum combustion. Oxidizing gas is fed into the left, injection well to maintain combustion in the stratum; oil expelled from the combustion zone comes out of the right, extraction well. The combustion zone is shown in color.

A fundamentally different direction of using coal is chemical processing of it into liquid and gaseous fuels, which unquestionably have a wider field of

application. But this path is significantly more expensive. The agenda again holds the question of underground gasification of coals as the least expensive method of obtaining gaseous fuel. The idea of underground gasification of coal, as is well known, was proposed by D. I. Mendeleev. In the prewar years this idea was realized in the Moscow basin, right on the nose, as they say: a wide shaft was dug out, combustion was organized at a moderate depth.... There was gasification, but no spread into industry, since great preliminary expenses were required.

Now underground gasification is being suggested for coals in a deep position (approximately a kilometer deep, where there are vast reserves of them, but processing them by conventional mining methods is economically unfeasible). In the oil and gas refining industry there are methods which make it possible to carry out the necessary hydraulic explosion of the coal stratum between two wells--one feeding the stratum with oxidant and one to extract the products of gasification--and also to accomplish the ignition of coal at great depths and under great pit pressures (on the order of 100 atmospheres).

Experience of using deep underground combustion has been accumulated recently in connection with the intensification of oil refining. It has turned out to be possible, by setting up combustion in the oil stratum, to extract the oil remaining in it which was impossible to reach by other methods. To do this, air or oxygen in pure form, or, still better, in a mixture with water, is fed into the injection well; the oil in the stratum is ignited, and the combustion zone, moving through the stratum, drives out the light fractions of oil through the extraction well. Only the heavy fractions, most difficult to drive out, burn; experiments show that a small quantity burns--5-10 percent of the total mass of oil in the stratum. The water and oxidant introduced promote more complete expulsion of the oil, since they play a role of transferring heat from the combustion zone into areas prepared under combustion, from which the extractable oil is expelled. Intrastratum combustion has turned out to be an effective means even for already fully flooded deposits, in which expelling the remaining oil by the old methods has turned out to be impossible.

In conclusion, let us mention the transport of the future--rockets. They require specific fuel with a high specific impulse of reactive force--not a natural fuel, but a specially synthesized one. In addition, rockets carry not only fuel but also oxygen. Expenses to produce these components are great and largely depend on the calorificity of the fuel. Its combustion products have a definite effect on the atmosphere, particularly on its upper layers. But this question requires special examination, and we will not dwell on it.

Combustion Synthesizes Substances

Relatively new "professions" have appeared in combustion. They can be called new because they turned up in a broad and persistent way only in the last 10-15 years.

Remember that combustion is a chemical reaction, although it occurs in a special form. So it is entirely natural that we should be interested also in the products of combustion, which are quite varied. In the traditional applications, which were discussed above, various forms of fuel are usually used

which produce the greatest energy effect, and, as a result of this, products which are uninteresting from the chemical point of view (water, carbon dioxide, and so forth). But processes of combustion can be set up especially to obtain valuable products. To do this, the original systems must be selected based on chemical considerations, while the power-producing aspect of the process is relegated to the second plane--it is important only insofar as it is necessary to carry out the actual combustion.

This approach was the basis for what is called technological combustion. One cannot say that the devices of technological combustion were previously unknown. Let us recall the reactions "from the fuse" which were carried out in preparative chemistry as early as last century. The obtaining of sulfur anhydride by burning sulfur, incomplete combustion of hydrocarbons to form ash, and "extra-furnace" aluminothermic smelting of ferroalloys have long since been accomplished in industry. And even the well-known blast furnace process can, by convention, be regarded as a version of technological combustion.

But all these processes were developed by themselves, in isolation from each other, without an overall ideology, without the necessary use of combustion theory. Technological problems of combustion for a long time received no serious attention--the vastness of power engineering tasks seriously fascinated specialists for a long time.

The situation began to change after 1967, when the USSR Academy of Sciences Institute of Chemical Physics discovered a new expanded class of reactions of technological combustion. These were reactions in powder mixtures of metals (titanium, zirconium, hafnium, niobium, tantalum, and so forth) with boron, carbon, silicon, and other non-metals; these reactions occur after local initiation under wave conditions. Then processes of burning metals in nitrogen were also implemented. The products of these reactions--valuable high-melting compounds (borides, carbides, silicides, nitrides)--possess unique physical properties. For example, tantalum carbide has a record melting temperature (4000 degrees C), boron nitride is a high-temperature insulator, titanium carbide is an outstanding abrasive, silicon nitride has no competitors for heat resistance, niobium carbonitride has superconductor properties, tungsten diselenide is a splendid electricity-conducting solid lubricant, and so forth. These and other analogous compounds are used to create materials which work under what are called extreme conditions--high temperatures and stresses, in currents of aggressive media, in high vacuum, exposed to penetrating radiation, and under conditions of high-speed combustion.

And so combustion intruded into the field of synthesis of these remarkable compounds. The new method was called self-propagating high-temperature synthesis (SHS).

Now the SHS method has produced more than 300 compounds. Their attractive characteristic is their high purity. Combustion not only synthesizes but also at the same time removes impurities from reagents! Furthermore, traditional furnace methods are low productive and energy-consumptive. And obtaining a high-quality product in furnaces is a very difficult business.

Recently the chemical capabilities of SHS have greatly expanded. It has begun to be used to obtain intermetallic compounds, complex oxides, semiconductors, unstable hydrides--in general, a broad scale of inorganic compounds. The chemical classes of reagents have also been expanded. Not only elements now participate in SHS reactions, but also various compounds (oxides, chlorides, fluorides, hydrides, hydrocarbons, azides, and so forth), and mineral raw materials. All of this has enabled SHS processes to win strong positions in the synthetic chemistry of inorganic compounds.

Synthesis by combustion. This is a very extraordinary process. In it the conditions for synthesis are not a given, as, for example, in furnaces, but are created as a result of combustion. Combustion and synthesis are closely linked, without one there cannot be the other. The formation of the product is both the cause and the consequence of combustion. Another thing is important too. The wave of synthesis, formed after triggering, spreads according to its own laws. To influence it in the course of its front movement and implement running control over the forming products is difficult, but this, it turns out, is not necessary. The foundations of success in obtaining high-quality results can be laid before beginning the process by a correct choice of input mixture and combustion conditions. So it is very important to understand how the process proceeds, to be able to visualize and predict it. In other words, SHS is more closely tied to macrokinetic science than furnace syntheses.

Let us examine several examples of these unusual syntheses. In combustion of especially high-melting mixtures of powders (for example, tantalum or niobium with carbon, and molybdenum with boron) all processes occur in the solid phase; this means not only the original substances but also the reaction products are in the solid state even at combustion temperature. This purely solid-phase combustion was previously unknown. Not only that, it was assumed that for such rapid processes as combustion, the presence of a liquid or gaseous phase was simply necessary.

Solid-phase reactions with solid products occur in a very unique fashion. In the initial moments at the contact sites of reagents, a phase of products in the form of a barrier layer is generated, which blocks the components and stops the reaction from proceeding further. In order for the reaction to continue, the reagents must diffuse toward each other, and this is a very slow process. Often these reactions, which interfere with their own flow (they are called self-braking), are practically completed in the initial stages, to very small degrees of conversion of reagents into products.

In that case, how does SHS occur, moreover with high completion of the reaction, and why is combustion itself possible?

It is because diffusion processes in the solid phase are strongly activated, and at high temperatures, characteristic for combustion, they can occur very energetically. So the mass exchange through the barrier layer (especially in high dispersion mixtures, where the diffusion way is not great) succeeds in controlling the process, not permitting it to die down. Moreover, it turns out that thanks to the great thermal effect of the reaction, to spread the

wave there is no need to fully convert the reagents--the wave can form at a rather minor extent of conversion, when the barrier layers are still small. The reaction proceeds further under afterburning conditions, in a broad zone behind the front of combustion, but this no longer has an effect on the spread of the wave.

Ensuring completion of the reaction in the afterburning zone is a task whose solution must be achieved in practical works on solid-phase syntheses. Usually this is achieved by decreasing the heat losses of combustion.

There is much that is surprising in self-propagating high-temperature synthesis. Projects of the Armenian Academy of Sciences Institute of Chemical Physics have discovered processes of combustion of metals in hydrogen to form thermally unstable hydrides. In them the metal is combustible and the role of oxidizing agent is played by hydrogen. It did not immediately become clear that the SHS method, during which high temperatures developed, could be used to synthesize unstable compounds.

Judge for yourself. In the formation of, for example, titanium dihydride, so much heat is generated that it can heat the product up to 2000 degrees C. But at temperatures above 800 degrees C the dihydride phase cannot exist--it dissociates and generates hydrogen. How does combustion occur in this case? Why is titanium dihydride synthesized during this? It turns out that in the course of combustion whose temperature does not exceed the temperature of dissociation, only weakly hydrogenated products form--solid solutions of hydrogen in metal. During this, the degree of dissociation of the products in the wave of combustion of titanium in hydrogen reaches 80 percent, while the hydride phase forms when the product cools, in the process of prehydrogenation; as a result of decreasing the temperature, equilibrium in the metal-hydrogen system is shifted to the side of hydride formation.

And here is an example of another sort. The Institute of Solid Chemistry and Processing Mineral Raw Materials in Novosibirsk has implemented SHS processes in mixtures of powders of metal oxides (for example, barium and tungsten). The question arises, what can burn here--all the components are already oxidized. It was discovered that under SHS conditions, the formation of a complex oxide (with spinel structure) from simple ones occurs. The low heat of this reaction turned out to be adequate for maintaining the self-spreading process.

Chemical syntheses based on SHS, as we have seen, are varied and interesting. In the technical part they are simple--blend, burn, produce. But behind the external simplicity lurks the need for deep understanding of the mechanism of the processes--without this it is impossible to obtain products satisfying the precise requirements of synthetic chemistry. "Theoretical synthesis" is what M. V. Keldysh called SHS processes in his day.

Synthesis → Structure → Form

All that we have discussed represents only the first task of self-propagating high-temperature synthesis. The most important thing here is how to set up

the process in order to synthesize a compound with a given chemical and phase composition. It has been successfully resolved, and a number of SHS products are already being produced on an industrial scale.

The second task is significantly more complex--obtaining material under combustion conditions while taking into account not only demands made on its composition, but also on its structure and properties. Of course, this is enticing. But, you will agree, obtaining powder structures with given granulometry, controlling the porousness of products, regulating grain sizes of crystallites in compact materials, and so forth--all this is very strange to combustion. The situation is not simple with the theory of this "burning" materials technology. The structure and properties of combustion products are usually formed far behind the reaction front as a result of post-processes whose nature is not considered in the theory of combustion. New approaches are needed, relying on the theory of solids and physicochemical metallurgical processes, but definitely in combination with combustion theory. Examining all this is the job of the future. Specialists are now obtaining combustion products in the form of materials--both simple monophase ones, and complex multicomponent ones.

The simplest of all is obtaining the required composition of the material. This is achieved mainly by the choice of input mixture. But it is necessary to keep in mind that the connection between the composition of the material and the composition of the input mixtures is nontrivial, since in combustion, especially in multicomponent systems, concurrent and secondary reactions can take place. Great help here is afforded by thermodynamic calculations of the composition of combustion products, which take into account the entire multitude of reactions. The introduction of inert fillers into the input mixture is being done--they do not participate in the reaction and move from the input mixture into the final material. Thus, for example, in synthesizing solid alloys, binding metals introduced into the input mixture (nickel, cobalt) blend only in the combustion wave and surround the grains of carbide formed in the SHS reaction; at the same time the necessary structure of the alloy is ensured.

In the general case of building the structure of the material, the question is complicated, but using semi-empirical techniques it can be resolved. The structure of the original medium (input mixture), the preliminary processing of the reagents, the conditions of combustion, the cooling regime of the product--these are the basic factors making it possible to construct materials with the desired structure.

Technological methods for obtaining materials (powdered, porous, solid) based on SHS are very effective. The most "advanced," with an output at an industrial level, is the technology of powdered materials. It is based on simple techniques of grinding SHS products with subsequent classification of powders for obtaining narrow fractions with various degrees of dispersion. These powders have taken over the "materials technology market" as raw materials for baking articles and applying coverings, abrasives, free-flowing media, catalysts, and so forth.

In many cases, when the combustion temperature is lower than the product's melting temperature, the product has a porous structure. So it is simple to obtain porous material. But regulating the number and size of pores, the ratio between closed and open porousness, and the strength of porous material is a difficult task. Here is an interesting fact: thanks to self-cleaning, the contacts between particles in a porous product during combustion are less contaminated by impurities and provide for greater linking strength than in analogous baked materials at the very same level of porousness. The SHS method is now being used to obtain porous high-melting materials for treating and manufacturing filters.

Techniques for obtaining compact, poreless materials are very effective. To do this, the SHS is carried out in special press molds, and the product, not allowed to grow cold, is compressed. Thus it is possible to obtain materials which have almost no pores (less than 0.2 percent).

With the appearance of SHS, classical techniques of heat-treating materials under pressure--extrusion, rolling, and so forth--began getting their "second wind." Combining them with SHS, in which the combustion actually synthesizes material and heats it to the necessary temperatures (that is, prepares it for deformation), makes it possible to create unique technological processes.

No less interesting and important are SHS processes in which products are formed in a melted state. This is possible if high-caloric compositions are specially created or additional energy is put into the hot medium. Here is one example. A mixture of powders of molybdenum trioxide, aluminum, and carbon is placed in a hermetic vessel with inert gas pressure on the order of a thousand atmospheres (the pressure is necessary in order to just partially "crush" the gasification of combustion products). In combustion of the mixture a high temperature develops, equal to approximately 4500 degrees C. And this vast temperature is reached almost without cost, moreover in fairly large volumes! And what about the combustion product? In our example it consists mainly of two unmixing liquid phases--molybdenum carbide (or, more precisely, a carbon-molybdenum melt) and aluminum oxide. In a gravity field they separate--molybdenum carbide sinks, and the lighter aluminum oxide floats. The material here is formed by a classical metallurgical method--ingot crystallization.

Many systems are now known which form molten products in combustion. They are also various in the chemical nature of reagents and conditions of combustion. Using them it is possible to obtain bars of welding fillers, heat-resistant and solid alloys, and special steels.

The possibilities of combustion in constructing materials are vast. That which has already been achieved is only a drop in the ocean. But the main thing has already been done--forming the basic directions of work.

Meanwhile, specialists have undertaken the solution of the third problem, consisting of direct production, using the SHS method, of articles with a definite form and size with a given set of usage properties, with minimum mechanical processing of the combustion product. Doing this, in order immediately to produce, by combustion, an article which is suitable for use, is very efficient. To do this, it is necessary to force the SHS process simultaneously (or rather, almost simultaneously) to synthesize the components of the material, form its structure, and provide for shaping. This is a monumental task, since its resolution can fundamentally restructure the technology of machine building.

The direction in which combustion processes synthesize substances and construct materials is developing rapidly, and we are not sure that the notices presented for readers' attention will not look outdated by tomorrow.

Technological Combustion: Advantages and Shortcomings

The discovery of self-propagating high-temperature synthesis has played a revolutionary role in the technical applications of combustion. And not only because it has broken ground for the science of combustion to resolve problems of materials technology which are new to it. More importantly, SHS has made it possible to take a fresh look at technological combustion, understand its principles, scale, and possibilities, and change the attitude toward it.

The idea that combustion products can be of technological value is easy to understand. The concrete examples convince us of this. But is it worthwhile, on the strength of this, to specially organize the combustion process? After all, there are other technological techniques, and often one and the same product can be obtained by different methods.

In order to produce thermally stable chemical products, metals, and inorganic materials, it is currently necessary to make universal use of high-temperature furnaces--electrical or induction. They are all-purpose, can work for a long time, and maintain a given temperature with adequate precision. Recently there have appeared plasmotrons which greatly expand the temperature capacities of furnace-type processes, laser heating has begun to be used, as well as explosion energy and many other things.

In such a situation, is combustion necessary too? Does it have an indisputable technological advantage? Will it be able to withstand the competition? On the example of SHS, and even certain "old" processes, we have become convinced that all these questions must be answered in the affirmative. But we are trying to examine this from general positions.

The technological features of combustion can be expressed in popular form using the motto of Aeroflot: "Fast, convenient, money-saving."

Let us examine it one part at a time.

"Fast!" Because the rate of combustion is high. The reaction time in the wave amounts to fractions of a second. The total time of burning in reactors is seconds, or, at the most, minutes. The productivity, therefore, of technological combustion is much greater than furnace processes. Even plasma, despite the very high temperature, is inferior to the technological productivity of combustion.

"Convenient!" Of course it is simpler to burn than to heat. Most importantly, complex high-temperature equipment (furnaces, plasmotrons) is not necessary. Combustion reactors are simple and long-lasting, and initiating the process presents no difficulty. So the technology of combustion products is easy to set up, as they say, "in any empty spot."

"Money-saving!" This proposition is completely clear. Above all, let us remember that combustion occurs by liberating internal chemical energy, and does not require outside energy outlays. So the use of technological combustion leads to economizing on electricity. Furnace and plasma processes, "squandering" a vast quantity of electricity, submissively bow their heads before this characteristic of technological combustion.

All the above leads to low expenses for organizing the process, and has a positive effect on the prime cost--combustion products are almost always relatively inexpensive. And if we take into account in addition the high quality of the goal product which is typical for technological combustion, the advantages are unquestionable.

What else may be recorded among the assets of technological combustion? Many things, but we will mention only one more, the perhaps unique capacity to work with large masses of substance and produce large articles. Heating from within, not from without, is especially basic. A chemical reaction is in a position to do that which a furnace cannot. In resolving such tasks, technological combustion has no analogs, no competitors.

Well, what about the liabilities? What is the price for all the virtues of technological combustion? The payment is simple--technological combustion is

not universal in the chemical sense. Not all systems are capable of combustion. Not every reaction, in contrast to furnaces, can be carried out in technological combustion; in order to do so, it must occur with a release of an adequate amount of heat. So the choice of systems plays a very important, fundamental role.

What can be said in defense? Fortunately, there are many reactions which release heat, and so the actual possibilities of technological combustion are great. Furthermore, it is possible to combine systems, to carry out thermally coupled processes in which the heat from one reaction aids the other.

Now let us use our imaginations! What can we expect in the future? First let us turn our attention to "great chemistry." How many exothermic processes there are in it is impossible to count, even to imagine it is difficult. But the use of technological combustion is held back by the fact that many valuable products are unstable and do not form even at high temperatures. For example, the oxidation of hydrocarbons is used in technology to obtain alcohols and other products of organic synthesis. But carrying out this process under more severe temperature conditions in a regime of technological combustion produces other, simpler and less interesting products--water, carbon dioxide. The solution, it would seem, is simple--lower the temperature of combustion, especially since doing this is easy. But the problem is that there are limit temperatures of combustion, below which it is extinguished, and frequently these temperatures turn out to be still too high. Combustion theory is pointing the way to decrease limit temperatures. The most convenient of these is increasing the rate of chemical conversion using catalysts.

Particularly great possibilities are hidden in heterogeneous catalysis of inorganic reactions. In this it is more simple to bring the maximum permissible process temperatures into line with the limit temperatures of combustion. And the use of high-melting SHS products as catalysts or catalyst carriers will make it possible in many cases to raise the temperature and effectiveness of catalytic processes.

In metallurgy the prospects of development of technological combustion are no less enticing. Let us take just the direct production of iron from ore, bypassing the blast furnace process. This is a problem of ferrous metallurgy of the highest class; it is being worked on actively all around the world, especially successfully in the FRG. The West German process, acquired by license, is also being carried out in the USSR. From the point of view of combustion theory, two aspects of this world-renowned technology provoke criticism: the use of pellets and the separate carrying out of processes of metal reduction and reducing-gas formation. Powdering the ore, rather than gathering it into pellets difficult to reduce because of diffusion, and combining the zones of combustion and reduction in order to use the active state of the reducer--these actions put the process into the class of technological combustion with all its advantages. Many other metals can also be reduced analogously. A laboratory facility created in the USSR Academy of Sciences Institute of Chemical Physics testifies to the great prospects of this direction in reduction metallurgy.

And processing sulfide ores? This is now done in a surprisingly inefficient way: in fluidized bed furnaces, at low temperatures, to obtain metal oxides (which then must be reduced). Technological combustion makes it possible to set up processes in highly productive combustion chambers to obtain reduced metals immediately.

We are sure that great prospects are also in store for the problem of precision casting (what is known as casting with melted models). This can be set up according to a simple scheme. Metal in the necessary quantity is "synthesized" in a combustion reaction, then poured into a mold. The metallic article formed after crystallization requires almost no mechanical processing. Thus it is possible to solve the same problems of saving metal which exist in powder metallurgy, but without using the classical scheme: metallurgists provide the ingot, and machine builders "reprocess it into shavings" (this is a widespread joke connected with the formation of a vast quantity of wastes in processing metals by cutting).

Combustion is being most actively adopted today in the technology of inorganic materials. Here technological combustion (SHS) is already standing firmly on its feet. The resolution of powder problems is increasing without pause. Methods, means, and techniques are being perfected and varied. The type of tasks is expanding. The chief prospect is the resolution of unique problems which are difficult to overcome by the usual methods (creation of materials with particularly extreme properties, direct production of large articles, and so forth). But all of this has already been discussed.

So, technological combustion has great claims and an argumentative striving for scope. Life will show how feasible they are. But one thing is still clear--we must work!

Instead of an Epilogue: More About Some Interesting Characteristics of Combustion

To the traditional idea that combustion is a source of heat and a means of creating material, we must add combustion's capacity to illuminate.

Usually the equilibrium luminescence of gases and solids heated by combustion to high temperatures is used. In recent times, greater attention has been focused on the chemiluminescent, nonequilibrium nature of the radiation of certain fuel mixtures. Take, for example, such curious fuel mixtures as a mixture of hydrogen and fluorine, and carbon disulfide and oxygen. In combustion of these under conditions of low pressure, the combustion products--hydrogen fluoride (in the first instance) and carbon dioxide (in the second)--have an excess of oscillation energy compared to assumed reserves according to thermodynamic equilibrium, an excess which in an optical resonator can be brought outside in the form of coherent radiation. And this has been implemented: continuous and impulse laser devices based on combustion have been built and are functioning successfully.

In addition, a flame is a source of radiation in the radio and acoustic ranges. In combustion of hydrocarbon fuels, as a result of associative ionization in the flame, there forms an excess quantity of charged particles

(positive and negative ions, electrons), which diffuse and recombine at various rates. As a result, there arises in the flame a volumetric electrical charge which, moving in a turbulent current, radiates electromagnetic waves. Thus, the flame "makes noise" in the radio range and has a shielding action which prevents the spread of the radio waves.

The acoustic noise of the turbulent flame is well known to people living near major airports. The "noise pollution" of the environment from the noise of reactive motors of airplanes occurs largely because of combustion.

All types of radiation arising in the process of combustion--the optical, radio, and acoustic ranges--can be successfully used for long-distance diagnosing of combustion zones, and to understand their internal thermal and chemical structure.

AUTHORS

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Author of books: "Ustoychivost' plamen" [Stability of Flames] (jointly with A. G. Istratov), Moscow, 1966; "Teoriya nestatsionarnogo goreniya porokha" [Theory of Nonstationary Combustion of Gunpowder] (with Ya. B. Zel'dovich and O. I. Leypunskiy), Moscow, 1975; and "Matematicheskaya teoriya goreniya i vzryva" [Mathematical Theory of Combustion and Explosion] (with Ya. B. Zel'dovich, G. I. Barenblatt, and G. M. Makhviladze), Moscow, 1980.

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FOOTNOTES

1. For a more thorough treatment, see: Arnol'd, V. I. "Catastrophe Theory," PRIRODA, 1979, No 7, p 86.
2. Recall that a flame, or wave of deflagration, is a slow spread of combustion, occurring at subsonic speeds, while detonation is a rapid spread of combustion at a supersonic speed.
3. For a more thorough treatment, see, for example: Kadomtsev, B. B., and A. I. Ryazanov. "What Is Synergetics?", PRIRODA, 1983, No 8, p 2.

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CSO: 1841/193

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RANGE OF THERMAL IGNITION FOR LIGHT-INITIATED UNBRANCHED CHAIN REACTION

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 58, No 12, Dec 84
(manuscript received 28 Feb 83) pp 2923-2927

BEGISHEV, I. R., POLUEKTOV, V. A., PAPLAUSKAS, A. B. and POLYAKOV, Yu. A.

[Abstract] Conduct is reported of a detailed theoretical analysis on the phenomenon of thermal explosion in the case of light-induced ignition of an equimolar mixture of H_2 and Cl_2 . Analysis of the rate of initiation of the reaction vs. temperature, and of induction time vs. temperature showed that, in the case of a $22 \text{ mole} \cdot \text{m}^{-3}$ concentration of H_2 and Cl_2 and a relatively low energy of activation for an unbranched chain reaction of 22 kJ/mole, a thermal explosion occurred under atmospheric pressure. With a heat effect of 184 kJ/mole, explosions will occur at $T_0 = 293^\circ\text{K}$ with a reaction rate of $9.4 \times 10^{-3} \text{ mole} \cdot \text{m}^{-3} \text{sec}^{-1}$ and at $T_0 = 673^\circ\text{K}$ with a rate of $1.7 \times 10^{-4} \text{ mole} \cdot \text{m}^{-3} \text{sec}^{-1}$. The induction time at the threshold of thermal ignition is equal to the time that it takes to reach the stationary phase immediately below the ignition range. The relationship between the rate of initiation of the reaction and the temperature at which the system shifts from the stationary phase to the explosive stage can be expressed by $1/W_i = 15(T_0 - T_i)$, where W_i = rate of ignition reaction. Figures 2; references 5 (Russian). [122-12172]

UDC 541.11

KINETICS OF CHEMICAL MEANS OF FIRE PREVENTION AND EXTINGUISHMENT

Moscow ZHURNAL VSESOYUZNOGO OBSHCHESTVA IMENI D. I. MENDELEYEVA
in Russian Vol 30, No 1, Jan-Feb 85 pp 4-12

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[Abstract] A review is provided of the kinetic aspects of fire prevention and extinguishment, with particular attention accorded to the homogenous

inhibitors and powdery compositions. The approach is based on the understanding that spontaneous ignitions and combustion processes involving chemicals proceed as chain reactions, with a key role played by active intermediate products. Such active intermediates are free atoms and radicals which favor a chain reaction rather than a molecular mechanism because of their high chemical reactivity and regeneration. Consideration of the kinetics of the various processes occurring in a combustion demonstrate that the effects of fire suppressants rest in transformation of the chemical energy of the free atoms and radicals into thermal energy which is released in recombination. The latter form of energy undergoes dissipation, as a result of which the overall reaction rate slows down or the reaction is inhibited. Figures 6; references 52: 32 Russian, 13 Western.
[200-12172]

UDC 614.841.12:66.007.7

APPLICATION OF FIRE INHIBITORS IN FIRE EXTINGUISHMENT

Moscow ZHURNAL VSESOYUZNOGO OBSHCHESTVA IM. D. I. MENDELEYEVA in Russian
Vol 30, No 1, Jan-Feb 85 pp 13-20

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[Abstract] Many of the difficulties encountered in planning for effective fire management and prevention and the application of fire suppressants in such programs are due to an inadequate understanding of the combustion mechanisms of various substances and materials, particularly in the area of macrokinetics of such processes. Recent studies with various chemical fire-quenching agents and analysis of the kinetic data, particularly with respect to the combustion of hydrogen and hydrocarbons, provided a better appreciation of the oxidative mechanism of combustion and its inhibition. Halohydrocarbon inhibitors were found to react selectively with hydrogen atoms. At temperatures below 950°K under high pressure the halocarbons promote spontaneous combustion of hydrogen and hydrocarbons, while at higher temperatures they inhibit such processes. In heterogeneous inhibition of fires by mineral salts it was found that, depending on the particle size of the powder, the active sites may either undergo heterogeneous recombination or sustain homogeneous extinction. Figures 8; references 48: 43 Russian, 5 Western.
[200-12172]

UDC 614.841.425

LIMIT PHENOMENA AS SCIENTIFIC AND THEORETICAL FOUNDATIONS OF FIRE AND EXPLOSION PREVENTION

Moscow ZHURNAL VSESOYUZNOGO OBSHCHESTVA IM. D. I. MENDELEYEVA in Russian
Vol 30, No 1, Jan-Feb 85 pp 21-27

ABDURAGIMOV, I. M., professor, Chair of Combustion Processes, Higher Engineering School of Fire Technology, USSR Ministry of Internal Affairs

[Abstract] An assessment was conducted of the various limit phenomena in fire and explosion processes, in order to obtain a better understanding of the various factors, and their relative contributions to combustion. Among the most important factors identified are the limit concentration of the combustible material or substance, temperatures of spontaneous ignition, transient flaming ignition, minimal critical energy of flaming, and the lower limit of the heat of combustion. These factors interact to favor a sharp, exponential acceleration of the chemical reaction of the flammable material with the oxidizing agent under the right temperature conditions, as well as to limit the reaction if the temperature at the zone of reaction is below a certain limit value. Mathematical analysis of these various factors for various combination has shown that dust suspensions and liquid air-dispersed systems present a greater danger of explosion than air-gas mixtures, due to the fact that in the former systems the concentration limit range is much wider for spontaneous combustion. Figures 1; references 23: 20 Russian, 3 Western.
[200-12172]

UDC 66.012-52

AUTOMATION AND SAFETY AT LARGE CHEMICAL PLANTS

Moscow ZHURNAL VSESOYUZNOGO OBSHCHESTVA IM. D. I. MENDELEYEVA in Russian
Vol 30, No 1, Jan-Feb 85 pp 27-30

KISIL', I. M., candidate of technical sciences, State Institute of Nitrogen Industry

[Abstract] With the increasing complexity of chemical processes and the concomitant increase in the size of chemical plants the hazard of chemical fires and explosions has also increased. In that respect, automation constitutes one of the most effective safety measures, making as it does not only for a more efficient operation of the entire plant, but also minimizing the risk to workers when all safety precautions are observed. Unfortunately, the safety of many automation systems has not been subjected to adequate scientific investigation, as have been the engineering aspects. In the long run, this cannot help but have negative consequences for the advancement of chemical technology. There is, as a result, an urgent need for the

development of a systematized approach to the safety of automated production systems, and the formulation of corresponding State Standards (GOST).
References 10: 9 Russian, 1 Western.
[200-12172]

UDC 621.646.8

NEW TECHNICAL SOLUTIONS IN APPARATUS PROTECTION FROM PRESSURE OVERLOAD

Moscow ZHURNAL VSESOYUZNOGO OBSHCHESTVA IM. D. I. MENDELEYEVA in Russian
Vol 30, No 1, Jan-Feb 85 pp 31-38

OL'KHOVSKIY, N. Ye., candidate of technical sciences, All-Union Scientific Research and Planning Institute of the Oil Refinery and Petrochemical Industry .

[Abstract] The current equipment of various petrochemical and refinery plants with complex, large-volume processing apparatus and devices, involved in large-scale management of flammable liquids and explosive gases, presents a special hazard both to the equipment and the workers. A number of rapid extinguishment and decompression devices have been designed, as well as methods of localization intended to stop or limit the spread of a conflagration or an explosion. Many of such safety devices encompass safety valves and bursting membranes, with the latter approach gaining prominence and importance in recent years with improvements in materials and design construction. Both Soviet and foreign experience in this field of safety measures show that bursting disc devices--allowing for rapid decompression under a variety of conditions--appears to be the most promising technology in the foreseeable future. Figures 8; references 6: 5 Russian, 1 Western.
[200-12172]

UDC 662.215.2+541.182.3

CONTROL OF FIRE AND EXPLOSION HAZARD OF DUST CONTROL DEVICES

Moscow ZHURNAL VSESOYUZNOGO OBSHCHESTVA IM. D. I. MENDELEYEVA in Russian
Vol 30, No 1, Jan-Feb 85 pp 38-47

TAUBKIN, I. S., candidate of technical sciences, All-Union Scientific Research Institute of Forensic Expertise

[Abstract] Advances in technology often involve processes relying on or creating dispersion of solid particles in gases, including air. In the case of pollution control, a variety of dust control devices have been designed all of which, however, have basic similarities in common. The dust control devices basically consist of baghouses, electrostatic precipitators, and collectors with an inherent danger of explosion regardless

of the chemical nature of the dust. To prevent such explosion, automated pressure detectors have been devised, as well as highly sensitive bursting membrane devices. Additional improvements include feedback-controlled injection of fire extinguishing agents into the closed area containing the dust in response to a signal from a sensor. In the USSR an automated system, designated Raduga, has been designed, in which a differential pressure sensor detects the rate of pressure increase and, thereby, precludes a false alert and unnecessary shutdown. Figures 7; references 67: 41 Russian, 26 Western.
[200-12172]

UDC 66.08

PREVENTION OF EXPLOSIONS AT CHEMICAL PLANTS

Moscow ZHURNAL VSESOYUZNOGO OBSHCHESTVA IM. D. I. MENDELEYEVA in Russian
Vol 30, No 1, Jan-Feb 85 pp 47-55

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[Abstract] Modern technology requires working conditions that approach near-critical levels (pressure, temperature, flammable material/oxidant ratio, etc.) in the processing of oil and various petrochemicals, carrying with it an increased risk of fires and explosions. In assessing the risk of an explosion or a fire careful attention has to be accorded to the prevailing process conditions as they influence the energy potential for an accident of that type. Pressure, temperature, and concentration are some of the more important factors that impact on spontaneous ignition, on the basis of which mathematical formulas can be proposed to provide a more rational basis for risk assessment. These include the implementation of automatic monitoring systems and fail-safe devices, more rational physical disposition of equipment and plant design, and off-limits areas. References 17 (Russian).
[200-12172]

UDC 621.643.55

INERT GASES IN FIRE AND EXPLOSION PREVENTION

Moscow ZHURNAL VSESOYUZNOGO OBSHCHESTVA IM. D. I. MENDELEYEVA in Russian
Vol 30, No 1, Jan-Feb 85 pp 55-63

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[Abstract] Current chemical technology involves extensive use and processing of various flammable and explosion-prone gases, liquids and dusts, and demands

special efforts and techniques to minimize the risk of a conflagration. Purging with an inert gas appears to be one of the more effective techniques that can be used in such safety measures, and offers the great advantage of relative simplicity. A number of inert gases have undergone extensive testing, alone or as combinations with other gases, with the general consensus that nitrogen is perhaps the most effective agent in a variety of conditions. There are, however, toxicity factors to be considered. This is particularly troublesome since human exposure to a nitrogen atmosphere containing 6-10% oxygen has an insidious onset leading to death, without any manifestations of anxiety. Recovered individuals often present with brain damage as a result of exposure to such a combination of gases. References 18: 12 Russian, 6 Western.
[200-12172]

UDC 614.834:614.838

ASSESSMENT OF FIRE AND EXPLOSION HAZARD AT PLANTS PROCESSING HEATED READILY INFLAMMABLE LIQUIDS

Moscow ZHURNAL VSESOYUZNOGO OBSHCHESTVA IM. D. I. MENDELEYEVA in Russian
Vol 30, No 1, Jan-Feb 85 pp 68-74

PCHELINTSEV, V. A., candidate of technical sciences, NIKITIN, A. G., candidate of technical sciences, and KHUZIAKHMETOV*, R. A., MISI [expansion unknown] imeni V. V. Kuybyshev; Kazan Engineering Construction Institute

[Abstract] Most of the fire and explosions at plants dealing with readily flammable liquids involved heated surfaces of machines and equipment. In contact with a readily flammable liquid, the latter then vaporizes, mixes with air, and forms a gaseous current rising perpendicularly to the heated surface. Criteria leading to such a phenomenon can serve as a basis for assessing actual flammability of a liquid and the risk of a conflagration. In the case of unheated liquids the vapors spread in a layer parallel to the surface of contact and subsequently, by convective mixing with air, gain altitude. In both cases convective air currents result in uneven distribution of the fumes within an enclosed area, with the danger of fire or of an explosion determined by actual concentrations. Thus, unless specific temperature and concentration conditions are met for an explosion or a fire, a plant can also be considered unsafe from other viewpoints, e. g., toxicity. Figures 2; references 20: 10 Russian, 10 Western.
[200-12172]

UDC 541.127+546.214

LOW TEMPERATURE PYROLYSIS OF OZONE

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 59, No 2, Feb 85
(manuscript received 19 Apr 83) pp 273-283

POPOVICH, M. P., YEGOROVA, G. V. and FILLIPOV, Yu. V., Chemistry Faculty,
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[Abstract] Under static conditions in a quartz reaction vessel, the rate of ozone pyrolysis was measured by pressure changes or by spectral analysis. Under dynamic conditions, initial and final ozone concentrations were determined at a constant flow rate through the reaction vessel. In both cases, high-purity ozone was generated electrically. Heterogenic dissociation on the reactor surfaces was reduced by careful prior desensitization of the surfaces with ozone prior to experimental measurements. Pyrolysis of concentrated (98-100%) ozone was measured at pressures of 15 to 100 mm Hg and temperatures of 110-150°C. In all cases the reaction was pseudo-first order, with the rate of dissociation dependent on pressure. The calculated energy of activation of the dissociation fell from 20 kcal/mol at 50 mm Hg to 15 kcal/mol at 5 mm Hg, with the change apparently related to changes in the relative amount of surface dissociation. Comparison with earlier experiments indicated the energy of activation of the homogenic dissociation was 22-23 kcal/mol. Higher pressure experiments (up to 200 mm Hg) also carried out with ozone-helium mixtures; linear dependence of the rate of dissociation on pressure was maintained. Figures 6; references 39: 20 Russian, 19 Western. [209-12672]

FERTILIZERS

MINERAL FERTILIZER OUTPUT GROWS

Moscow SEL'SKAYA ZHIZN' in Russian 2 Mar 85 p 2

[Article: "The Capacities Are Growing"]

[Text] Industrial chemistry [bol'shaya khimiya] received an important reinforcement at the end of last year. New capacities for the output of mineral fertilizers were put into operation at enterprises in the Ukraine. Having taken the baton from the construction workers and installation workers, the operating workers have been assuredly increasing the production volume since the very first days.

One more complex for ammonia production, constructed at the Gorlovskiy Association, Stirol', has begun to work for the harvest. It is estimated that the output yielded by it in a year will make it possible for farmers to obtain over 1.5 million tons of additional grain.

The enterprise's collective decided to utilize the planned capacity of the complex a month ahead of schedule--by the 50th anniversary of the Stakhanov movement. This had to have a sound basis. The future instrument control men studied the special features of the industrial equipment while it was still in the process of being installed and adjusted. Experienced specialists from two similar complexes already operating at Stirol' came to their assistance. Party groups, formed in all the shifts, direct the collective's efforts.

"Each of us tries to maintain and develop the shock rate of the originators of the complex, who successfully coped with a large and complicated work volume," said instrument control person I. Malakhova. "The capital invested in the new production should quickly provide an increase in the harvests. This will become our real contribution to implementing the country's Food Program. The speech made by Comrade K.U. Chernenko to the electorate gave new impetus to the collective's competition."

The meters at the new carbamide complex of the Odessa Port Plant have registered the figure "1000". This many tons of the granulated product were produced in a day for the first time since the launching. This means that the planned capacity was reached eight months earlier than specified by the normative deadline.

The foundation for success here was also laid when the production lines were being installed. The future operators took an active part in the work and went through on-the-job training at related enterprises.

The cleaning unit of the new structure, placed in the granulation tower, was especially difficult to set up. The faults noted were efficiently eliminated in the course of the start-up and adjustment work. In the final analysis it took not five months, but only one and a half months to finish the unit.

The ahead-of-schedule development of the complex to the planned productivity will make it possible, as early as the first quarter of this year, to send to the farmers about 10,000 additional tons of valuable fertilizers. The enterprise, receiving the raw material along the Tol'yatti-Odessa ammonia pipeline, is increasing the flow of the fertility salts.

The ammonia output doubled at the Dneprodzerzhinskiy Association, Azot, with the launching of one more complex. It will yield 450,000 tons of the product yearly.

The complex, planned in consideration of the latest achievements of science and technology, is distinguished not only by high productivity, but also by its economy.

The chemists are planning to bring the complex to planned capacity by this September--a month ahead of the normative deadline. The construction workers already have new worries: by the end of the year they should turn over a large carbamide production facility for operation.

The industry of fertility continues to increase its power.

12151

CSO: 1841/207

INORGANIC COMPOUNDS

UDC 62.987:546.27

EFFECTS OF HIGH PRESSURES AND TEMPERATURES ON PHASE TRANSITIONS IN TERNARY BORON SYSTEMS

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 58, No 12, Dec 84
(manuscript received 16 Mar 83) pp 2946-2949

LYSENKO, A. V., IVAKHNENKO, S. A., TOVSTOGAN, Y. M. and BELYANKINA, A. V.,
Institute of Superhard Materials, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] Metallographic and x-ray structural studies were conducted on ternary boron systems to determine the effects of high temperatures and pressures in the synthesis of novel superhard materials. The experiments were conducted in the interval of quasihydrostatic pressures ($p = 7-9$ GPa) and temperatures ranging from 1600 to 2200°K, while the duration of barothermic exposure varied from 10 to 600 sec. In B-C-O systems the amorphous phases underwent crystallization, with C transformed into graphite and amorphous B into a highly baric form. The crystalline tetragonal network had the parameters $a = 0.508$ nm, $c = 0.554$, and $c/a = 1.09$. With a B-N-O system a tetragonal lattice was obtained with $a = 0.564$, $c = 0.573$ and $c/a = 1.02$. The synthesis of superhard boron materials appears to be limited by diffusion processes. Figures 1; references 12: 10 Russian, 2 Western.
[122-12172]

UDC 541.8.127

REACTION EQUILIBRIUM OF URANYL ION HYDROLYSIS IN POTASSIUM NITRATE SOLUTIONS

Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA: KHIMIYA in Russian Vol 25, No 6, Nov-Dec 84 (manuscript received 17 Oct 83) pp 551-554

KOTVANOVA, M. K., YEVSEYEV, A. M., BORISOVA, A. P., TORCHENKOVA, Ye. A. and ZAKHAROV, S. V., Chair of Inorganic Chemistry

[Abstract] Mathematical modeling and pH measurements were conducted in studies on the equilibrium reaction of uranyl ion hydrolysis in 0.1 M

potassium nitrate, employing ionic strength conditions of 0.1, 10^{-3} M uranyl nitrate, and a temperature of $25 \pm 0.2^\circ\text{C}$. Measurements over a pH range of ca. 3.0 to 6.0 and evaluation of the equilibrium constants by nonlinear least squares method yielded tabulated hydrolysis constants involving formation of polynuclear $[(\text{UO}_2)_p(\text{OH})_q]^{2p-q}$ complexes. The data on the pH range of the complexes can be applied to other processes, e.g., complex formation, extraction, ion exchange, occurring in the presence of uranyl ions over a similar pH range. Figures 1; references 9: 3 Russian, 6 Western. [135-12172]

UDC 537.226.33

PHYSICAL CHARACTERISTICS OF LEAD GERMANATE MONOCRYSTALS AND CERAMICS UNDER HIGH PRESSURE

Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA: KHIMIYA in Russian Vol 25, No 6, Nov-Dec 84 (manuscript received 25 Jul 83) pp 600-604

POLANDOV, I. N. and ISAYEV, G. P., Chair, Physics and Chemistry of High Pressures

[Abstract] The ferroelectric properties of lead germanate ($\text{Pb}_5\text{Ge}_3\text{O}_{11}$) monocrystals and ceramics were studied over a wide temperature range--from -80 to $+250^\circ\text{C}$ --under high pressures reaching 40 kbar. Experimental data were compared with those based on theoretical calculations and found to agree within 15%. Essentially, the data demonstrated that as the pressure on the crystalline structure increased the dielectric permeability maximum was shifted to lower temperatures and markedly decreased. Figures 2; references 18: 11 Russian, 7 Western. [135-12172]

UDC 537.531.8:(546.19'22'682.546.19'23'682)54-161.6

SPECTRA EMISSION DATA ON STATUS AND DISTRIBUTION OF ATOMS IN GeX_rIn_x (X = S, Se) GLASSES

Kiev TEORETICHESKAYA I EKSPERIMENTAL'NAYA KHIMIYA in Russian Vol 20, No 6, Nov-Dec 84 (manuscript received 19 Dec 83) pp 689-696

BATRAKOV, Yu. F., ZAYTSEV, Yu. M., GUTENEV, M. S., KARPOVA, Ye. A., MAKAROV, L. L. and KHRAMTSOV, K. G., Leningrad University

[Abstract] The status and distribution of atoms in GeX_rIn_x (X = S, Se) glasses were assessed on the basis on chemical shifts in x-ray emission $K_{\alpha 1}$ lines of Ge, Se and In. The resultant data on chemical shifts and effective charge are presented in a tabular form in relation to a specific glass and its phase, and indicate that for GeSe_r glasses with $r > 2$, a model

consisting of random distribution of $\text{SeGe}_{2/4}$ and $\text{SeGe}_{2/2}$ structural units

applies. The In atom always appears to be charged positively, and its state approximates the situation in $\alpha\text{-In}_2\text{X}_3$ chalcogenide glasses, indicating that the In atoms form a polyhedron. Modification of the glass due to introduction of small concentrations of In is due to the localized perturbations induced by the molecularly dispersed $\text{SeIn}_{2/3}$ structures. Analysis of $K_{\alpha 1}$ lines for Ge and In in $\text{GeS}_{1.5}\text{In}_x$ glasses demonstrated that Ge and In compete for binding to S. Figures 3; references 12: 7 Russian (1 in English), 5 Western.

[146-12172]

UDC 669.715.892

EFFECTS OF ADDITIONS OF MAGNESIUM AND STRONTIUM ON PROPERTIES OF ALUMINUM

Dushanbe DOKLADY AKADEMII NAUK TADZHIKSKOY SSR in Russian Vol 27, No 10, Oct 84 (manuscript received 4 Jul 84) pp 587-589

MAKHMUDOV, M., VAKHOBOV, A. V. and GANIYEV, I. N., Institute of Chemistry imeni V. I. Nikitin, Tadzhik SSR Academy of Sciences

[Abstract] A study of the effects of adding up to 12% magnesium and 1.0% strontium on Brinell hardness and corrosion resistance of aluminum shows that magnesium additions tend to increase hardness and decrease electrical conductivity to a greater extent than strontium. Alloying aluminum with both magnesium and strontium enhances formation and spread throughout the triple system of regions of higher corrosion resistance. Figures 1; references 7 (Russian).

[194-12765]

ORGANOMETALLIC COMPOUNDS

UDC 541.49:546.763+541.182+543.226/227

SOLID-PHASE REPLACEMENT OF LIGANDS IN AMINE COMPLEXES WITH CHROMIUM(III)
EMBEDDED IN ORGANOSILOXANE MATRIX

Leningrad ZHURNAL OBSHCHEY KHMII in Russian Vol 55, No 2, Feb 85
(manuscript received 19 Mar 84) pp 405-412

YATSIMIRSKIY, K. B., SHEVCHENKO, Yu. N., YASHINA, N. I., SAMODUMOVA, I. M.,
NAZARENKO, V. A. and KISELEVA, L. I., Institute of Physical Chemistry
imeni L. V. Pisarzhevskiy, Ukrainian SSR Academy of Sciences

[Abstract] A study was made of the stoichiometry of solid-phase substitution reaction of ligands in amine-chromium(III) complexes embedded in organo-siloxane matrix, with the general formulas $[\text{Cr}(\text{Am})_3\text{L}(\text{O}_{1.5}\text{SiCH}_3)_n]$, where $\text{Am} = \text{NH}_2\text{CH}_2\text{CH}_3$ or $1/2\text{en}$, and $\text{L} = \text{Am}$ or $\text{O}_{1.5}\text{SiCH}_3$. In these complexes chromium(III)³ ions form 3 or 4 bonds with amines, while the remaining coordination sites are occupied by the oxygen atoms of the matrix. The rate of solid-phase replacement of the amine by the oxygen atoms of the matrix can be described by kinetic equations applicable to random nuclei formation and their growth in three dimensions. The energy of activation for the replacement process was calculated at 15-25 kJ/mole, a value about 3- to 5-fold lower than for analogous processes in solution. The entropy of activation was much more negative (-260 to -290 J/(mole·deg)) than for a solution, indicating a highly ordered transitional state. Figures 1; references 13: 9 Russian, 4 Western.
[215-12172].

UDC 541.49:547.27

COMPLEX FORMATION BETWEEN SELENO- AND THIOCYANATES WITH IODINE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 2, Feb 85
(manuscript received 4 Apr 84) pp 422-427

CHMUTOVA, G. A., KAZYMOVA, M. A. and YERMOLAYEVA, L. V., Kazan State
University imeni V. I. Ul'yanov-Lenin; Institute of Organic and Physical
Chemistry imeni A. Ye. Arbuzov, Kazan Branch, USSR Academy of Sciences

[Abstract] An assessment was made of the reactivity of methyl- and phenylselenocyanates with iodine, along with comparison of the spectral and thermodynamic characteristics of compounds with the groups $EC\equiv N$ ($E = \text{Se}, \text{S}$) and $C\equiv N$ in the donor molecule. Electron spectroscopy revealed the formation of weak complexes between CH_3SeCN and $\text{C}_6\text{H}_5\text{SeCN}$ (donors) and iodine (acceptor) in CCl_4 with a reactant ratio of 1:4. Comparative analysis of the electron and photoelectron spectroscopies and quantum chemical calculations of the donor structure indicated that the most probable coordinating site consists of the selenium (or sulfur) atom. In the case of nitriles, complex formation involves the nitrogen atom of the nitrile group. Figures 2; references 28: 11 Russian, 17 Western.
[215-12172]

ORGANOPHOSPHORUS COMPOUNDS

UDC 547.56+535.34:542.91

MECHANISM OF PERMUTATIONAL ISOMERIZATION OF AMIDINOFLUOROPHOSPHORATES:
TAUTOMERIC MIGRATION OF PHOSPHORANYL GROUPS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 2, Feb 85
(manuscript received 13 Mar 84) pp 271-282

NEGREBETSKIY, V. V., KAL'CHENKO, V. I., RUDYY, R. B. and MARKOVSKIY, L. N.,
All-Union Scientific Research Institute of Chemical Plant Protection,
Moscow; Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences,
Kiev

[Abstract] Factors contributing to the configurational stability of hexa-coordinated phosphorus atom of amidino fluorophosphorates were studied in order to determine the mechanism of permutational isomerization. Dynamic ^1H and ^{31}P NMR data analysis was applied to a series of N,N-dialkyl substituted amidino fluorophosphorates with different substituents on the phosphorus atom, and at the carbon and nitrogen atoms of the N-C-N triad. Permutational isomerization in the tetragonal bipyramidal coordination of phosphorus atom involved an irregular mechanism with dissociation of the P-N or of the P-O bonds of the ligand, and formation of pentacoordinated intermediates. The study represents the first analysis of reversible intramolecular migration of pentacoordinated phosphorus groups in the amidine N-C-N triad. Figures 2; references 18: 7 Russian, 11 Western.
[215-12172]

UDC 546.18

REACTION OF DIIMIDOPHOSPHENIC AND IMIDOTHIO(SELENO)PHOSPHENIC ($\sigma^{3\lambda 5}$ -PHOSPHORYLIDES) ACID AMIDES WITH ORGANOALUMINUM COMPOUNDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 2, Feb 85
(manuscript received 27 Mar 84) pp 282-291

ROMANENKO, V. D., SHUL'GIN, V. F., SKOPENKO, V. V., CHERNEGA, A. N.,
ANTIPIN, M. Yu., STRUCHKOV, Yu. T., BOLDESKUL, I. Ye. and MARKOVSKIY, L. N.,
Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences, Kiev;
Institute of Heteroorganic Compounds imeni A. N. Nesmeyanov, USSR Academy of
Sciences, Moscow

[Abstract] Standard NMR and ESR techniques were employed in continuing studies on the reaction of $\sigma^{3\lambda 5}$ -phosphorylides with organometallic compounds, which demonstrated that reaction of phosphenimidic acid and the imidithio- (or seleno) congeners react with trimethyl- or triphenylaluminum. The reaction mechanism involves transfer of a methyl or phenyl group to the phosphorus atom with the formation 1,3,2,4-diazaphosalumethidines or 1,3,2,4-thiaza(selenaza)phosphalumethidines. In the case of polyfunctional organo-aluminum compounds, e.g., methylaluminum chlorides or dimethylaluminum hydrides, the most nucleophilic ligand bound to the aluminum atom is transferred to the phosphorus atom. On the basis of x-ray analysis structural formulas are presented for 1,3-bis(trimethylsilyl)-2-bis(trimethylsilyl)-amino-2-phenyl-4,4-diphenyl-1,3,2,4-diazaphosphalumethidine and 2-bis(trimethylsilyl)-amino-2-phenyl-3-tert-butyl-1,3,2,4-thiazaphosphalumethidine. Figures 3; references 13: 6 Russian, 7 Western.
[215-12172]

UDC 547.26'118

REACTION OF POLYFLUORINATED ALIPHATIC ALDEHYDES WITH TRIVALENT PHOSPHORUS ACID CHLORIDES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 2, Feb 85
(manuscript received 24 Feb 84) pp 291-297

SHERMOLOVICH, Yu. G., SOLOV'YEV, A. V., DANCHENKO, Ye. A. and
MARKOVSKIY, L. N., Institute of Organic Chemistry, Ukrainian SSR Academy
of Sciences, Kiev

[Abstract] In view of the ease of reaction of fluorinated aldehydes with trialkyl and trispolyfluoroalkylphosphites for the synthesis of cyclic alkoxyphosphoranes, an attempt was made to expand the reaction mechanism to halogenated derivatives of trivalent phosphorus in order to synthesize halophosphoranes with a 1,4,2-dioxaphospholane ring. The experimental studies showed that 2,2,3,3-tetrafluoropropanal and 2,2,3,3,4,4,5,5-octafluoropentanal failed to react at 150°C with PCl_3 , PBr_3 ,

propyldichlorophosphite, phenyldichlorophosphine and bis(2,2,3,3-tetrafluoropropyl)chlorophosphite. However, dipropylchlorophosphite reacted with chlorophosphoranes to form cyclic chlorophosphoranes on the basis of NMR data. The high thermal stability of the products was due to the exocyclic substituents on the phosphorus atom in the 1,4,2-dioxaphospholane ring. Figures 2; references 9: 5 Russian, 4 Western.
[215-12172]

UDC 546.98:547.241

SYNTHESIS AND STRUCTURE OF DIMETHYLPHOSPHITE-RHODIUM HYDRIDE COMPLEX

Leningrad ZHURNAL OBSHCHEY KHMII in Russian Vol 55, No 2, Feb 85
(manuscript received 3 Jan 84) pp 298-304

NIFANT'YEV, E. Ye., KUKHAREVA, T. S., ANTIPIN, M. Yu. and STRUCHKOV, Yu. T.

[Abstract] Experimental studies were conducted on the synthesis of complexes between rhodium and dimethylphosphite to further expand available knowledge on complexes of transition metals, and compare the structural data with the information now available for diethylphosphite-palladium complexes. Reaction of an excess of dialkylphosphites in an inert gas with acetylacetonaterhodium carbonyl resulted in the formation of hydride complexes of rhodium. On the basis of elemental analysis and IR and NMR spectroscopies, a crystalline structure for bis(dimethylphosphito)hydridocarbonyl-bis-dimethylphosphite-rhodium has been proposed in conjunction with data yielded by x-ray structural analysis. Figures 1; references 12: 7 Russian, 5 Western.
[215-12172]

UDC 547.288.1

C-PHOSPHORYLATION OF 2,6-DI-TERT-BUTYLPHENOL BY PHOSPHORUS TRIHALIDES

Leningrad ZHURNAL OBSHCHEY KHMII in Russian Vol 55, No 2, Feb 85
(manuscript received 3 Jan 84) pp 304-307

NIFANT'YEV, E. Ye. and KUKHAREVA, T. S., Moscow State Pedagogical Institute imeni V. I. Lenin

[Abstract] Since arylphosphonous acids have been identified as putative sources of pharmacologically active compounds, particularly those containing functional groups with mobile hydrogen atoms, it appeared reasonable to complement such studies by using phosphorus trihalides for C-phosphorylation of 2,5-di-tert-butylphenol. Experiments conducted in an atmosphere of an inert gas demonstrated that phosphorylation of the butylphenol by phosphorus trichloride or tribromide involves a slow phosphorylation of the phenol hydroxyl group and rapid phosphorylation of C-4 of the benzene ring. The

latter reaction is a reversible process. In addition, dephosphorylation was hindered by the addition of a tertiary amine. Description is provided of preparative methods for the synthesis of 4-hydroxy-3,5-di-tert-butylphenylphosphonous acid, 4-hydroxy-3,5-di-tert-butylphenylphosphonic acid, and 4-hydroxy-3,5-di-tert-butylphenylthiophosphonic acid. References 4:

1 Russian, 3 Western.

[215-12172]

UDC 547.26'118

1,3-DIBENZYL-1,3,2-DIAZAPHOSPHOLANES AND -PHOSPHORINANES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 2, Feb 85
(manuscript received 30 Jan 84) pp 308-315

NIFANT'YEV, E. Ye., SOROKINA, S. F., VOROB'YEVA, L. A. and BEKKER, A. R.,
Moscow State Pedagogical Institute imeni V. I. Lenin

[Abstract] Description is provided for the synthesis of 1,3-dibenzyl-1,3,2-diazaphospholanes and -phosphorinanes by the reaction of N,N'-dibenzylethylene- or -propylenediamines with phosphorus trichloride in the presence of triethylamine in absolute benzene. The procedure yielded previously undescribed N,N'-dibenzyl-1,3,2-diazaphospholanes and -phosphorinanes, with alkyl and phenyl substituents on the nitrogen atom. The stability of these products was comparable to that of the parent compounds. NMR and ESR spectroscopies showed that the phosphorinanes exist largely in a chair conformation with an axially-oriented substituent on the phosphorus atom. In addition, the two geminal protons of the $-\text{CH}_2\text{CH}_2\text{CH}_2-$ groups were nonequivalent, with the degree of nonequivalence predicated on the substituent on the phosphorus atom.

Figures 2; references 6: 4 Russian, 2 Western.

[215-12172]

UDC 547.558.1

REACTION OF p-NITROPHENYLSULFENAMIDE WITH $\text{Ph}_3\text{P}/\text{CCl}_4$

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 2, Feb 85
(manuscript received 16 Feb 84) pp 321-323

ZHMUROVA, I. N., YURCHENKO, V. G. and PINCHUK, A. M., Institute of Organic Chemistry, Ukrainian SSR Academy of Sciences, Kiev

[Abstract] In distinction to the reaction of o-nitrophenylsulfenamide with the binary system $\text{Ph}_3\text{P}/\text{CCl}_4$ which proceeds according to the Appel scheme [Appel, R., Angew. Chem., 14: 801-811, 1975], the reaction of $\text{Ph}_3\text{P}/\text{CCl}_4$ with p-nitrophenylsulfenamide follows an unusual course with the formation triphenylphosphonium-bis(p-nitrophenylsulfenyl)methylide (I). The synthesis of I was confirmed by elemental analysis, MW determination, and independent

synthesis. Under the conditions employed, I was synthesized in a 52% yield.
References 8: 3 Russian, 5 Western.
[215-12172]

UDC 547.241

SYNTHESIS AND CHARACTERISTICS OF 1,2,4-AZADIPHOSPHETIDINES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 2, Feb 85
(manuscript received 7 Feb 84) pp 331-340

NOVIKOVA, Z. S., KABACHNIK, M. M., MONIN, Ye. A., BORISENKO, A. A. and
LUTSENKO, I. F., Moscow State University imeni M. V. Lomonosov

[Abstract] Description is provided of the synthesis of bisalkylamides of methylenediphosphorus(III) acids via the interaction of dichloroanhydrides with primary amines at 0°C in ether, with a reactant ratio of 1:4. By means of thermal cyclization of the methylenediphosphorus(III) acid bisalkylamides, the first reported synthesis of 1,2,4-azadiphosphetidine was achieved. NMR studies on the product demonstrated that it represents a mixture of cis- and trans-isomers. In addition, one of the congeners, 2,4-dialkoxy-1,2,4-azadiphosphetidine--with a tert-butyl group on the nitrogen atom--underwent transformation from the trans form into the thermodynamically more stable cis form. Figures 1; references 7: 2 Russian, 5 Western.
[215-12172]

UDC 547.241

¹³C-NMR STUDIES ON (MONO-, DI-, TRIHALOMETHYL)DIHALOPHOSPHINES AND THEIR DERIVATIVES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 2, Feb 85
(manuscript received 8 FEB 84) pp 340-346

PRISHCHENKO, A. A., YASHINA, N. S., GEFEL', Ye. I. and GROMOV, A. V.,
Moscow State University imeni M. V. Lomonosov

[Abstract] A series of mono-, di-, and trihalomethyl)dihalophosphines and their derivatives were subjected to ¹³C-NMR analysis, as an ideal method for structural confirmation since rearrangement of halomethylphosphines into the corresponding P-halo ylides involve the carbon atom of the halomethane fragment. The data for chlorine compounds are summarized in tabular form. Analysis of the information on the chemical shifts and spin-spin interactions for the compounds of interest demonstrated that this technique is suitable for structural determinations of organophosphorus compounds with the P-C-Hlg fragment in the molecule. Figures 1; references 6 (Russian).
[215-12172]

UDC 547.341

NICKEL(II) AND COBALT(II) COMPLEXES WITH CYCLIC AND ACYCLIC DERIVATIVES OF
PHOSPHORUS DITHIONIC ACIDS: STABILITY AND STRUCTURE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 2, Feb 85
(manuscript received 4 Jun 84) pp 357-360

OVCHINNIKOV, V. V., GALKIN, V. I., GARIFZYANOV, A. R., TOROPOVA, V. F. and
CHERKASOV, R. A., Kazan State University imeni V. I. Ul'yanov-Lenin

[Abstract] An analysis was conducted on the stability and structure of several types of dithionic phosphorus acids (dithiophosphinic, dithiophosphonic, dithiophosphate) complexes formed with nickel(II) and cobalt(II), based on an evaluation of the steric effects of substituents on the ligands. Correlation analysis of stability vs. structure for the cyclic and acyclic ligands demonstrated that the stability of the ligand-nickel(II) or -cobalt(II) complexes in both cases was dependent on the steric factors of the substituent on the phosphorus atom. The complexes can be classed into different reactive series with the stability within each series determined by the steric characteristics of the substituent. However, differences among the series are due largely to the electronic configuration of the R, RO, and O-R-O groups in the dithiophosphate ligands. Figures 2; references 3 (Russian).
[215-12172]

UDC 547.26'118

REACTION OF o-PHENYLENEDIISOTHIOCYANATE WITH DIBUTYLPHOSPHONOUS ACID

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 2, Feb 85
(manuscript received 23 Apr 84) pp 452-453

ZIMIN, M. G., MIRONOV, A. V., CHERKASOV, R. A. and PUDOVIK, A. N.,
Kazan State University imeni V. I. Ul'yanov-Lenin

[Abstract] o-Phenylenediisothiocyanate was found to react with dibutylphosphonous acid at room temperature, in ether, with the formation of 13H-[1,3,5]-thiodiazino-[3,2-a,5,6-a']bisbenzimidazole-13-thione and N-(dibutylphosphinoxidothiocarbonyl)benzimidazoline-2-thione. The reaction mechanism involves both isothiocyanate groups and results in the formation of an imidazolinethion ring. References 2: 1 Russian, 1 Western.
[215-12172]

UDC 547.26'118

RETENTION OF PHOSPHORUS COORDINATION IN REACTION OF THIOPHOSPHITES WITH CCl_4

Leningrad ZHURNAL OBSHCHEY KHMII in Russian Vol 55, No 2, Feb 85
(manuscript received 29 Apr 84) pp 453-454

SINYASHIN, O. G., KARIMULLIN, Sh. A., BATYYEVA, E. S. and PUDOVNIK, A. N.,
Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan
Branch, USSR Academy of Sciences

[Abstract] Triethyltrithiophosphite was found to react with CCl_4 (2:1 reactant ratio) with the formation of S,S-diethylchlorodithiophosphite, diethyldisulfide, and trichloromethyldithiophosphonic acid diethyl ester. Tripropyltrithiophosphite reacted in an analogous manner with CCl_4 .
References 5: 3 Russian, 2 Western.
[215-12172]

UDC 547.26'118+547.241

REACTION OF DIALKYLIODOPHOSPHITES WITH AZOMETHINES

Leningrad ZHURNAL OBSHCHEY KHMII in Russian Vol 55, No 2, Feb 85
(manuscript received 24 May 84) pp 456-457

NOVIKOVA, Z. S., KABACHNIK, M. M., MASHCHENKO, N. V. and LUTSENKO, I. F.,
Moscow State University imeni M. V. Lomonosov

[Abstract] In distinction to chlorophosphites, dialkyliodophosphites were found to react readily with various azomethines with the formation of 1,4,2-diazaphospholanes. In ether, the reaction proceeded readily at room temperature with a reactant ratio of 1:2. The initial step involved formation of a quasiphosphonium compound which formed a white precipitate, and gradually underwent transformation into 1,4,2-diazaphospholane.
References 2 (Russian).
[215-12172]

UDC 546.183+547.585

OXAZAPHOSPHORINANES FROM ANTHRANILIC ACID

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 2, Feb 85
(manuscript received 18 May 84) pp 457-458

KULIYEV, A. K., MOSKVA, V. V., AKHMEZADE, D. A., SAKHNOVSKAYA, Ye. B. and GUSEYNOVA, M. M., Institute of Petrochemical Processes, Azerbaijan SSR Academy of Sciences, Baku; Kazan Institute of Chemical Technology

[Abstract] 2-Chloro-4,5-benzo-1,3,2-oxaphosphorinane-6-one (I) was formed by boiling a mixture of anthranilic acid and PCl_3 (excess) for 5 h. Subsequent reaction of I with diethylamine at 20°C resulted in the formation of the amide--2-diethylamido-4,5-benzo-1,3,2-oxazaphosphorinane-6-one. [215-12172]

UDC 547.558.1

p-BROMOBUTYROPHENONE TETRAARYLPHOSPHONIUM SALTS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 55, No 2, Feb 85
(manuscript received 1 Jan 84) pp 346-350

SHEVCHUK, M. I., BUKACHUK, O. M. and ZINZYUK, T. A., Chernovtsy State University

[Abstract] Conditions are described for the reaction of p-bromobutyrophenone with triphenylphosphine to synthesize a tetraarylphosphonium salt, containing several reactive groups (triphenylphosphonium, carbonyl, alkyl). The presence of a triphenylphosphonium group at the p-position of the phenyl ring activates the carbonyl group of p-butyrylphenyltriphenylphosphonium bromide(I) in reactions with arylhydrazines. I enters readily into condensation reactions with aldehydes via the alpha-methylene group to yield phosphonium alkonos. Description is also provided of the synthesis of previously unreported bromophosphonium and bisphosphonium salts containing the carbonyl group. References 4: 3 Russian, 1 Western. [215-12172]

PETROLEUM PROCESSING TECHNOLOGY

EFFICIENT USE OF PETROLEUM PRODUCTS REQUIRED

Moscow EKONOMICHESKAYA GAZETA in Russian No 7, Feb 85 p 4

[Article by V. Yefimov, doctor of Economic Sciences, academic secretary of the Interdepartmental Commission on Economy and Efficient Use of Material Resources: "How Petroleum and Petroleum Products are Used"]

[Text] On 8 February the Interdepartmental Commission on Economy and Efficient Use of Material Resources heard L.P. Karpenko, deputy minister of the USSR Petroleum Refining and Petrochemical Industry, speak about losses of petroleum and petroleum products at enterprises of the USSR Ministry of Petroleum Refining and Petrochemical Industry. In the course of the discussion it was revealed that a cautious attitude toward "black gold" and the products produced on its basis is still not found everywhere. For example, at 15 oil refineries and production associations checked by organs of USSR Gosnab, above-norm industrial losses of petroleum and petroleum products exceeded hundreds of thousands of tons. Moreover, the Groznefteorgsintez Production Association permitted a third of them.

The experience of the Ministry of Petroleum Refining and Petrochemical Industry itself is convincing proof that the potentials for saving are quite large. In 1984 on the whole for the sector, irrevocable losses of petroleum and petroleum products were reduced by 0.03 percent as compared with the norm. The result could be more impressive if the plans adopted for organizational and technical measures to reduce loss were carried out everywhere. At some enterprises, these plans are not drawn up at all. Some plants obtained the loss norms for 1984 from the USSR Ministry of Petroleum Refining and Petrochemical Industry only in June 1984.

The "efficiency" is no better this year, either. January has passed, but many of the ministry's enterprises still do not know the loss norms for 1985--hence the placid mood.

The Mozyrskiy Oil Refinery in Belorussia and the Achinskiy Oil Refinery in Krasnoyarskiy Kray are equipped with uniform modern equipment. In Mozyr', however, the losses are lower by almost half, while in Achinsk they are 50 percent higher than on the average for the sector. Nevertheless, the ministry sets the norm for the Achinskiy Oil Refinery at the level of the actual losses.

Petroleum products are also irrevocably lost due to the fact that from 50 to 80 percent of the pumps are not equipped with face seals. The average yearly content of petroleum products in the waste waters of Yaroslavnefteorgsintez exceeds the established norms by sevenfold. These irrevocable losses of petroleum products are added to by the unnecessary energy input to collect and process the so-called trapped petroleum products.

Maintaining the reservoirs, receiving-distributing accessories and pipelines in poor condition costs dearly. At the Pavlodarskiy Oil Refinery, a total of about 10 sixty-ton railroad tanks was spilled on the ground due to leakage in the valves and joints of the pipelines. Losses of oil due to its insufficient discharge from the tanks is a mass phenomenon.

Interdepartmental Commission discussions revealed the fact that even today there have been few changes. The workers of the USSR Ministry of Petroleum and Petrochemical Industry could not give any precise answer to the question of how they intend to form resources for above-plan saving this year.

The Interdepartmental Commission committed the USSR Ministry of Petroleum Refining and Petrochemical Industry to quickly adopt measures for a realistic change in the state of affairs pertaining to the use of petroleum and petroleum products.

12151
CSO; 1841/207

UDC 66.022:621.311.2+665.63.634

STABILIZATION OF FUEL T-6 WITH MIXTURES OF ANTIOXIDANTS

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 1, Jan 85, pp 16-17

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[Abstract] The effectiveness of mixtures of additives with N,N'-di(3,5-di-tert-butyl-4-hydroxybenzyl)urea (KF-1) as jet fuel stabilizers was studied by heating fuel T-6 12 times to 120°C and determining its acidity, optical density and peroxide number. The amount of additive added was $5 \cdot 10^{-5}$ mole/kg. The mixture of KF-1 and dilaurylthiodipropionate (DLTDP) had a synergistic effect, which was attributed to the reduction in hydrogen peroxide yield by the phenol antioxidant (KF-1) and decomposition of hydrogen peroxide by the sulfur-containing DLTDP. The effect of mixtures of KF-1 and zinc diethyldithiocarbamate (DEDTCZn), an organometal compound, was determined by the molar ratio of components. Thus, the mixture of KF-1 and DEDTCZn exhibited synergism at molar ratios above (9-4):1. An especially high synergistic effect was observed at a KF-1:DEDTCZn ratio of 1.5:1. The mechanism of action was typical for dialkyldithiocarbamates, which inhibit oxidative processes at higher concentrations. A synergistic effect was observed at all component ratios of the mixture of KF-1 and di(3,5-di-tert-butyl-4-hydroxyphenyl)-methane (MB-1), which is a side product in the production of KF-1; the highest effect was observed at a KF-1:MB-1 ratio of 4:1. Consequently, it is not necessary to remove MB-1 admixtures from KF-1. This also contradicted literature data in that two sterically hindered phenols acted synergistically. Mixtures of KF-1 and four phenosanes also had a synergistic effect, which was attributed to the inhibition of oxidation of antioxidant conversion products. Figures 1; references 5 (Russian).

[173-9307]

UDC 665.765:404.038.2

EFFECT OF SULFONATE ADDITIVES ON LACQUER FORMATION IN ENGINE AT HIGH TEMPERATURES

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 1, Jan 85, pp 22-23

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[Abstract] The effect of neutral and highly alkaline sulfonate additives, based on synthetic alkyl aromatic ($R = C_{20}-C_{28}$) compounds (alkyl toluene, alkyl naphthalene, and alkyl phenol), on lacquer formation was studied with motor oil M-11 as the example. S-300, a highly alkaline additive widely used in Soviet motor oils, was used for comparison. All tested additives reduced the tendency for lacquer formation over the entire temperature range tested (270-350°C). Although no lacquer deposits were formed at piston wall temperatures of 270-300°C, the effectiveness of additives declined at 300-350°C. The effectiveness of additives increased with an increase in alkalinity; this is apparently due to the greater detergent and dispersing properties of highly alkaline additives in comparison with neutral additives. The highly alkaline sulfonates were also more effective than S-300. Compounds based on alkyl phenol, which also possesses antioxidant activity, were the most effective. The additives were most effective at a 5% concentration in oil, since higher concentrations did not significantly reduce lacquer formation. Tests with the most effective additives IKhP-223 (alkyl toluene) and IKhP-227 (alkyl phenol) in oil M-10G₂ designated for use in automotive diesel engines showed that M-10G₂ with these additives met the standard requirements for G₂ oils. Consequently, the synthetic sulfonate additives can be used to create motor oils for heavy duty use with a reduced tendency for lacquer formation. Figures 2; references 5 (Russian).
[173-9307]

UDC 543.422:541.183

PHASE TRANSITIONS IN INDUSTRIAL ALUMINUM OXIDE AS CATALYST CARRIER

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 1, Jan 85, pp 26-27

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[Abstract] The effect of the type of original aluminum hydroxides on the temperature of γ - α Al_2O_3 phase transitions was studied by IR spectroscopy. Products studied were chemically pure samples of gibbsite $Al(OH)_3$, boehmite $AlO(OH)$ and bayerite $Al(OH)_3$ and commercially produced samples of aluminum oxide and hydroxide: aluminate Al_2O_3 calcined at 550°C (IV), aluminum hydroxide AO-TA-308 obtained by thermal dispersion (V), microspherical Al_2O_3 obtained by spray drying (VI), Al_2O_3 obtained by hydrolysis of crude aluminum (VII), and aluminate Al_2O_3 (VIII). Calcination of AO-TA-308 at 1000°C resulted in

the formation of ϵ - Al_2O_3 and at 1200°C in the formation of α - Al_2O_3 . IR spectroscopy was more sensitive than X-ray analysis in determining a small number of phases and can be successfully used for monitoring phase transitions in Al_2O_3 . The γ - ϵ Al_2O_3 transition in the tested samples occurred at 800-1000°C and the ϵ - α Al_2O_3 transition at 1000-1200°C. Variation in phase transition temperature for samples from various sources was 50-100°C. The model hydroxides were arranged as follows according to rate and degree of transition: gibbsite $\rightarrow$ boehmite $\rightarrow$ bayerite; and the industrial samples: Al_2O_3 (VII) $\rightarrow$ Al_2O_3 (VI) $\rightarrow$ AO-Ta-308 (V) $\rightarrow$ Al_2O_3 (VI). Figures 1; references 3 (Russian).
[173-9307]

UDC 665.644.2.022.1

AGGREGATE STABILITY OF HEAVY DISTILLATE STOCK IN PRESENCE OF ACTIVATING ADDITIVES

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 1, Jan 85, pp 28-29

ABDUL'MANOV, R. G., SERIKOV, P. Yu., SMIDOVICH, Ye. V. and SYUNYAYEV, Z. I., Moscow Institute of the Petrochemical and Gas Industry imeni I. M. Gubkin

[Abstract] The aggregate stability of oil disperse systems, i.e., the capacity to maintain uniform disperse phase consistency throughout the system, is important for the storage, mixing and processing of oil stock and affects the high-temperature processes of heating, evaporation and destructive conversion of stock. A method is proposed for evaluating the aggregate stability of mixtures of vacuum distillate and activating additives, which have a positive effect on the aggregate state; this method is based on determining structural viscosity on a standard capillary viscometer. However, repeated viscosity tests on the same batch of vacuum distillate decreased viscosity, for example, from 232.6 mm²/s in the first determination to 146.1 mm²/s in the fiftieth, due to the transition from a disperse to a highly disperse state in the viscometer. The temperature of the preliminary heat treatment in a drying oven had a similar effect on viscosity. The proposed method consists of the following stages: preparation of an untreated sample and a sample with modifiers, preliminary heat treatment of mixtures at 60°C for 15 min, determination of viscosity 2-3°C below the cloud point (viscosity of untreated sample should be 140-340 mm²/s), incubating the capillary viscometer with sample for 20 min, determination of viscosity, and plotting structural viscosity versus the amount of modifier in the system. Samples were used only once; the most suitable diameter for the capillary viscometer was 1.7-2 mm. Two series of tests with the extract from selective purification of oils and thermal cracking residue showed that a system with 2% extract had the highest dispersion and highest aggregate stability. Higher quantities of extract increased system structural viscosity. Similar findings were obtained for the cracking residue with highest aggregate stability found with 0.3% cracking residue. The viscosity of the distillate and its mixtures with additive

was 70.8 mm²/s for the extract and 97.7 mm²/s for the cracking residue; consequently, the mixture of distillate and cracking residue had a higher aggregate stability than the extract mixture. The cracking residue was a more effective additive since smaller amounts produced a greater effect. The viscosity test was highly temperature sensitive: a 0.5°C drop in temperature increased viscosity from 232.6 to 315.2 mm²/s. The method can be used in the temperature range between the temperature of system transition from the disperse to the molecular state and the solidifying point of the analyzed product. Figures 1; references 5 (Russian).

[173-9307]

UDC 621.892.401.7

ESTABLISHMENT OF SERVICE LIFE OF OILS IN AIRCRAFT GAS-TURBINE ENGINES

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 1, Jan 85, pp 31-33

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[Abstract] The dependence of physicochemical and service properties of oils on the length of their use in engines was studied in various types of engines for different climate zones to increase oil service life in various types of gas-turbine engines used in nonmilitary aircraft. The physicochemical parameters studied were oxidative stability, foaming capacity, lubricating properties and iron and copper content. Flash and solidifying points and water content changed minimally and stabilized within the first 100-150 h of oil use. Mechanical admixtures did not accumulate in lubrication systems. Viscosity was found to change most extensively, and acid numbers were the most stable. Study of lubricating properties of mineral oils showed that wear spot diameters and critical loads stabilized with use. The increase in kinematic viscosity and deterioration in oxidative stability of oils preceded changes in other parameters, and these two parameters can therefore be used as serviceability criteria. Oxidative stability can be determined from the antioxidant content, and kinematic viscosity according to GOST [State Standard] 33-82. Changes in oil viscosity and additive concentration were either exponential or linear, and equations were derived for predicting the service life of oil. The above test results and equations were the basis for "A method for assessing the service life of oils in gas-turbine engines of nonmilitary aircraft," and this method was incorporated into a State Standard for introducing new mineral oils and increasing their service life. Use of this procedure doubled or tripled the life of various oils in engines, and showed that service life of mineral oils in gas-turbine engines was limited. Figures 1; references 6 (Russian).

[173-9307]

UDC 621.892.21:543.432

DETERMINATION OF WATER CONTENT IN TURBINE OIL FOR GAS PUMPING UNITS

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 1, Jan 85,
pp 33-35

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[Abstract] The method developed for determining the water content in turbine oil Tp-22 for gas pumping units was based on oil surface tension; the effect of gas condensate on oil surface tension was also taken into account. Surface tension was studied in a three-component system of turbine oil Tp-22, gas condensate and distilled water at 20°C. The gas condensate in oil was determined from its optical density at a wavelength corresponding to peak light absorption of oil; for Tp-22 this peak was 450 nm. The surface tension of oil at its interface with air was determined by the method of the highest bubble pressure on a Rebinder device. The graph of oil optical density versus the gas condensate content was a straight line passing through the origin, which indicates that the test solution was governed by Beer's law. Graphs are presented which can be used to determine the water content from the gas condensate content and surface tension. Oil surface tension was also determined in the binary systems: oil--gas condensate and oil--water. Oil surface tension increased minimally with addition of up to 10% gas condensate, and dropped abruptly with higher amounts. Addition of even a small amount of water (0.01% by mass) to oil produced an abrupt increase in surface tension, which continued to increase with higher amounts of water. Water and gas condensate content can be determined by this method within 5-10 min after oil samples are obtained from an operating gas pumping unit. Test time can be shortened by continuously monitoring the optical density of circulating oil from a gas pumping unit with an in-line photocolormeter. Test error for an artificial mixture of known composition did not exceed 3%. Figures 4; references 4 (Russian).
[173-9307]

UDC 665.644.2:665.635:665.642.4

CATALYTIC CRACKING OF LIGHT GAS OIL FROM COKING

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 2, Feb 85 pp 11-14

FARKHADOVA, G. T., RUSTAMOV, M. I., MYURTYCHEV, A. A., GUSEYNOV, A. M., MAYOROVA, N. S. and GYSEYNOVA, S. B., Institute of Petrochemical Refining, AzSSR Academy of Sciences, Novo-Baku Oil Refinery imeni Vladimir Il'ich

[Abstract] Light gas oil resources are expected to increase significantly with the growing capabilities of slow coking installations, and since refineries using light gas oil as a rule also have catalytic cracking units, it becomes feasible to study the possibilities of incorporating the light gas oil obtained from coking in the catalytic cracking feedstock. Results of a study on catalytic cracking of a light gas oil obtained from slow coking of a sulfur-free bottoms stock show that this may be successfully combined with vacuum gas oil cracking in a two-stage operation. Figures 2; references 5 (Russian). [199-12765]

UDC 665.637.6:621.892.261

EFFECT OF COOLING CONDITIONS ON BULK-MECHANICAL PROPERTIES OF LITHIUM GREASES

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 2, Feb 85 pp 17-20

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[Abstract] A study was made of the effects of the cooling rate on the bulk-mechanical properties of lithium greases as a function of the content of synthetic oils in the dispersion medium. Two commercial grade petroleum base oils (MS-20 and S-220) and two synthetic oils (poly-alpha-olefin M9-S and dioctylsebacinate DOS) were used. The greases were made by adding 10% air-dried LiSt to the oil followed by heating to 210°C and then cooling at 1°-2°C/min. (slow), 40°C/min. (rapid) or subjecting it to isothermal crystallization at 130°C. The results indicate that greases containing 5% DOS and 95% S-220 have optimum bulk-mechanical and heat resistant properties regardless of the cooling conditions. Figures 2; references 10: 6 Russian, 4 Western. [199-12765]

UDC 620.193.7:621.892

EFFECTS OF OILS AND ADDITIVES ON FRETTING-CORROSION OF STEEL

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 2, Feb 85 pp 22-25

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[Abstract] While it is known that by adding lubricating oils to the contact area of metals bulk wear is reduced many times, but the intensity of corrosion is increased greatly as compared with dry friction. To evaluate the effects of lubricants and additives on the fretting corrosion of steel, a special device was built consisting of a spring-loaded vibrator in which a steel ball is subjected to friction against the flat surface of a roller bearing under controlled amplitude of vibration and load. Fretting corrosion was observed through a metallographic microscope. Various mineral and synthetic oils and additives were tested and their effects on fretting corrosion were shown to depend on such factors as the capability of the oil to penetrate the friction area and remain there; the ability of the additive to form strong protective films; and the effects of the oils and additives on chemical and electrochemical corrosion processes under dynamic conditions. Optimum results were obtained with medium viscosity mineral oils and dioctylsebacinate, and phosphorus-containing additives. Figures 2; references 9: 3 Russian, 6 Western.

[199-12765]

UDC 621.313.37+621.89

EFFECTIVENESS OF LUBRICATING ACTIVITY OF SULFUR-, PHOSPHORUS- AND
NITROGEN-CONTAINING POLYMETHACRYLATES

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 2, Feb 85 pp 25-26

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[Abstract] A study was made of the antiwear and antiscuffing properties of alkylmethacrylate and diethylaminoethylmethacrylate copolymers modified with dithiophosphoric acids of various structures. The results show that modification of nitrogen-containing copolymer additives such as polymethacrylates with heteroorganic acids broadens their functional activity, the diameter of wear spots being almost half that of oils without additives. References 3 (Russian).

[199-12765]

UDC 665.767:667.5.033.37

POLYBUTENEAROMATIC COMPOUNDS AS THICKENERS FOR MINERAL AND SYNTHETIC OILS

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 2, Feb 85
pp 27-28

PROKOF'YEV, K. V., ALEKSEYEVA, L. P., MARKOVA, L. D., LOBANOVA, G. N. and SANGALOV, Yu. A., All-Union Scientific-Research Institute of the Oil Industry; Institute of Chemistry Bashkir Branch, USSR Academy of Sciences

[Abstract] A study was made of the viscosity-temperature properties, mechanical stability, thickening and lubricating capabilities of a polybutenearomatic compound - Octol-600M. The compound was prepared by polymerization of lower olefins followed by alkylation of aromatic hydrocarbons and compared with various known viscosity additives. The results show that Octol-600M has as great a thickening effect and the same resistance to mechanical destruction, viscosity index and lubricating capabilities as the other known additives. Octol-600M may therefore be recommended as a viscosity additive. Figures 2; references 2 (Russian).
[199-12765]

UDC 621.892.096.1:621.431.74-729.3

CLEANSING OIL IN INTERNAL COMBUSTION ENGINES

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 2, Feb 85 pp 28-30

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[Abstract] Full flow fine oil filters (FTOMp) in heavy duty diesel engines fail to provide both deep cleansing of motor oil from insoluble products and dependable protection of moving parts from mechanical impurities caused by abrasive wear. This failure has been overcome by using the new combined oil-cleansing complexes (KMOK) in conjunction with centrifuging. The effectiveness of KMOK was proved in operation on heavy duty marine diesel engines 4ChN22/24 and 6ChN18/22. The intensity of wear and other factors demonstrated the superiority of the KMOK over that of the FTOMp filter. Figures 2; references 3 (Russian).
[199-12765]

UDC 621.665

EFFECT OF gamma-RADIATION ON GREASE TsIATIM-221

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 2, Feb 85
pp 36-38

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[Abstract] A detailed study of the effects of ionizing radiation on TsIATIM-221 grease (polyethylenesiloxane thickened with a stearate soap and calcium acetate) shows that the grease first liquefies and then thickens. Dosages of gamma-radiation greater than 200 Mrad harden the grease and cause it to puff up as a result of abundant gas formation. Infra-red spectrum analysis of the solid phase shows the presence of fatty acid salts. The most significant changes observed at high dosages (up to 500 Mrad) are due to the low radiation resistance of the dispersion medium. Dispersal of thickener fibers at low dosages may be due to rupture of certain bonds in the crystal formation of the soaps. Figures 2; references 4 (Russian). [199-12765]

UDC 543.544(088.8)

CHROMATOGRAPHIC METHOD FOR DETERMINING AROMATIC HYDROCARBONS IN AVIATION GASOLINES

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 2, Feb 85
pp 38-39

KRASNAYA, L. V., POSTNIKOVA, N. G. and ZRELOV, V. N.

[Abstract] The presently used sulfonation method (GOST 6994-74) to determine the aromatic hydrocarbon content in aviation gasolines does not give reliable results because part of the paraffinic and naphthenic hydrocarbons pass over to the acid layer and some of them become oxidized and sulfonated. In the present work a chromatographic procedure was developed and attested in three laboratories in accordance with regulation RD-50-262-81. The method provides reliable determination of the aromatic hydrocarbon content in aviation gasolines. Figures 1; references 5 (Russian). [199-12765]

UDC 543.544.45:621.982

USE OF GRAPHITIZED THERMAL BLACK FOR GAS CHROMATOGRAPHIC SEPARATION OF SYNTHETIC OILS

Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 2, Feb 85
pp 39-40

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[Abstract] It is impossible to determine the composition of synthetic lubricating oils from the composition of the reagents they were synthesized from. In the present work a gas adsorption chromatographic method was developed that employs a graphitized thermal black modified with a single layer of apezone L or lubricants VNII HP-300A by which it is possible to separate synthetic lubricating oils. Figures 4; references 7: 5 Russian, 2 Western.

[199-12765]

UDC 665.753.2:542.943:541.127

KINETIC PATTERNS OF T-6 FUEL OXIDATION

Moscow NEFTEKHIMIYA in Russian Vol 25, No 1, Jan-Feb 85
(manuscript received 28 Oct 83) pp 78-83

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[Abstract] Fossil fuels often contain natural inhibitors, hydroperoxides and traces of metals, whose oxidation is worthy of special study. The present article reports on research and comparison of kinetic patterns and oxidation mechanisms found in two separate manufacturers' T-6 fuel. The fuels were alike in most respects, but fuel #1 had lesser thermooxidational stability at 150°C and had no sulfur impurities, while fuel #2 had 0.008% sulfur compounds (by weight). Oxidation kinetics were studied under auto-oxidation and induced oxidation regimens. Results showed autoacceleration with periods of induction related to natural inhibitors that remained after hydrogenization. At high rates of initiation, oxidation rates were constant, attesting to the development of natural inhibition of the process. Variations in the induction period for concentrations of natural inhibitors and the autocatalytic segment of the kinetic curves of the two fuels affected the braking of oxidation in the tests. Products of oxidation such as ketones and acids affected the process of degenerative branching of the two fuel variants. As the oxidation process deepened, the fuel with the lesser thermooxidation stability produced more free radicals than hydroperoxides. Figures 5; references 3 (Russian).

[206-12131]

UDC 665.753.2:542.943.8:541.127:547.873

MECHANISM OF ANTIOXIDATIONAL ACTION OF TRIAZINE DERIVATIVES IN HYDROCARBON FUEL

Moscow NEFTEKHIMIYA in Russian Vol 25, No 1, Jan-Feb 85
(manuscript received 19 Dec 83) pp 90-95

GOLUBEVA, I. A., VISHNYAKOVA, T. P., KHARITONOV, V. V., MALOVA, O. V. and SHUBINA, O. V., Moscow Institute of Petrochemical and Gas Production imeni I. M. Gubkin

[Abstract] Aviation fuels demand higher refinement and antioxidational stability. Derivatives of sym-triazine with phenol fragments show promise as additives, but they have received little attention. The present article reports on synthesis and study of sym-triazine derivatives with 1 to 6 fragments of spatially restricted phenols connected to the phenol ring through various nitrogen-, oxygen- or sulfur-containing groups. The triazine with 6 such fragments at a nitrogen group had the highest effectiveness. It, along with one with 3 fragments attached to sulfur, were the focus of the study of T-6 fuel, with boiling point of 200-315°C, density of 0.840 g/cm³, and ca. 10% aromatic fractions. A bubbling oxidation device was used to obtain fuel samples with varying content of hydroperoxides. Comparison of test results showed that the S-3 triazine was more active in initiating oxidation. In the presence of N-6 triazine, the oxidation rate did not depend significantly on hydroperoxide concentration. The high effectiveness of the compounds studied is connected to their rapid reaction with peroxide radicals and low reaction rate with the medium that inhibited conversion. Figures 5; references 5 (Russian).
[206-12131]

UDC 665.61.033.52:543.422

ORGANIC SULFUR COMPOUNDS AND HYDROCARBONS OF 65-200°C DISTILLATE OF USINO CRUDE OIL

Moscow NEFTEKHIMIYA in Russian Vol 25, No 1, Jan-Feb 85
(manuscript received 6 Jun 83) pp 115-121

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[Abstract] The Usino deposit of the Timano-Pechora Province, Komi ASSR, contains predominantly thiophene compounds, but there are clear differences between fractions at 200-350 and those at 360-410°C boiling points. The present article reports on study of organic sulfur compounds and hydrocarbons in the 65-200°C fractions of Usino crude oil. Results indicated that sulfur content was 0.6%, of which 65% was in the form of sulfides. Infrared

and mass-spectra showed no absorption of aromatic compounds in these sulfides. The nature of the sulfide compounds is discussed. They included 0.59% saturated sulfides, of which 0.43% were alkylthiamonocycloalkanes, and 0.09% alkylthiopenes. Basic hydrocarbons were naphthenes (58.6%), paraffins (37.4%) and aromatic compounds (5.0%). References 13: 11 Russian, 2 Western.
[206-12131]

UDC 665.666.62

NITROGEN BASES OF 180-360 C FRACTION OF WESTERN SIBERIAN CRUDE OIL

Moscow NEFTEKHIMIYA in Russian Vol 25, No 1, Jan-Feb 85
(manuscript received 29 Nov 83) pp 122-126

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[Abstract] Along with other heteroatomic compounds, nitrogen bases form the heavy high-molecular weight part of crude oil. The present article reports on study of the structural and group composition of nitrogen bases of the 180-360°C fraction from Western Siberian crude oil of the Omsk Scientific Production Association. Composition was studied by fragmentation and molecular mass spectrometry, infrared and ultraviolet spectroscopy. The maximum molecular weight distribution was found in compounds of 16-19 atoms of carbon. The predominant compounds were alkyl-quinolines, cyclo- and dicycloalkyl quinolines, 5,6- and 7,8-benzoquinolines, and cyclo-benzoquinolines, among numerous other compounds. Further study by direct programmed introduction of samples into the ion source of a mass spectrometer is recommended. Figures 3; references 14: 11 Russian, 3 Western.
[206-12131]

UDC 547.759.32:665.61.033.53

CARBAZOLS OF SURAKHAN CRUDE OIL

Moscow NEFTEKHIMIYA in Russian Vol 25, No 1, Jan-Feb 85
(manuscript received 13 Jan 84) pp 127-131

FROLOV, Ye. B., BANYUKOVA, N. A., MARKOVA, Ye. I., MIKAYA, A. I. and SANIN, P. I., Institute of Petrochemical Synthesis imeni A. V. Topchiyev, USSR Academy of Sciences

[Abstract] Nitrogen compounds in crude oil are traditionally divided into bases that can be extracted by mineral acids, and nitrogen-containing neutral compounds. Difficulties in isolating carbazols and purifying them of impurities have hindered their analysis by chromato-mass-spectrometry. The present article describes production of carbazol concentrates from

Surakhan crude oil and their spectral analysis. The precise Baku drill hole and other parameters of the oil are given. The heavy acid extracts, at above 350°C, were analyzed by thin-coat and column adsorption chromatography on silica gel, as well as by chromato-mass-spectrometry, and these methods showed the content of carbazol, C₁-C₆-alkylcarbazols, C₁-C₄-alkylbenzocarbazols and C₁-C₂-alkylphenylcarbazols. Figures 3; references 14: 5 Russian, 9 Western.
[206-12131]

UDC 665.612.:665.64/65

STUDY OF PYROLYSIS OF PARAFFINACEOUS GASEOUS CONDENSATE

Moscow NEFTEKHIMIYA in Russian Vol 25, No 1, Jan-Feb 85
(manuscript received 11 Aug 83) pp 132-137

SERGIYENKO, S. R., KHANKULIYEV, K. and KUL'DZHAYEV, B. A., Chemical Institute, TSSR Academy of Sciences

[Abstract] The lower olefins, particularly ethylene and propylene, are used widely in industry, but price increases in the 1970s have reoriented production of such products as ethylene from natural gas to petroleum. The present article reports on study of a gas condensate lacking sulfur compounds with high paraffin and low aromatic and naphthene components. The condensate was produced by pyrolysis at 800-850°C for 0.3-1.5 seconds, using an uncracked condensate from the Shatlyk deposit. The light (60-180°C) fraction of the condensate was found to have 12% aromatic and 10% naphthene hydrocarbons; these were found especially in the lightest fractions (60-95 and 95-120°C). The optimum temperature for pyrolysis was determined to be 825-850°C, where the highest yields of ethylene were obtained. The gas condensate was better than propane or any petroleum fraction for producing ethylene and other olefins, and was surpassed only by ethane and standard butane. Maximum production of C₃-C₄ and C₂-C₄ olefins was reached at 0.3-0.5 seconds of reaction, while best ethylene yields were at 0.7-1.3 seconds, indicating that much of the ethylene formed in secondary conversions of C₃-C₄ olefins. References 6: 1 Russian, 5 Western.
[206-12131]

PHARMACOLOGY AND TOXICOLOGY

UDC 615.462:615.451.35/0,3:617

DOUBLE ADHESIVE POLYMERIC FILMS WITH HEMOSTATIC ACTIVITY

Yerevan ARMYANSKIY KHIMICHESKIY ZHURNAL in Russian Vol 37, No 10, Oct 84
(manuscript received 12 Jun 84) pp 657-662

CHUKHADZHYAN, G. A., SARKISYAN, F. A., KARAPETYAN, S. A. and
GABRIYELYAN, E. S., Yerevan State University

[Abstract] Adhesive films consisting of double polymeric films [Chukhadzhyan, G. A. et al., Arm. Khim. Zh., 36: 255, 1983] were used for the preparation of biocompatible films possessing hemostatic activity. The hemostatic component consisted of $\text{FeCl}_3:\text{CaCl}_2 = 9:1$ salt mixture in ϵ -aminocaproic acid polymer, with which the outer hydrophobic layer was impregnated. The films were used successfully in insuring hemostasis when applied to 1 cm-deep cuts in male rats, with the hydrophilic layer of the double membrane film assuring tissue adhesion. Such hemostatic films appear to have considerable potential in the management of small internal and external wounds. References 15: 7 Russian, 8 Western.
[124-12172]

UDC [615.462:615.451.35].03:617

BILAYER POLYMERIC FILMS WITH EMBEDDED ANTIBIOTICS

Yerevan ARMYANSKIY KHIMICHESKIY ZHURNAL in Russian Vol 37, No 9, Sep 84
(manuscript received 15 Mar 84) pp 586-590

CHUKHADZHYAN, G. A., SARKISYAN, F. A., KARAPETYAN, S. A., KOCHARYAN, K. M.,
MASHINYAN, A. Kh., GERVORKYAN, G. A. and GABRIYELYAN, E. S., Yerevan Medical
Institute

[Abstract] Description is provided of the preparation of a variety of bilayer polymeric films containing imbedded antibiotics and preservatives. Intended for application in the treatment of wounds, such films can be expected to exhibit considerable antibacterial effectiveness. The hydrophilic layer with the imbedded antibiotic should also possess high affinity for the moist

tissue surface, while the hydrophobic layer provides protection from the environment and shows selective gas permeability. Studies with films sterilized by gamma- or UV-irradiation demonstrated that films with 1-5% lincomycin, gentamycin, ceporin, tetracycline, streptomycin, etc., retained antibiotic activity for over a year. References 13: 6 Russian, 7 Western. [123-12172]

POLYMERS AND POLYMERIZATION

POLYMER COMPOSITES AND THEIR PROSPECTIVE ADVANCES

Moscow KRASNAYA ZVEZDA in Russian 8 Dec 84 pp 3, 4

[Article by Yuriy Sergeyevich Lipatov, director of Institute of Chemistry and Macromolecular Compounds, Ukrainian Academy of Sciences]

[Abstract] The article is a lengthy general survey of the development of polymer composite materials. The author notes performance characteristics of composites with such reinforcing fillers as carbon fibers and boron filaments. Applications of composites and prospects for broadening them are mentioned. The author notes that his institute has developed composites with binders that can be used to patch damaged surfaces of ships in any atmospheric conditions, including surfaces that are covered with petroleum products, and also under water.

Looking ahead, the author says that by 1986 the country's production of plastics and synthetic resins will be between 6 and 6.5 million tons annually. More than 300 types of new plastics will be introduced, and there will be over 2,500 new plastic products for automobiles, electrical machinery, and radio and electrical equipment. Production of chemical fibers and filaments will reach 1.6 million tons. Among advances the author sees around the year 2000, he says there will be new materials which will be non-combustible, whose performance will not be affected by high temperatures, and which will possess rubberlike elasticity at temperatures close to absolute zero. He says it will not be long until a film is developed on which it will be possible to store millions of bits of information in one square centimeter of its area. Also, he says it is possible to impart such properties to synthetic polymers that they can become substitutes for natural food products. Regarding the production technology of polymer materials, the author predicts that as petroleum and natural gas reserves become depleted, man will learn to obtain polymer materials from inorganic raw materials.

FTD/SNAP
CSO: 1841/137

POLYMER COMPOSITES FOR INDUSTRIAL APPLICATIONS

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 9 Jan 85 p 2

[Article by S. Shysungin, TASS correspondent, Riga]

[Text] Experimental Plant for Hydrometric Instruments has begun to use fiberglass to produce cases for measuring devices to be submerged in the sea. This has made it possible to conserve expensive titanium. Research has shown that the new material withstands pressure to 650 atmospheres and can protect equipment even at a depth of 4 km.

This is only one development by scientists and industry specialists, whose efforts have been combined by the republic's scientific-technical program for introducing polymer composite materials.

"Twenty enterprises, organizations, and scientific institutions have been brought together to realize this program," said L. Irgens, head of the laboratory of the Institute for Polymer Mechanics of the Latvian Academy of Sciences. "We can judge the effect of cooperation between science and industry by such examples."

There is a great deal of interest in "Ripor" foam plastic, an outstanding thermal insulator. This material, created by Latvian scientists, is easy to spray on any surface. It can be conveniently used to insulate vegetable warehouses or to cover openings in large-panel structures. Builders value the features of exceptional polyethylene strips and bands which make it possible to quickly and reliably join pipes. These substitutes for metal couplings, pretreated with gamma rays, form tight hermetic joints when heated.

Ship repair workers are taking advantage of another innovation. Before, ship decks damaged by corrosion had to be repaired with welded-on patches, but now mastic made of polyester resins is being used. This saves tens of thousands of rubles.

12809
CSO: 1841/138

UDC 541.64:546.212

GRAFT COPOLYMERIZATION OF ACRYLIC ACID TO OZONIZED POLYVINYL ACETATE

Yerevan ARMYANSKIY KHMICHESKIY ZHURNAL in Russian Vol 37, No 10, Oct 84
(manuscript received 31 Jan 83) pp 612-615

YEGOYAN, R. V., GRIGORYAN, V. V., GINOSYAN, S. M. and BEYLERYAN, N. M.,
Yerevan State University

[Abstract] The kinetics of graft copolymerization of acrylic acid and methacrylic acid to ozone-treated polyvinyl acetate were studied in methanol and water-methanol solvents. The presence of water in the system enhanced the rate of polymerization more than 3-fold, with the energies of activation under various conditions in the 68.75 to 83.3 kJ/mole range. Graft copolymers were also formed with unoxidized polyvinyl acetate via matrix polymerization mechanisms. The viscosity of the acrylic acid-polyvinyl acetate copolymers was markedly greater than for the polyvinyl acetate or the methacrylic acid copolymers. Figures 3; references 3 (Russian).
124-12172]

UDC 531.30+542.952+678.744+678.046.3

FILLER EFFECTS ON VINYL ACETATE POLYMERIZATION KINETICS

Yerevan ARMYANSKIY KHMICHESKIY ZHURNAL in Russian Vol 37, No 10, Oct 84
(manuscript received 30 Mar 84) pp 649-653

POKRIKYAN, E. V., AYRAPETYAN, S. M., GERVORKYAN, S. B., AKOPYAN, L. A. and MATSOYAN, S. G., Institute of Organic Chemistry, Armenian SSR Academy of Sciences, Yerevan

[Abstract] Filler effects on vinyl acetate polymerization were studied in a system employing potassium persulfate initiation and chlorosilane-treated perlite as the filler, in the presence of a protective colloid (polyvinyl alcohol) under conditions optimal for polymerization. Evaluation of the polymerization kinetics demonstrated that the filler had no essential effect on the reaction. In the absence of the filler the order of the reaction with

respect to vinyl acetate, potassium persulfate and polyvinyl alcohol was, respectively, 0.37, 0.51 and 0.22. In the presence of the filler the first two values remained unaltered, but the order with respect to polyvinyl alcohol was decreased to 0.17, a phenomenon which was ascribed to the adsorption of the perlite to the monomer and diminished role of the emulsifying agent. Figures 5; references 14: 11 Russian, 3 Western.
[124-12172]

UDC 541.127+547.362

SOLVENT EFFECTS ON RADICAL COPOLYMERIZATION OF DIMETHYLAMINOETHYL METHACRYLATE AND VINYL ACETATE

Yerevan ARMYANSKIY KHMICHESKIY ZHURNAL in Russian Vol 37, No 9, Sep 84
(manuscript received 14 Oct 83) pp 543-547

YEGOYAN, R. V., GRIGORYAN, V. V., SOGOMONYAN, V. A. and BEYLERYAN, N. M.,
Yerevan State University

[Abstract] Solvent effects on the copolymerization of dimethylaminoethyl methacrylate with vinyl acetate were studied by comparison with the reaction process in methanol, methanol + water, and methanol + water + KCl systems. In the methanol + water system the resultant copolymer was enriched in the dimethylaminoethyl methacrylate monomers over the polymers obtained in methanol in reactions carried out at 60°C. Inclusion of KCl into the methanol + water system was seen to inhibit electrostatic effects and promoted alternating succession of the two monomeric moieties in the copolymer. In addition, the presence of water enhanced cross-linking and resulted in polymers with a higher MW than obtained in the methanol solvent, while viscosity determinations showed that the presence of KCl favored the formation of polymers with a more compact structure. Figures 2; references 5 (Russian).
[123-12172]

UDC 541.127+678.744.422

BENZOYL PEROXIDE INITIATED POLYMERIZATION OF ACRYLONITRILE IN DIMETHYLFORMAMIDE

Yerevan ARMYANSKIY KHMICHESKIY ZHURNAL in Russian Vol 37, No 9, Sep 84
(manuscript received 4 Jul 83) pp 547-552

SOGOMONYAN, B. M. and SIMONYAN, G. S., Yerevan State University

[Abstract] Kinetic studies were conducted on the polymerization of acrylonitrile (AN) in dimethylformamide, which demonstrated that in reactions initiated by benzoyl peroxide (BP) the rate expression follows the equation $W_{bp} = K_{eff}[BP]^{1/2}[AN]^n$, where $n = 1.0-1.5$. At the lowest BP concentrations,

the order of the reaction with respect to AN was equal to unity, whereas at high BP concentrations it increases to 1.5. Thermodynamic determinations yielded values of 29.3-30.0 kcal/mole for the energy of activation for polymerization, and 19.1-19.8 kcal/mole for the energy of activation of initiation. Figures 2; references 4 (Russian).
[123-12172]

UDC 678.13+547.538.141+547.724

COPOLYMERIZATION OF 5-NITROFURFURAL AND STYRENE

Yerevan ARMYANSKIY KHIMICHESKIY ZHURNAL in Russian Vol 37, No 9, Sep 84
(manuscript received 21 Jun 83) pp 578-585

DURGARYAN, A. A. and BEGINYAN, R. M., Yerevan State University

[Abstract] The nature of copolymerization of 5-nitrofurfural (NF) with styrene was studied at -25.0, 0 and +25°C in chlorobenzene, with the reaction initiated by $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$. NF was shown, on the basis of IR and ESR data, to react with styrene via its aldehyde group. The last reaction in the copolymerization involves replacement of the terminal NF by a nitrofuran ring. Consequently, at higher temperatures, the mole fraction of NF in the copolymer decreases even as the greater fraction of NF in the original mixture is increased from 0.15 to 0.95. Determination of the copolymerization constant at -25°C yielded $r_1 = 0.87$ and $C_{22} = 0.46$, at 0°C $r_1 = 2.3$ and $C_{22} = 0.26$, and at 25°C $r_1 = 3.15$ and $C_{22} = 0.44$. Comparison with published data on such constants in the literature shows that NF is far less active than other aldehydes, and that the energy of activation of the final substitution reaction is greater than that of the addition reaction. In copolymerization with alpha-methylstyrene, substitution did not take place. References 11: 8 Russian, 3 Western.
[123-12172]

UDC 541.64

POLYMERIZATION OF MONOMERIC QUATERNARY AMMONIUM SALT OF N,N-DIMETHYL-AMINOETHYL METHACRYLATE WITH IODOPROPANE

Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 6, Nov-Dec 84
(manuscript received 16 Jan 84) pp 28-31

MAKSUMOVA, A. S., ISMAILOV, I. I. and DZHALILOV, A. T., Tashkent Order of Peoples' Friendship Polytechnic Institute imeni Abu Raykhan Beruni

[Abstract] IR, PMR and UV spectroscopies and standard kinetic techniques were used in monitoring the polymerization of the monomeric quaternary ammonium salt of N,N-dimethylaminoethyl methacrylate (I) with iodopropane,

initiated with 2,2-dinitryl-azobisisobutyric acid, in dimethyl sulfoxide at 293-323°K. The order of the polymerization with respect to the initiating agent was 0.5, and 1.54 with respect to I. The energy of activation of the reaction calculated from changes in rate constants with an increase in the reaction temperature was 10.1 kcal/mole, which was considerably lower than the activation energies for radical polymerization usually reported (25-30 kcal/mole). The novel complex was characterized by unique spectral characteristics, and demonstrated that redox mechanisms can be utilized for such synthesis at relatively low temperatures. Figures 3; references 8: 6 Russian, 2 Western.
[130-12172]

UDC 547.563+547.222+547.51

ALKYLATION OF PHENOL AND ANISOLE BY SUBSTITUTED BENZYL CHLORIDE IN PRESENCE OF LOW CATALYST CONCENTRATIONS

Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 6, Nov-Dec 84
(manuscript received 16 Jan 84) pp 31-34

ABDURASULEVA, A. R., TADZHITUKHAMEDOV, Kh. S. and AKHMEDOV, K. N., Tashkent Order of the Red Banner of Labor State University imeni V. I. Lenin

[Abstract] An analysis was conducted on the efficiency of different derivatives of benzyl chloride in the alkylation of phenol and anisole, the former at 140°C and the latter at 90°C. The activities of the substituted benzyl chlorides ranked as follows (data for Ar in ArCH₂Cl): 4-CH₃OC₆H₄>4-CH₃C₆H₄>

alpha-C₁₀H₇>2-CH₃C₆H₄>3-CH₃C₆H₄>C₆H₅>4-Cl C₆H₄>2-ClC₆H₄ 3-ClC₆H₄>4-NO₂C₆H₄.

The products were 2- and 4- (and in the case of 4-methoxybenzylation, also 3-) substituted benzyl phenols, enriched in the 2-isomer in the case of phenol alkylation. References 11: 8 Russian, 3 Western.
[130-12172]

UDC 541.64:547.538.241:546.77

MECHANISM OF PHENYLACETYLENE POLYMERIZATION CATALYZED BY Mo(V)/KAOLIN

Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 6, Nov-Dec 84
(manuscript received 17 May 84) pp 54-56

ARISLANOV, S. S., YUSUPBEKOV, A. Kh., POMOGAYLO, A. D. and ABDURASHIDOV, T. R.,
Tashkent Order of Peoples' Friendship Polytechnic Institute imeni Abu Raykhan
Beruni

[Abstract] Polymerization of phenylacetylene was carried out at 343°C on Mo(V)/kaolin catalyst to determine the effectiveness of the supported catalyst. Chromatographic analysis of the polymeric and oligomeric products led to definition of conditions favoring polymerization, with ESR indicating that polymerization is accompanied by reduction of Mo(V) to Mo(IV). The polymers ranged in MW from 21,000 to 25,000 with a $\bar{M}_w/\bar{M}_n$ ratio of 1.09 to 3.17. Polymerization involved either a coordination or a organometallic mechanism, with termination of the reaction due either to chain transfer to a monomeric unit or virtually complete reduction of Mo(V). Figures 1; references 6: 2 Russian, 4 Western.
[130-12172]

UDC 541.64:536.6:547.1'128

CALORIMETRIC STUDY OF 1,1,3,3,5,5-HEXAETHYLCYCLOTRISILOXANE, POLYDIETHYLSILOXANE AND POLYMERIZATION PROCESS OF 1,1,3,3,5,5-HEXAETHYLCYCLOTRISILOXANE AT 13-330K

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 26, No 12, Dec 84
(manuscript received 10 Mar 83) pp 2476-2482

LEBEDEV, B. V., KULAGINA, T. G., SVISTUNOV, V. S., PAPKOV, V. S. and ZHDANOV, A. A., Scientific-Research Institute of Chemistry at Gor'kiy State University imeni N. I. Lobachevskiy; Institute of Heteroorganic Compounds imeni A. N. Nesmeyanov, USSR Academy of Sciences

[Abstract] The heat capacities of 1,1,3,3,5,5-hexaethylcyclotrisiloxane and polydiethylsiloxane were determined at 13-330K in an adiabatic vacuum calorimeter within 0.2% error. Other thermodynamic properties and functions such as enthalpy and entropy were calculated for both the monomer and the polymer. The monomer exists in three crystal forms and the liquid state, while the polymer is part crystal and part liquid, the crystals being in two modifications. The upper limit of polymerization temperature was calculated to about 520K. Figures 2; references 21: 13 Russian, 8 Western.
[127-12765]

UDC 541.64:539.3

LOW TEMPERATURE RELATIONSHIP TO STRENGTH OF POLYIMIDE FIBERS

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 26, No 12, Dec 84
(manuscript received 11 Mar 83) pp 2483-2488

BRONNIKOV, S. V., VETTEGREN', V. I., KORZHAVIN, L. N. and FRENKEL', S. Ya.,
Institute of High Molecular Weight Compounds, USSR Academy of Sciences

[Abstract] Tensile strength as a function of temperature was studied for 14 oriented polyimide fibers of various structure within the temperature range 100-650K. While the coefficient of thermal expansion, α , is known to be independent of temperature within the classical range, and tensile strength decreases linearly with rising temperature, at low temperatures where $T < \text{effective Debye temperature}$, α decreases and as T approaches 0, α also approaches 0. It was established that at low temperatures $T < \text{Debye temperature}/3$, and the relationship of tensile strength to temperature is non-linear. This is apparently due to the change in α in this temperature range, as confirmed by spectroscopic observation. Figures 5; references 15: 14 Russian, 1 Western.
[127-12765]

UDC 541.64:542.952.66.022.32

POLYMERIZATION MODIFICATION OF FILLERS AND ITS EFFECT ON PROPERTIES OF FILLED POLYVINYL CHLORIDE

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 26, No 12, Dec 84
(manuscript received 14 Mar 83) pp 2489-2495

POPOV, V. A., GUZEYEV, V. V., ZVEREVA, Ye. A., GRISHIN, A. I., PALAYEVA, T. V.,
SAVEL'YEV, A. P. and POTEPALOVA, S. N.

[Abstract] Adding large amounts of filler to polyvinyl chloride worsens the physical-mechanical and working properties of this material. This may be offset to a considerable degree by polymerization filling. A study was made of the modification to inorganic fillers by graft radical (co)polymerization and its effect on the properties of the filled PVC. The grafting of the polymer to the surface of the filler is shown to have a significant effect on the physical-mechanical properties of the filled PVC composition. The size and composition of the polymer shells on the solid particles of the dispersed phase is shown to have an effect on the rheological, physical-mechanical and working properties of filled PVC. Figures 7; references 7 (Russian).
[127-12765]

UDC 541.64:539.2

STRUCTURE OF HIGH DENSITY POLYETHYLENE OBTAINED BY HYDROEXTRUSION IN SOLID STATE

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 26, No 12, Dec 84
(manuscript received 18 Apr 83) pp 2529-2533

KORCHAGIN, A. G., MARTYNOV, M. A. and TSYGANKOV, S. A., Okhtinskiy Scientific-Production Association "Plastopolimer"

[Abstract] Polymeric objects high in strength and elasticity may be produced by hydroextrusion in the solid state. A study was made of the structural changes in high density polyethylene obtained by solid state hydroextrusion at 393 and 353K and various degrees of die-stretching to clarify the effects of these parameters on the change in modulus of elasticity. Increased die-stretching is accompanied by a thinning out and joining of microfibrils until transverse axes are formed between alternate amorphous and crystalline layers and some fraction of the dense strands between them. The rise in modulus of elasticity with the degree of die-stretching is determined first by the increase in degree of molecule-crystallite orientation and crystallinity of the polymer, and second by the uniform distribution of mechanical load on all fibrils and intercrystalline strands. Figures 3; references 13: 6 Russian, 7 Western.
[127-12765]

UDC 541(24+64+14)

CHANGE IN MOLECULAR WEIGHT DISTRIBUTION OF PHOTSENSITIZED LOW DENSITY POLYETHYLENE UNDER CONDITIONS OF ATMOSPHERIC AGEING

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 26, No 12, Dec 84
(manuscript received 26 Apr 83) pp 2548-2552

BUDTOV, V. P., PONOMAREVA, Ye. L., KONDRASHKINA, N. I. and ZELENKOVA, T. N., Okhtinskiy Scientific-Production Association "Plastopolimer"

[Abstract] A study was made of the changes in molecular weight distribution and physical-mechanical and optical properties of low density polyethylene containing photosensitizers under moderately cold climatic conditions. A limited cross linking of macromolecules takes place during the induction period which varies, depending on whether the polyethylene sample was produced in a tubular reactor or in an autoclave. Molecular weight distribution of the polymers changes in accordance with the laws of statistical degradation. Figures 4; references 10: 9 Russian, 1 Western.
[127-12765]

UDC 541.64:66.022.32

MECHANISM OF MODIFYING ACTION OF OLIGOMERS IN FILLED POLYETHYLENE COMPOSITIONS

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 26, No 12, Dec 84
(manuscript received 5 May 83) pp 2553-2556

SKRIPACHEV, V. I., KUZNETSOV, V. I. and IVANCHEV, S. S., Okhtinskiy
Scientific-Production Association "Plastpolimer"

[Abstract] The properties of polymers can be altered by using fillers, although the organic polymer, especially polyolefins, is often poorly compatible with the inorganic filler. One way to overcome this is by using a modifying additive which forms an intermediate layer between the polymer phase and the filler. In the present work a study was made of the effect of oligomeric compounds having terminal or chain functional groups on the properties of filled polyethylene. The results indicate that the oligomers are not only physically bound to the filler, but also react chemically with the functional groups located on its surface. Mechanisms for the formation of a transitional zone in the filled polyethylene are proposed. Figures 2; references 7 (Russian).

[127-12765]

UDC 541.64:537.226

EFFECT OF CHEMICAL ISOMERISM OF GLYCIDIC ESTERS OF DIPHENOL AND AROMATIC DICARBOXYLIC ACIDS ON DIELECTRIC RELAXATION IN EPOXY POLYMERS

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 26, No 12, Dec 84
(manuscript received 10 May 83) pp 2557-2561

YURECHKO, N. A., YEVTUSHENKO, G. T., YERMILOVA, Yu. Ye., SHOLOGON, I. M.
and ROZENBERG, B. A., Ukrainian Scientific-Research Institute of Plastics

[Abstract] The chemical structure of a polymer chiefly determines the molecular mobility of its chain and the nature and intensity of relaxation processes taking place therein. It may be assumed then that the position of the functional groups in the aromatic nucleus of phenylenediglycidic esters, and the type of ester group (simple or complex) should have a major effect on molecular mobility. In the present work molecular mobility in epoxy polymers was investigated by studying dielectric relaxation in diphenol glycidic esters (pyrocatechol, resorcinol and hydroquinone), and aromatic dicarboxylic acids (ortho-, iso- and terephthalic). Relaxation spectra of the polymers are presented and the alpha- and beta-transition parameters are calculated. Figures 3; references 8: 6 Russian, 2 Western.

[127-12765]

UDC 541.64:542.954:532.2

SYNTHESIS OF HIGH MOLECULAR LIQUID CRYSTAL POLYESTERS BY POLYCONDENSATION OF A MESOGENIC MONOMER

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 26, No 12, Dec 84
(manuscript received 13 May 83) pp 2570-2576

BILIBIN, A. Yu., TEN'KOVITSEV, A. V., PIRANER, O. N. and SKOROKHODOV, S. S.,
Institute of High Molecular Weight Compounds

[Abstract] A method for synthesizing high molecular weight alkylene-aromatic polyesters capable of forming liquid crystal melts is presented. It is based on two sequential systems of ester bonds in triad polymers. A mesogenic monomer is prepared in a first stage from which an entire series of various mesomorphic polymers can be obtained in a second stage. Terephthaloyl-bis-(4-oxybenzoic) acid served as the mesogenic monomer from which terephthaloyl-bis-(4-oxybenzoylchloride) was prepared for the first time. Polycondensation of the latter with various aliphatic and oxyaliphatic diols resulted in polymers having liquid crystal transition temperatures ranging from 40° to 360°. Polydecamethyleneterephthaloyl-bis-(4-oxybenzoate) was prepared by this method and its molecular weight - phase transition temperature characteristics determined. Figures 5; references 15: 7 Russian, 8 Western.
[127-12765]

UDC 541.64:539.199

STRUCTURE OF TERMINAL GROUPS IN POLYVINYLIDENE FLUORIDE OBTAINED WITH beta-OXYETHYL-ter-BUTYL PEROXIDE

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 26, No 12, Dec 84
(manuscript received 17 May 83) pp 2577-2581

MADORSKAYA, L. Ya., SAMOYLOV, V. M., OTRADINA, G. A., AGAPITOV, A. P.,
BUDTOV, V. P., MAKEYENKO, T. G., KHARCHEVA, Ye. Yu., LOGINOVA, N. N.,
Okhtinskiy Scientific-Production Association "Plastpolimer"

[Abstract] It was previously shown that the properties of hydrogen fluoride-containing polymers depend essentially on the structure of the terminal groups. Specifically, vinylidene fluoride homo- and copolymers prepared with organic peroxides such as beta-oxyethyl-ter-butyl peroxide have high resistance to heat. In the present work the structure and terminal group content were determined for a vinylidene fluoride copolymer containing 5-7 mole % tetrafluoroethylene. Radioactive methyl groups predominate in the polymer. The content of $(CH_3)_3CO-$ and $HOCH_2CH_2O-$ terminal groups comprised only 2 and 1%, respectively, of their total content in the polymer, which has 1.5 branchings per 100 monomer units. References 7: 5 Russian, 2 Western.
[127-12765]

UDC 541.64:547(1'128+241)

ACTION OF DIETHYLPHOSPHITE AND DIETHYLPHOSPHINE OXIDE ON POLYDIMETHYLVINYL-SILOXANES

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 26, No 12, Dec 84
(manuscript received 8 Jun 83) pp 2588-2592

ZHDANOV, A. A., KURASHEVA, N. A. and KUTEYNIKOVA, L. I., Institute of Heteroorganic Compounds imeni A. N. Nesmeyanov, USSR Academy of Sciences

[Abstract] Polysiloxanes containing phosphorus can resist heat, hydrolysis and air only if the phosphorus atom is linked to the silicon atom through a hydrocarbon bridge containing at least two methylene groups. A study of the action of diethylphosphite and diethylphosphine oxide on various polydimethylvinylsiloxanes in the presence of peroxide initiators and platinum catalysts at high temperatures shows that phosphorylation does not take place. Only in the presence of ultraviolet radiation is it possible to conduct partial phosphorylation of polydimethylvinylsiloxane with diethylphosphine oxide. References 8: 3 Russian, 5 Western.
[127-12765]

UDC 541(64+14):542.952

GRAFT POLYMERIZATION OF VINYL MONOMERS ON SURFACES OF SOLID INORGANIC MATERIALS, PHOTO-INITIATED WITH SYSTEM $R-CCl_3$ -CARBONYL OF TRANSITION METALS

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 26, No 12, Dec 84
(manuscript received 11 Jun 83) pp 2599-2603

ANDRIANOV, A. K., OLENIN, A. V., SAPRYGIN, O. N., GARINA, Ye. S., ZUBOV, V. P., KASHUTINA, E. A. and ZHDANOV, A. A., Moscow State University
imeni M. V. Lomonosov; Institute of Heteroorganic Compounds
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[Abstract] Most known methods for grafting polymers to the surfaces of inorganic fillers (to give modified fillers, pigments and highly filled composite materials) cannot be conducted under mild conditions. However, the optical clarity in the visible region of the spectrum of many heterogeneous reaction mixtures consisting of a dispersed filler and a monomer makes it possible to use photochemical initiation to conduct liquid phase graft polymerization on inorganic materials. In the present work silica gel and aerosil were modified with (methyldichlorosilyl)propyl trichloroacetate to give organo-silicas having grafted $R-CCl_3$ groups. By using $R-CCl_3-Mn_2(CO)_{10}$ as an initiating system, it is possible to conduct graft polymerization of methylmethacrylate and styrene in visible light. Reaction time, concentration of $Mn_2(CO)_{10}$ and CCl_3 groups as functions of yield, molecular weight and molecular weight distribution were studied. Figures 4; references 13: 8 Russian, 5 Western.
[127-12765]

UDC 541.64:539.2

RELAXATION PROPERTIES OF HEAT RESISTANT POLYMERS AT LOW TEMPERATURES

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 26, No 12, Dec 84
(manuscript received 13 Jun 83) pp 2604-2610

BANYAVICHYUS, R. B., MIGONENE, Z. B. and ASKADSKIY, A. A., Kaunas Polytechnic Institute imeni Antanas Sneckus; Institute of Heteroorganic Compounds imeni A. N. Nesmeyanov, USSR Academy of Sciences

[Abstract] Heat resistant polymers have been shown to have high resistance also to cryogenic temperatures (-270°), and therefore they appear promising for use as cold resistant structural materials. However, the mechanical behavior of these polymers is not well known. In the present work, stress relaxation and creep analysis were used to determine relaxation transitions in two aromatic polymers of different structures (polybenzoxazole, and polyoxydiazole). Both exhibited considerable deformation at low temperatures and both have high resistance to stress at low temperatures. Figures 8; references 10: 9 Russian, 1 Western.

[127-12765]

UDC 541(64+24)

MOLECULAR CHARACTERISTICS OF OLIGOMERS OBTAINED IN PRESENCE OF OXIDATIVE-REDUCTIVE SYSTEMS

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 27, No 1, Jan 85
(manuscript received 3 May 83) pp 36-40

MIN'KO, S. S., KUZAYEV, A. I., PUCHIN, V. A. and VORONOV, S. A., L'VOV Polytechnic Institute imeni Lenin Komsomol; Division of the Institute of Chemical Physics, USSR Academy of Sciences

[Abstract] The molecular characteristics of oligomers produced from 1,3-butadiene and styrene in the presence of various large organic hydroperoxides, benzoin and iron naphthenate were studied using gel permeation chromatography. The oligomers obtained had $\bar{M}_w/\bar{M}_n$ of 1.4 to 1.6, with an average functionality of 1.5 to 1.8. Changing the ratio of the redox system components permits regulation of oligomer molecular mass distribution. While the polydisperseness of the product was close to the theoretical value, the molecular weight and average functionality were less. This appears to be connected with chain transfer to the hydroperoxide. The nature of the hydroperoxide or the solvent did not affect oligomer molecular parameters. Figures 2; references 15: 14 Russian, 1 Western.

[157-12126]

UDC 541.64:547(313+256.2)

ALTERNATING COPOLYMERIZATION OF ISOPRENE WITH ETHYLENE USING $TiCl_4$ -ELECTRON DONATING COMPOUND - AlR_3 CATALYTIC SYSTEM

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 27, No 1, Jan 85
(manuscript received 3 May 83) pp 41-45

MYAGKOVA, L. A. and KROPACHEVA, Ye. N., All-Union Scientific Research
Institute of Synthetic Rubber imeni S. V. Lebedev

[Abstract] The alternating copolymerization of isoprene and ethylene was studied using as the catalytic system $TiCl_4$ -acetophenone-tris-isopropyl aluminum. At an Al to Ti ratio of one, only isoprene homopolymers formed, with the 1,4-trans structure predominating. Copolymerization began at Al:Ti greater than three. On increasing the ratio, reaction rate, number of C_2-C_5 diads and 3,4-chain content increased, while viscosity and polyethylene yield decreased. At Al:Ti of 15, increasing the relative amount of ethylene in the reaction mixture accelerated the reaction, while at Al:Ti of 5, more ethylene retarded the reaction. The C_2-C_5 diad content and polymer microstructure were unchanged. Increasing $TiCl_4$ concentration from 0.0021 to 0.0074 mole/L increased reaction rate and polyethylene yield while decreasing polymer viscosity. Increasing the temperature from 30° to 10° increased reaction rate while decreasing polyethylene yield and polymer viscosity. Substituting benzophenone for acetophenone lowered reaction rate, using acetone further retarded the reaction. These substitutions decreased C_2C_5 diad and 3,4-chain content. In the absence of ketone electron donor, reaction rate was markedly decreased. The results indicate that copolymer structure is strongly dependent on reaction conditions. References 5: 4 Russian, 1 Western. [157-12126]

UDC 541(64+183.12)

EFFECT OF PROTEIN AMINO ACID COMPOSITION ON ITS BINDING TO CARBOXYLIC CATIONITES

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 27, No 1, Jan 85
(manuscript received 3 May 83) pp 46-50

SHATAYEVA, L. K., KREYER, V. G., POKROVSKAYA, S. S., RADZYAVICHYUS, K. I.
and SAMSONOV, G. V., Institute of High Molecular Weight Compounds, USSR
Academy of Sciences

[Abstract] The binding of pepsin, insulin, chymotrypsin-A-lysozyme, poly-endo-galacturonase and alkaline protease from *Str. spheroides* to carboxylic cation exchangers was studied using resins prepared from acrylic or methacrylic acids. The dependence of protein adsorption on pH of the equilibrium solution was similar in form for all the systems studied, but for the basic proteins, chymotrypsin and protease, the maximum was shifted in the

acid direction. This indicates that polar interactions play a predominant role in the process. Potentiometric titration of the protein-polymer complexes showed that the nature of the adsorbed protein strongly affects the acid composition of the polyelectrolyte, even though the number of titratable groups on the protein is small. Protein adsorption increased the exchange capacity of the resin. The binding of the basic protein protease to the methacrylic acid polymer increased the adsorptive properties of the resin towards the other proteins. It appears that ion-ion interactions between the carboxylic acid groups of the resin and the protein amino groups increases the ability of the undissociated carboxylic group to interact with other macromolecules. This may cause decreased selectivity of adsorption observed when a complex protein mixture, containing zwitterions and basic macromolecules, is passed over this type of resin.

Figures 3; references 14: 9 Russian, 5 Western.
[157-12126]

UDC 541.64:539.2

EFFECT OF POLYMER-POLYMER COMPOSITE PHASE STRUCTURE FORMATION METHOD ON THEIR RELAXATION PROPERTIES

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 27, No 1, Jan 85
(manuscript received 5 May 83) pp 51-57

LISHANSKIY, I. S., POMERANTSEV, V. I., YEVSEYEVA, T. G., KRASNER, L. V., SHEVELEV, V. A., AFANAS'YEVA, N. V. and CHICHAGOVA, Ye. R., Institute of High Molecular Weight Compounds, USSR Academy of Sciences

[Abstract] A study was conducted on the effect of sequential mixed polymerization of ethylacrylate and butylmethacrylate on relaxational properties, in comparison to polymers obtained by mixed latex polymerization, using NMR, and dielectric and mechanical loss. The temperature dependence of dielectric loss angle tangent was characterized by two maxima, indicating predominant segregation. Changes in relaxation parameters indicated that mixed areas were also formed. The free nuclear induction signal of the glass-like and rubber-like components were described as the superposition of two exponential terms. The greatest changes in relaxational properties, connected with interphase interactions, were observed for components which polymerize at the second stage at low concentrations. A temperature shift in the relaxation region of polyethylacrylate was accompanied by an increase in activation energy, caused by interphase interactions. Four possible composite structures were represented by the composites formed, including latex particles in a mixed matrix, mixed particles in a latex matrix, mixed particles with coalesced latex and inclusion of small mixed areas in the latex matrix. Figures 7; references 11: 9 Russian, 2 Western.

[157-12126]

UDC 541.64:539.2

EFFECT OF HYDROEXTRUSION PARAMETERS FOR LOW DENSITY POLYETHYLENE ON ITS
PROPERTIES AND STRUCTURE

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 27, No 1, Jan 85
(manuscript received 25 May 83) pp 99-104

TSYGANKOV, S. A., DEMENCHUK, N. P., MYASNIKOV, G. D., KORCHAGIN, A. G.,
and MARTYNOV, M. A., Okhtinskiy Scientific Research Association "Plastpolymer"

[Abstract] The hydrostatic extrusion of low density polyethylene was studied in detail. The degree of extrusion reduction had a strong nonlinear effect on the pressure required for extrusion. Increasing the temperature reduced the pressure required. Poor extrudate quality was observed at temperatures above 363°K. Exit angles of 30° gave more uniformly distributed plastic deformation, compared to angles of 60° and 90°, while pressure requirement was lowest at 60°. Increasing the pressure led to more rapid extrusion with poorer surface properties and more deformation. The best extrudates were produced at 1.7 mm/sec or less. Transparency increased with extrusion ratio, due to greater structural homogeneity. Swelling depended on temperature and degree of reduction. Elasticity and durability increased with extrusion ratio, up to a value around six, and decreased with increasing temperature. Very little change in density or melting point was observed. Wide-angle X-ray diffraction demonstrated that molecular-crystalline orientation was increased at higher extrusion ratios. Figures 5; references 9: 7 Russian, 2 Western.

[157-12126]

UDC 541.64:547.458.82

MECHANISM OF LOWERING COMBUSTIBILITY FOR VISCOSE-FIBER REINFORCED COMPOSITES

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 27, No 1, Jan 85
(manuscript received 26 May 83) pp 105-113

VILKOVA, S. A., KOSTIN, K. B., GUSEV, A. P. and KOGERMAN, A. R., Saratov
Polytechnic Institute

[Abstract] A study was conducted of the processes which occur at the surface of viscose-fiber reinforced polymers during burning and of the mechanism of combustibility reduction. Epoxide resin, strengthened with polyethylene-polyamide and reinforced with viscose fibers which had been treated with diamidomethylphosphonate-urea, was used. The structure of the coke formed during burning was studied with "Superprobe JXA7B" electronic microprobe X-ray spectral analysis and elemental analysis. Derivatography of thermo-oxidative destruction and multistage pyrolysis gas chromatography were also used. The phosphonate was found to be evenly distributed in the fibers of the composite, but not in the binder. In untreated composites, slow rates of combustion propagation led to melting of the binder so that, after

extinguishing, the carbonized area was pitted, due to diffusion of gaseous products. At oxygen levels of 40% friable, sooty blisters formed after combustion, while at 50% oxygen a uniform, light coke layer containing increased oxygen was seen. Greater unevenness was seen in the surface of composites reinforced with untreated viscose. In composites treated with flameproofed viscose, nitrogen and phosphorous were found in the surface coke after combustion. The surface coke layer was separated from the base by a protective air seal. These results indicate that combustion occurs at lower temperatures in the flameproofed composites. The flameproofed composites also demonstrate a lesser degree of burn-off. Figures 8; references 8: 6 Russian, 2 Western. [157-12126]

UDC 541.64:539.3

TIME-TEMPERATURE CHANGES IN PHYSICOMECHANICAL PROPERTIES OF SLIGHTLY PLASTICIZED AMORPHOUS POLYMERS

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 27, No 1, Jan 85
(manuscript received 20 Jun 83) pp 138-143

OVCHINNIKOV, Yu. V., GOLUB, I. G., TEPOV, B. F. and GORSHENKOV, Yu. M.

[Abstract] Previous work by the authors on the time-temperature changes in the physico-mechanical properties of slightly plasticized amorphous polymers has been extended. Polymethylmethacrylate containing dibutyl phthalate, chlorinated polyvinyl chloride, vinylchloride-vinylacetate copolymer and polyvinylchloride containing di-2-ethylhexylphthalate were studied. The samples were subjected to thermal treatment at a temperature 50° below their plasticizing temperatures. Tensile strength was maximum at a thermal processing temperature near the glass transition temperature. This is due to acceleration of the transition to an equilibrium state, as the glass transition temperature is approached, and destabilization of the polymer above this point. Changes in physical-mechanical properties with time are characterized by complex curves, some with several plateaus. Patterns observed depended on the material involved. The existence of two characteristic regions for changes in stability and deformational properties suggests that there is more than one stabilizing process connected with chain migration and with nucleation and growth of microheterogeneous regions of stabilization. Similar two-stage shifts are observed for the endothermic peaks obtained by differential thermal analysis. The S-shaped curves were not observed in the absence of plasticizer. Figures 6; references 18: 14 Russian, 4 Western. [157-12126]

UDC 541.64:536.7

PHASE STRUCTURE FORMATION AND PROPERTIES OF POLYMETHYLMETHACRYLATE POLY-CARBONATE BLENDS

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 27, No 1, Jan 85
(manuscript received 27 Jun 83) pp 184-191

RAZINSKAYA, I. I., GALLE, B. S., OTT, L. I., BUBNOVA, L. P., BATUYEVA, L. J.,
PUPUKINA, N. I., ADAMOVA, L. V. and SHTARKMAN, B. P.

[Abstract] In order to elucidate the mechanism of pearl shine, a study was conducted of polymethylmethacrylate polycarbonate blend phase structure as a function of composition, polymethylmethacrylate molecular weight, mixing conditions and properties of the blend. Electron microscopy and glass transition temperatures demonstrated that the blends are biphasic at 0.5-99.5 weight % polycarbonate. A sharp minimum in newtonian viscosity was found at 0.25% polycarbonate. Polycarbonate glass transition temperatures and density were depressed in the biphasic region. The dielectric relaxation properties of the blends were similar to those of the pure polymethylmethacrylate, indicating that chain mobility was independent of polycarbonate presence. Solubility in methylmethacrylate and carbon tetrachloride indicated that the surface layer of 30% and 50% blends was polymethylmethacrylate. The surface of a 70% blend was soluble in carbon tetrachloride, indicating that it was polycarbonate. In 30% blends, the polycarbonate has a drop dispersion structure, while in 50% and 70% blends it has a banded or layered structure. This transition corresponds to the appearance of pearl shine. The logarithms of newtonian viscosity was less than additive for blends above 10-15% polycarbonate. At the phase inversion point of 50% polycarbonate the efficiency zone of the blends begins to shift toward that of pure polycarbonate. Relaxation parameters exhibit similar shifts, with the mole activation energy of relaxation reaching a minimum at 70% polycarbonate. The data indicate that polycarbonate molecular structure is loosened when blended with polymethylmethacrylate. Figures 8; references 20: 15 Russian, 5 Western.

[157-12126]

UDC 541.64:542.943

MECHANISM OF INHIBITION OF THERMAL AND THERMOOXIDATIVE DEGRADATION OF
POLYMERS BY POLYARYLENEALKYLENES AND POLYMERIC HYDROCARBONS

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 27, No 1, Jan 85
(manuscript received 11 Jul 83) pp 192-197

SHOPOV, I., Central Polymer Laboratory, Bulgarian Academy of Sciences,
Sofia, Bulgaria

[Abstract] It is proposed that polyarylenealkylenes and other conjugated polymeric hydrocarbons inhibit thermal and thermooxidative degradation by forming charge-transfer complexes with the radicals which arise during degradation. This concept can also be used to explain various literature reports that these conjugated compounds are inhibitors of polymerization. The proposition is supported by the fact that increasing electron donor capacity improves inhibitory properties, as does increasing the number of aromatic groups on the inhibitor. The pressure of oxygen increases the electron acceptor capacity of the radicals formed during degradation. The charge-transfer complexes are less stable in low-viscosity media, so that inhibition does not occur. At least two aromatic nuclei complex with each radical. Poly-1-vinyl naphthalene, poly-9-vinyl anthracene and poly-N-vinyl carbazol were prepared and shown to inhibit the thermal degradation of polycarbonate in an argon atmosphere or in air. These additives do not have aromatic moieties attached to methylene groups, indicating that such methylene groups are not involved in inhibition. Figures 1; references 23: 12 Russian, 11 Western.
[157-12126]

UDC 678.7:678.664

COPOLYMERIZATION OF UNSATURATED URETHANES WITH ACRYLATES

Ivanova IZVESTIYA VYSSHIKH UCHEBNIKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA
TEKHNLOGIYA in Russian Vol 28, No 1, Jan 85
(manuscript received 14 Apr 83) pp 91-94

SOROKIN, M. F., ONOSOVA, L. A., SHODE, L. G. and GUSEVA, O. F., Chair of
Chemical Technology of Varnishes, Paints and Paint-and Varnish Coatings,
Moscow Chemico-Technologic Institute imeni D. I. Mendeleev

[Abstract] Copolymerization of unsaturated urethanes with acrylates makes it possible to obtain products having elasticity, weather resistance, decorative properties characteristic of acrylates, and, at the same time, to impart properties of polyurethanes such as high resistance to abrasion and temperature changes. The copolymerization of butylmethacrylate and triethylene glycol dimethylacrylate with unsaturated urethanes having two types of double bonds was studied and the rate constants for the four monomer pairs were determined. The results show that regardless of the double bond

type, unsaturated urethanes have about the same activity in radical copolymerization with methylacrylate monomers. Figures 3; references 8: 7 Russian, 1 Western.
[196-12765]

UDC 678.652:62-405.8(088.8)

FEATURES OF SYNTHESIS OF UREA RESINS FOR PREPARING UREA-FURANE PLASTIC FOAM

Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHNLOGIYA in Russian Vol 28, No 1, Jan 85 (manuscript received 10 Jun 83) pp 95-98

OKUNEV, P. A. and POKROVSKIY, S. L., Chair of Technology of Plastics Refining, Vladimir Polytechnic Institute

[Abstract] A study was made of the changes in basic physical chemical properties of urea resins that take place during their synthesis. Methodology was developed for the synthesis of urea resins and their furfurylic alcohol modifications, making it possible to obtain from them plastic foam of 50-150 kg/m³ density and low flammability (oxygen index 36-48 and calorimetric coefficient not greater than 0.5 without fire-retardant additives). These foam products may be recommended for heat insulation in buildings requiring high resistance to fire. Figures 2; references 9: 6 Russian, 3 Western.
[196-12765]

UDC 541.127 + 527.821

ACRYLAMIDE POLYMERIZATION KINETICS INITIATED BY PERSULFATED DIMETHYLAMINOETHYL METHACRYLATE SYSTEM IN AQUEOUS SOLUTIONS

Yerevan ARMYANSKIY KHIMICHESKIY ZHURNAL in Russian Vol 37, No 11, Nov 84 (manuscript received 1 Aug 83) pp 675-679

AKOPYAN, R. M., KAYFADZHYAN, A. M. and BEYLERYAN, N. M., Yerevan State University

[Abstract] In previous studies, it was shown that systems consisting of potassium persulfate (PP), tertiary amines or aminoalcohols were effective initiators of radical polymerization of acrylamide (AA) in aqueous solutions. In this work, macrokinetics of the polymerization of AA in aqueous solutions was studied when the reaction was initiated by PP in presence of small quantities of dimethylaminoethylmethacrylate (DMAEM). This system indeed initiated effectively polymerization of AA at room temperature. The polymerization rate in the stationary region could be described by the classical equation $W_p = k_{ef} [P]_0^{1/2} [DMAEM]_0^{1/2} [AA]$ for $[AA]_0 \gg [DMAEM]_0$. Under the

experimental conditions used, it was not possible to get the polyacrylamide completely dissolved in water. In general, a gel was obtained making it impossible to determine the average degree of polymerization. Figures 4; references 7: 5 Russian, 2 Western.
[205-7813]

UDC 547.541.64/678-547.58:58.1.5

SYNTHESIS AND POLYMERIZATION OF SOME CYANOETHYLATED BIS-AMIDES OF VINYLBenzoic ACIDS

Yerevan ARMYANSKIY KHIMICHESKIY ZHURNAL in Russian Vol 37, No 11, Nov 84 (manuscript received 5 Nov 83) pp 712-716

SHAKARYANTS, M. V., KARAPETYAN, T. G. and POTOSYAN, G. M., Institute of Organic Chemistry, ArmSSR Academy of Sciences, Yerevan

[Abstract] In an attempt to obtain novel polyfunctional divinyl compounds, a series of cyanoethylated bisamides of isomeric vinylbenzoic acids was synthesized and their polymerization regularities were studied. These compounds were obtained by reacting 2,3- and 4-vinylbenzoic acid chlorides with N,N'-bis(β -cyanoethyl)ethylene and N,N'-bis(β -cyanoethyl)hexamethylene diamines. The polymerization activity of these monomers increased in the following order: O-bis-amides < m-bis-amides < p-bis-amides. Figures 4; references 6: 4 Russian, 2 Western.
[205-7813]

UDC 542.94.459 + 547.22

DEHYDROHALOGENATION OF HALOORGANIC COMPOUNDS USING INTERPHASE TRANSFER CATALYSTS. 12 COMMUNICATION. SYNTHETIC METHOD FOR VINYL CHLORIDE

Yerevan ARMYANSKIY KHIMICHESKIY ZHURNAL in Russian Vol 37, No 11, Nov 84 (manuscript received 24 Feb 84) pp 719-721

ROSTOMYAN, I. M., ISRAYELAN, A. G., MATOSYAN, V. A. and CHUKHADZHYAN, G. A., Scientific Production Association "NAIRIT", Yerevan

[Abstract] An attempt was made to dehydrochlorinate dichloroethane into vinyl chloride (VC) in various organic solvents and in presence of quaternary ammonium salts and crown esters. In presence of quaternary ammonium salts and KOH the dehydrochlorination occurred with quantitative yield of the product; when crown esters were used, the yield of VC was about 94-95%. Replacement of KOH by NaOH dropped the yield to 80%. In absence of catalysts only insignificant yield of VC was obtained (about 5%). The best yields were obtained in benzene and toluene. References 6: 4 Russian, 2 Western.
[205-7813]

RUBBER AND ELASTOMERS

UDC 678.031

DEVELOPMENT OF LATEX BASED ANTICORROSION COVERS

Moscow KAUCHUK I REZINA in Russian No 2, Feb 85 pp 5-7

LIPKIN, A. M., KOVALENKO, G. A., GONCHAROVA, T. P. and MAYZELIS, B. A.

[Abstract] Water soluble elastomeric compositions were developed for chemically stable seamless covers requiring no high temperature treatment of toxic or flammable agents. Because of the fact that films have normally poor adhesive capability to cement and iron, special primers and interphase layers were developed for such application. For cement these layers were based on a mixture of natural and synthetic latexes ("Polan-B"), for metals a special binder and the same cover as for cement were used ("Polan-M"). Adhesion between layers is an important factor, especially between the outer latex layer and the interphase. This process is a function of the drying time of interphase. For equipment with complex configuration a special semiebonite cover "Polan-PE" was developed with high adhesive strength to the metal surfaces. Mechanical properties of these latex covers are tabulated.

Figures 2; references: 5 (Russian).

[208-7813]

UDC 678.4.063.048

NOVEL PRODUCTION FORM OF PHENOLIC STABILIZERS FOR LIGHT RUBBERS

Moscow KAUCHUK I REZINA in Russian No 2, Feb 85 pp 7-8

GURVICH, Ya. A., KUMOK, S. T., LOPATIN, V. V. and YAROVIKOVA, M. M.

[Abstract] Agidol 20 and Agidol 123 are used normally as phenolic stabilizers for protection of white and colored rubbers. However, because Agidol 20 is a viscous fluid and Agidol 123 a tarry substance, their application is difficult. To convert them to powdery material, they were absorbed on mineral carriers from benzene solution. Silica gel BS-30 and BS-50 were the best of the studied carriers: kaolin, chalk, silica gel and aerosol. The powder disperses well in rubber mixtures, does not lump and forms little dust during operations. References 5: 3 Russian, 2 Western.

[208-7813]

UDC 678.05-52:685.3

AUTOMATED CUTTING OF RUBBER-TEXTILE MATERIALS WITH LASER BEAM

Moscow KAUCHUK I REZINA in Russian No 2, Feb 85 pp 8-9

FEDOTOVA, S. Ye., ZAYDENBERG, G. A., KHAVKIN, V. P. and MOROZOV, A. V.

[Abstract] The use of a laser beam machine in automation of textile and leather form cutting has been described. In particular, the performance of a unit LURM-1600, developed at the All Union Scientific Research Institute of Light and Textile Machine Construction, was described. Almost all synthetic, artificial and natural materials can be cut to the predetermined pattern, including sack cloth, double and triple woven fabrics, etc. Due to the precision obtained and because of careful arrangement of the pattern, large savings could be expected to result from the use of this new cutting method. Figures 2.

[208-7813]

UDC 678.4.06:675:678-405.8

REPLACEMENT OF NUTRITIONAL AMMONIUM CARBONATE IN PRODUCTION OF RUBBER SPONGE AND MEDICAL SUPPLIES

Moscow KAUCHUK I REZINA in Russian No 2, Feb 85 pp 12-13

BOL'SHAKOVA, S. S., VYSHEGORODSKAYA, R. A., MEL'NIKOVA, G. K. and STOLYAROVA, L. B.

[Abstract] Nutritional ammonium carbonate (NAC) is used as the pore forming agent in production of rubber sponges, catheters and rectal tubes. This is an expensive material in short supply. It was shown in this study that NAC could be effectively replaced by carbon-ammonium salts (CAS). CAS can be easily measured out, they are introduced into the reaction mixture directly, without preliminary solution, they do not require strong alkaline media and do not generate excessive volume of ammonia gas. Field testing of finished products obtained with CAS showed quite comparable properties with materials obtained with NAC. No irritating effects on experimental animals were noted. Thus it was shown that NAC could be replaced effectively with CAS in manufacturing of various medicinal rubber products. Figures 2.

[208-7813]

UDC 678.4.031:678.762.2

COLLOIDAL-CHEMICAL PROPERTIES OF LATEX MIXTURES BASED ON CHLOROPRENE WITH
CARBOXYL CONTAINING BUTADIENE LATEX

Moscow KAUCHUK I REZINA in Russian No 2, Feb 85 pp 24-25

KUZNETSOV, V. L., RAYMAN, I. R., KRAYUSHKINA, Ye. I. and TUTORSKIY, I. A.

[Abstract] Effect of the composition of latex mixtures based on chloroprene and carboxyl containing butadiene latex on their colloidal-chemical properties was studied. The experimental objects included homopolymeric chloroprene latex L-7, latex L-M based on a copolymer of chloroprene and metacrylic acid and latex SKD-1. These latexes were mixed with SKD-1 taken at different ratios. It was shown that addition of SKD-1 increased frost resistance of the formed films. It was concluded that when new compositions of latexes are being developed, it is necessary to consider the changes in colloidal-chemical properties which depend to a large extent on the nature of each polymer. Figures 2; references 5 (Russian).
[208-7813]

UDC 678.014.32;678.06:82;416;678.061

CHANGE IN ANTIOZONANT CONTENT DURING OZONE AGING PROCESS OF RESINOUS AND
LATEX FILMS

Moscow KAUCHUK I REZINA in Russian No 2, Feb 85 pp 28-30

RAZUMOVSKIY, S. D., VINITSKAYA, Ye. L., KEFELI, A. A. and GURVICH, Ya. A.

[Abstract] Increased resistance of polymers to ozone related cracking can be achieved by addition of antiozonants (AO). The effect of the structure of latex films, the presence of surfactants and their chemical structure was studied in relationship to the consumption of AO up to the moment of the appearance of visible cracks. Tri-n-butylthiourea used as a 75% emulsion stabilized with potassium oleate was used as AO. It was shown that the characteristics of ozone aging of stabilized latex films in comparison with rubber films are related to the presence of emulsifiers in latex vulcanizates. The presence of surfactants, their chemical structure and distribution within the latex affect the behavior of AO, its kinetics of consumption and consequently the effectiveness of the protective action. Figures 4; references 11: 9 Russian, 2 Western.
[208-7813]

2 July 1985

UDC 678.06:685.4

AGENTS FOR INDIVIDUAL HAND PROTECTION BASED ON POLYMER MATERIALS

Moscow KAUCHUK I REZINA in Russian No 2, Feb 85 pp 40-42

ALEKSANDROVA, Ye. A., VAS'KOVSKAYA, A. A., GRUBMAN, Yu. V. and
FILIMONOVA, A. M.

[Abstract] Protection of hands continues to be an actively investigated area. The role of protective gloves is discussed: latex based gloves with rough surface, gloves reinforced with fabrics designed to prevent punctures and tears and gloves designed for protection from organic solvents and concentrated mineral acids. Special polymers are used in each case depending on the end-use. Rough surface gloves made of dual layer latex and gloves resistant to acids and bases (made of PVC) are being mass produced at the present time. The others have been field tested and recommended for production. Figures 1; references 5 (Russian, 1 by Western author).
[208-7813]

WATER TREATMENT

NEW PUMPS IMPROVE LAND RECLAMATION

Moscow SEL'SKAYA ZHIZN' in Russian 21 Feb 85 p 2

[Interview with V.A. Reznichenko, USSR deputy minister of Chemical and Petroleum Machine Building, by I. Kalashnikov: "That Hand-Created Rivers Flow..."; date and place not specified]

[Text] [Question] In connection with the rapid development of land reclamation, the editorial staff receives many letters from readers requesting an account of the type of new equipment being developed for this. Tell us please, Viktor Aleksandrovich, about today's technical equipment for the reclamation workers.

[Answer] As we know, a great deal of land suitable for irrigation today is located above the water sources, and because of this the moisture must be raised dozens and even hundreds of meters. It is precisely this characteristic feature that distinguishes a considerable number of land areas in the Volga area, in the Ukraine and in Moldavia, Kazakhstan and Central Asia, where the water is lifted by machine, on the average up to 50-150 meters, and in a number of cases--even to 250 meters. In order to give water to these fields, high-pressure pumping stations and even whole series of them are being built. The enterprises of the USSR Ministry of Chemical and Petroleum Machine Building supply modern equipment to fit out these stations.

We are now turning out about 70,000 various pumps yearly for the needs of reclamation and water resources. Among them are highly productive units, capable of pumping dozens of cubic meters of water per second. Use of them has made it possible to carry out construction of large irrigation systems, unequalled in world practical work. In the last decade the sector's enterprises have supplied over 1000 pumps with a large unit capacity for use on over 20 main canals and large irrigation systems.

As an example I should like to refer to the Karshinskiy main canal in the Uzbek SSR, introduced at the planned capacity a few years ago. It is about 100 kilometers long. Six stations, at which 36 vertical pumping units are established, have been built on the canal. Each of them gives almost 150,000 cubic meters of water per hour. The canal is a water course several times greater than the Moscow River, and makes it possible to irrigate 350,000 hectares.

An even more powerful main arterial is the Amu-Bukharskiy Canal, extending 233 kilometers in the Kyzylkum desert. About a million cubic meters of water pass along it in one hour. The pumping equipment ensures the water's rising 112 meters.

Pumping equipment produced by enterprises of the Ministry of Chemical and Petroleum Machine Building is also operating successfully on the Irtysh-Karaganda Canal, the largest in Kazakhstan, extending about 500 kilometers, on the first section of the Dnepr-Donbass Canal, the Saratov and Severo-Krymskiy canals and other irrigation systems.

By 1990 we, the machine builders, should considerably increase the supplies of equipment for reclamation and considerably expand its product list. At the same time, development is specified of units unique for their power, for the Volga-Don, Rostov-Krasnodar, Volga-Chogray and Dunay-Dnepr canals, and for transferring part of the flow from the northern rivers into the Volga basin.

[Question] How will this idea itself be realized if one looks at it from the technical point of view?

[Answer] The problem is very complex if one considers that just the first stage of implementing this idea calls for a yearly transfer of 5.8 cubic kilometers of water. The complexity lies in the fact that it is to be directed upstream, against the current—that is, the rivers should practically go backwards.

Only modern equipment can cope with this difficult task. The scientists, designers and specialists of our department have taken on the task of developing and mastering production of unique super-powerful pumping equipment.

At present several machines with a unit feed of 25, 80, 125 and 200 cubic meters of water per second are being developed. These pumps are analogous in class to medium and large hydroturbines: their impeller diameters reach 4-7 meters. Output of the first super-powerful pumps is outlined for readiness in the 11th Five-Year Plan. They will assume the entire burden of transferring the huge masses of water from the northern rivers to the southern regions, which have available large areas of unused arid lands and at the same time experience a severe moisture shortage. The machine builders are now actively preparing for practical fulfillment of this complicated and responsible task.

[Question] Water in nature is, as we know, a corrosive medium. Reliable, higher quality equipment is needed to cope with it. How is this problem being solved?

[Answer] This is correct. Machines that pump water from some sources to others must withstand colossal loads at times. The point is, that many rivers carry with them huge masses of sand and clay. All of this gets into the pump units. The rivers of the Central Asian latitudes are particularly characterized by this corrosiveness.

For example, on the Karshinskiy and Dzhizakskiy canals, each pump, along with the water, pumps up to 600 tons of suspended matter in an hour. It is not surprising that this leads to the units wearing out rapidly.

Specialists of many sectorial institutes and design bureaus are working on heightened reliability and durability for the pumps. Five types of large centrifugal pumps have already been developed for Central Asia. Due to original design solutions, their reliability has sharply increased. Development of new units, resistant to the effect of "corrosive" water, is being called for.

We have many years of contact with the USSR Ministry of Land Reclamation and Water Resources as the basic purchaser. We improve the equipment and increase its reliability and durability jointly. We also reveal the current and long-term needs for equipment together. The need for pumps and other equipment up to 1990 and in the following period has been determined.

We also have a fruitful collaboration with the USSR Ministry of Electrical Equipment Industry, the enterprises of which supply us with electric motors, and with the Ministry of Power Machine Building—it provides us with castings. I should like to note that for a further improvement in quality and increase in reliability of the pump units, we need polyamide materials, rolled dynamo steel and improved types of rolled metal. So far we obtain all of this in insufficient quantity.

It appears that the large tasks facing us in land reclamation will give a powerful impetus for intensifying the activity of our related industries and suppliers of complete-equipping items. Through combined efforts, all the difficulties in the development of modern equipment for reclamation needs will be successfully surmounted.

12151

CSO: 1841/207

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ELECTROFILTRATION BASED ON ION EXCHANGE MEMBRANES AND DIFFUSION PHORESIS

Kiev KHIMIYA I TEKHNLOGIYA VODY in Russian Vol 6, No 6, Nov-Dec 84
(manuscript received 16 Mar 83) pp 491-495

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[Abstract] Mathematical and experimental data were analyzed for electro-filtration based on ion exchange membranes and diffusion migration of charged particles. Particles bearing the same charge as that imparted to the membrane were seen to concentrate at a defined distance from the membrane which was determined by the charge and applied potential. The actual distance between the zone of particle concentration and the membrane was determined by the ratio of dipole phoresis to the electrodiffusion rate of transport. Figures 4; references 9: 8 Russian, 1 Western.
[148-12172]

UDC 628.1.16.08

ULTRASONIC ENHANCEMENT OF ULTRAFILTRATION

Kiev KHIMIYA I TEKHNLOGIYA VODY in Russian Vol 6, No 6, Nov-Dec 84
(manuscript received 12 Apr 83) p 496

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[Abstract] Nuclear membranes with a 10% porosity and 0.6-0.7 μm pore diameters were subjected to 50-400 W ultrasonication to determine the effects of the latter treatment on ultrafiltration efficiency. Maximum improvements in filtration were obtained with 400 W ultrasound applied directly to the side exposed to water requiring purification under a pressure of 10^3 Pa. Discontinuation of ultrasonication resulted in a gradual loss of efficiency, while resonation resulted in an instantaneous improvement

in efficiency. The mechanism underlying such changes remain to be elucidated. Figures 1; references 2 (Russian).
[148-12172]

UDC 622.765:546.49.-386:661.185.1

FLOTATION REMOVAL OF MERCURY THIOCYANATES

Kiev KHIMIYA I TEKHNLOGIYA VODY in Russian Vol 6, No 6, Nov-Dec 84
(manuscript received 10 Mar 83) pp 502-505

SKRYLEV, L. D., BULYGINA, L. M. and SIN'KOVA, L. A., Odessa State University imeni N. I. Mechnikov

[Abstract] Acetate derivatives of rosin amines and hydrochlorides of primary aliphatic amines were tested for their effectiveness in the removal of mercury thiocyanates from water by the flotation method. Virtually complete (>99%) removal of mercury was obtained with the rosin at pH 2.5-7.5, and with the aliphatic amines containing 11-16 C atoms at pH 6.5-7.5, i.e., at those pH values at which the agents are largely ionized. The high degree of mercury elimination required excess rosin (150%) and amines (50%), with the process enhanced in the case of the rosin by raising the temperature from 5 to 40°C, while the aliphatic amines showed a maximum at 20°C. The flotation process followed first order kinetics, giving a rate constant for the rosin of 0.08 min⁻¹, and for the amines 0.29 min⁻¹. Figures 5; references 15: 13 Russian, 2 Western.
[148-12172]

UDC 628.3:541.183

PURIFICATION OF WASTE WATERS FROM INSECTICIDE PLANTS BY ACTIVATED CHARCOAL

Kiev KHIMIYA I TEKHNLOGIYA VODY in Russian Vol 6, No 6, Nov-Dec 84
(manuscript received 21 Mar 83) pp 506-508

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[Abstract] Activated charcoal AG-3 was tested for its effectiveness in the removal of organic compounds (from the waste waters of a plant manufacturing the insecticides Prima-71 and dichlorvos) using two column filtration devices in tandem. Analysis of removal plots for kerosene, xylene and the insecticides demonstrated this system to be highly effective in reducing the level of contaminants to allowable levels. Optimum conditions for decontamination included a charcoal concentration of 0.6 g/liter and a flow rate of 2 m/h. The system can be utilized in a recirculating operation, with the cost for the purification of one cubic meter of water being 14- to 18-fold

lower than the cost of combustion decontamination. Figures 1; references 8 (Russian).
[148-12172]

UDC 628.543.49.081.32(088.8)

ELECTROCHEMICAL REGENERATION OF ACTIVATED CHARCOAL SATURATED WITH
p-NITROTOLUENE

Kiev KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 6, No 6, Nov-Dec 84
(manuscript received 4 Apr 83) pp 509-511

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[Abstract] A system was designed for the electrochemical regeneration of activated charcoal used for the purification of waste waters polluted with organic compounds. Trials conducted with AG-3 activated charcoal saturated with p-nitrotoluene demonstrated that using the charcoal as an anode, and a steel cathode (employing the column casing), resulted in regeneration of AG-3 in a system consisting of 0.2-0.6 M NaCl electrolyte and 20-40 A/m² current. A four cycle operation of the column system yielded 97-98% regeneration with a current of 30 A/m² and respective initial and final pH values of 6.5 and 10.6. The effectiveness of this method was apparently due to reactions on the carbon electrode which facilitated oxidation of the adsorbed p-nitrotoluene. Figures 1; references 4: 2 Russian, 2 Western.
[148-12172]

UDC 543.42:628.312

ASSAY OF BERYLLIUM IN MINE WATERS BY CHEMICAL AND SPECTRAL METHODS

Kiev KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 6, No 6, Nov-Dec 84
(manuscript received 28 Mar 83) pp 534-536

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[Abstract] A method has been developed for the analysis of beryllium in neutral or acid coal mine waters based on preliminary extraction and subsequent spectral quantification. Beryllium alone was not extracted by various chelating agents, but in combination with other metals (Al, Fe, Mn, Ni, Co, Zn, Cu, Bi, Cd, Pb, etc.) was cochelated by acetylacetone, acetylacetone + hydroxyquinoline, and acetylacetone + hydroxyquinoline + diethyldithiocarbamate combinations. The latter combination of chelating agents proved to

be most effective at pH 5 in the case of neutral water. For acid waters, the pH was adjusted to 8 and extraction was conducted with dithizone or EDTA (komplekson III) as a preliminary step, followed by further extraction with acetylacetone and diethyldithiocarbamate. The extract was distilled, ashed at 350°C, and the samples analyzed with an ISP-30 quartz spectrograph. The method makes possible detection of beryllium down to a concentration of 0.04 µg/liter with $S_r = 0.16$ for neutral waters, and 0.05-100 µg/liter with $S_r \leq 0.20$ for acid waters. References 7 (Russian).
[148-12172]

UDC 628.165

REGENERATION OF RAPID WATER FILTERS BY ADDITION OF FLOCCULANTS DURING FLUSHING

Kiev KHEMIYA I TEKHOLOGIYA VODY in Russian Vol 6, No 6, Nov-Dec 84
(manuscript received 28 Feb 83) pp 551-552

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[Abstract] Trials were conducted on an effective means of improving the performance of quartz-sand water filters for water clarification at water treatment plant during wintertime. Addition of flocculants prior to final flushing at 4°C was evaluated in the case of 0.5% silicic acid and 6% polyacrylamide gel. The latter yielded superior results and extended the working lifetime of a filter 2.5- to 3-fold before retreatment with the flocculant had to be re-employed. Optimum concentrations of the polyacrylamide ranged from 12 to 30 g per one cubic meter of the filler. Figures 2; references 8: 7 Russian, 1 Western.
[148-12172]

UDC 628.3

TREATMENT OF WATER AT GORKIY AUTOMOBILE PLANT

Kiev KHEMIYA I TEKHOLOGIYA VODY in Russian Vol 6, No 6, Nov-Dec 84
(manuscript received 27 Dec 82) pp 553-555

NAYDENKO, V. V., VASIL'YEV, L. A., ALEKSEYEV, V. I. and NEFEDOVA, T. A., Gorkiy Engineering and Construction Institute imeni V. P. Chkalov

[Abstract] An analysis was conducted at the water treatment facility of the Gorkiy Automobile Plant to assess its efficiency in removing petroleum hydrocarbons. The efficiency of the process was found to be only 35-45% effective and, as a result, several modifications of flotation and coagulation techniques were tested separately and in combination to improve elimination

of the hydrocarbons. Best results--removal of 80% of the hydrocarbons and 90% of suspended particulates--were obtained with a combination of coagulants and flocculants. For flotation, the water was subjected to a pressure of 0.3-0.5 MPa with a saturation time of 1.5-3.5 min and a flotation time of 10 min, followed by treatment with a coagulant (5% $\text{Al}_2(\text{SO}_4)_3$) and a flocculant (1% polyacrylamide). The final step in the closed system involved filtration via a polyurethane foam. Figures 2; references 5 (Russian).
[148-12172]

UDC 628.33

ELECTROMAGNETIC DOUBLE-FLOW FILTER

Kiev KHIMIYA I TEKHOLOGIYA VODOY in Russian Vol 6, No 6, Nov-Dec 84
(manuscript received 17 Jun 83) pp 555-559

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[Abstract] The relative efficiencies of solenoid and toroidal double-flow magnetic filters are discussed from theoretical and experimental viewpoints. Under identical trial conditions, the toroidal double-flow electromagnetic filter system was demonstrated to offer superior water treatment to the solenoid filter. In addition, the experimental data confirmed hypothetical speculations that a parallel arrangement of the elements offers greater efficiency than a series connection of the filtering elements. These observations indicate that the electromagnetic separators will find growing application in continuous filtering systems. Figures 5; references 17: 6 Russian, 11 Western.
[148-12172]

UDC 539.23.535.24

LASER DEVICE FOR TURBIDITY ANALYSIS OF WATER SUSPENSIONS

Kiev KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 6, No 6, Nov-Dec 84
(manuscript received 21 Feb 83) pp 560-561

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[Abstract] Mathematical analysis is presented for turbidimetric water assays using a He-Ne laser emitting at 630 nm, and kaolin and formasin [sic] as turbidity standards. Light scattering data are presented for both standards, as well as bell-shaped histograms depicting particle-size distribution. Experimental analysis and evaluation have shown that such a system,

employing kaolin and formasin standards, can be useful in routine water analysis. Figures 2; references 3 (Russian).
[148-12172]

UDC 628.16.067+621.317.333

FILTER MEDIA COMPACTION IN RAPID FILTERS

Kiev KHEMIYA I TEKHNOLOGIYA VODY in Russian Vol 6, No 6, Nov-Dec 84
(manuscript received 21 Mar 83) pp 562-563

OVCHINNIKOV, G. A., ALESHICH, N. K., GORONOVSKIY, I. T. and
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[Abstract] Conductometric studies were conducted on charcoal-sand rapid filters at a water-treatment plant in Kiev to assess filter medium compaction as a factor in diminished filtration efficiency. The approach essentially consisted of a correlation between effective porosity and electrical conductivity in relation to compaction. Analysis of the factors in question demonstrated that the initial loss of efficiency was due to hydrodynamic instability of the pore size, and that silt accumulation is accompanied by compaction of the filter media. Since compaction is neglected in standard theories of filtration, it appears that the effects of compaction on the intergranular volume in the filter media may account for the discrepancies between laboratory studies and actual findings on filtration rates at water-treatment plants. Figures 1; references 11: 10 Russian, 1 Western.
[148-12172]

UDC 541.183

STUDY OF EFFECTIVENESS OF CATIONITE FLOCCULANTS IN CLARIFYING FLUORITE ORE FLOTATION EFFLUENT

Ivanova IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHEMIYA I KHEMICHESKAYA
TEKHNOLOGIYA in Russian Vol 28, No 1, Jan 85 (manuscript received 28 Jul 82)
pp 70-73

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[Abstract] The lack of effective flocculants and coagulants to treat effluent from fluorite ore enrichment plants lowers the productivity of cationite water softening units. In the present work, four new water-soluble

quaternary salts of chloromethylated polystyrene having pyridine, beta- and gamma-picoline and isoquinoline chloride groups were synthesized and tested. The data show that these flocculants are more effective than the currently used polyacrylamide-aluminum sulfate combination. The correlation between flocculant structure and its effectiveness was established. Figures 3; references 6: 5 Russian, 1 Western.
[196-12765]

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