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UDC 547.491.4:661.833:543.42

Aqueous Alkali Solutions in Reactions With Isocyanate

18410055d Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 61 No 8 Aug 88 (manuscript received 13 May 87) pp 1872-1876

[Article by R. A. Veselovskiy, S. S. Ishchenko, T. I. Novikova, and N. L. Zbanatskaya, High-Molecular Compound Chemistry Institute, Ukrainian Academy of Sciences]

[Abstract] A study is made of the interaction of aqueous caustic soda solutions of various concentrations, modeling the state of the hydrated sodium cation in liquid sodium glasses with various silicate moduli and 2,4-toluylene diisocyanate (2,4-TDI). IR spectroscopy was used to identify the end products of the reaction of 2,4-TDI with water and NaOH solutions of 5.8 to 42 percent concentration. At up to 20 percent alkali concentrations, disubstituted urea and amine are formed, whereas at higher concentrations, a trimer of isocyanate and sodium salts of carbaminic acid are also formed. The quantitative yield of disubstituted urea, amine, the trimer, isocyanate, and the acid salts is determined by the hydration status in the NaOH-H₂O system and the ratio of NCO and OH groups. Figures 2, references 17: Russian.

UDC 621.315.616.7:620.17:536.485

New Method For Estimating Rubber Brittleness Temperature Limit

18410056e Moscow KAUCHUK I REZINA in Russian No 9 Sep 88 pp 34-36

[Article by A. M. Kucherskiy, M. Ye. Varaksin, V. P. Perelygina, and L. V. Vikhlyayev]

[Abstract] A study is made of the influence of certain methodologic factors on the results of brittleness temperature testing of rubber. It was found that variations in the clamping force and thus in the compression of rubber specimens can cause variations in test results. Specimens can be clamped between rubber inserts, or the clamping force can be standardized to avoid this. Cantilever holding of specimens that are then struck by a pendulum hammer, the speed of which after impact can be measured to determine the brittleness of rubber fractures, is suggested to reduce the variations in test results. Figures 3, references 4: 3 Russian, 1 Western.

UDC 678.065:66.015.24

Experimental Determination of Tire Heat Transfer Characteristics at Various Rolling Speeds

18410056f Moscow KAUCHUK I REZINA in Russian No 9 Sep 88 pp 38-39

[Article by L. S. Gluskina]

[Abstract] Previously suggested equations for calculating the heat transfer of tires yield results differing by a factor of more than 5. Additional studies were performed to

determine the true heat transfer characteristics of tires with the surrounding environment. The method developed for estimating the heat transfer coefficient can determine the quantity of heat liberated by the tread, sidewalls, and rims at various rolling speeds. Special sensors with microthermistors were used to measure the temperatures of tire structural elements at 60 and 80 km/hr and air temperatures of 18 and 30°C. It was found that the tire tread surface liberated 70 percent of the heat, the sidewalls 26 percent, the rim 4 percent. An increase in heat transfer from the tire tread can therefore significantly reduce the usage temperature of tires and improve their serviceability. Figures 3, references 8: Russian.

UDC 535.24:523.42

Analysis of Venusian Atmosphere by Mass Spectrometry and Gas Chromatography

18410059a Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 43 No 8, Aug 88 (manuscript received 22 Jun 87) pp 1371-1382

[Article by Yu. A. Surkov and M. L. Ryvkin, Institute of Geochemistry and Analytical Chemistry imeni V. I. Vernadskiy, USSR Academy of Sciences, Moscow]

[Abstract] This review presents Soviet experience in gathering mass spectrometric and gas chromatographic data on Venus atmosphere when using the Venera, Vega, and Pioneer-Venera space probes. The information obtained by mass spectrometric techniques was derived at a height of 30 to 50 km above the surface and yielded values of 97 percent by vol. CO₂, 2 +/- 0.5 percent by vol. N₂, 2 x 10⁻² percent by vol. Ar, 10⁻² percent by vol. COS, and 5 x 10⁻⁴ percent by vol. NH₃. However, the value for ammonia was found to be elevated. The gas chromatographic apparatus used to obtain altitude profiles for gases in the Venusian atmosphere is also described. This also resulted in the first reported values for H₂ (2.5 +/- x 10⁻³ percent by vol. at 49 to 58 km), H₂S (8 +/- 4 x 10⁻³ percent at 29 to 37 km), and COS (4 +/- 2 x 10⁻³ percent by vol. at 29 to 37 km). Although the data compiled in these experiments are preliminary, they delineate the usefulness of gas chromatography and mass spectrometry in analyzing atmospheric gases on Venus and the improvements that need to be made in the instruments for greater reliability. Figures 9; tables 4; references 13: 9 Russian, 4 Western.

UDC 543.51:543.8

Quantitative Mass Spectrometry of Multicomponent Mixtures with Direct Introduction of Sample into Ionization Chamber

18410059b Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 43 No 8, Aug 88 (manuscript received 28 Apr 87) pp 1406-1410

[Article by Yu. P. Turov, T. A. Sagachenko, and F. G. Unger, Institute of Oil Chemistry, Siberian Department, USSR Academy of Sciences, Tomsk]

[Abstract] Direct introduction of various petroleum fractions (180-360, 350-400, and 350-540 degrees C) into the

ionization chamber was employed for quantitative mass spectrometry based on a single spectrum. The mass spectra were continuously scanned as the evaporated samples were introduced into the ionization chamber where they were subjected to electron impact ionization. The spectra were converted into an integrated mass spectrum to reflect the composition of the gas phase at a given moment in time. Evaluation of the multicomponent sample was based on a comparison of mass spectra obtained on different parts of the full ionic current with the integrated spectrum, with the latter treated as the spectrum of a standard reference sample. This approach was shown to yield reliable information with an error range of 5-19 percent, i.e., a typical range for mass spectrometric analyses. The single mass spectrum may be recorded either at the peak region of the total ion current with variable heating of the ampule of vaporization or at a fixed ampule temperature corresponding to the peak region of the current. Figures 1; tables 1; references 10: 9 Russian, 1 Western.

UDC 543.42:546.661

Enhanced Accuracy of Determination of Isotope Composition of Europium Sample by Atomic Emission Spectroscopy Without Reference Standard

18410059c Moscow ZHURNAL ANALITICHESKOY KHMII in Russian Vol 43 No 8, Aug 88 (manuscript received 13 Sep 87) pp 1437-1439

[Article by A. I. Drobyshv, Yu. I. Turkin, and N. M. Yakimova, Leningrad State University imeni A. A. Zhdanov]

[Abstract] Atomic emission spectroscopy has been applied to the determination of the isotope composition of a europium sample without a reference sample, based on the fact that the sum of fractional concentrations of each species equals unity (i.e., $c_1 + c_2 = 1$). The relationship between concentration and intensity of emission leads to the following equation: $c_1 = [A_1/(A_1 + A_2)] \times [(1 + v)/(1 - v)] - [v/(1 - v)]$, where v is the transposition factor representing a fraction of the peak intensity of one of the isotopes at the peak intensity of the spectrum of the other isotope and A_1 and A_2 represent the emission intensities of the two isotopes. The analytical signal $OC = A_1/(A_1 + A_2)$ was combined with v for each order of interference pattern to calculate the percentage of ^{151}Eu in a europium chloride sample from the equation for calculating c_1 . The value of v was derived as the ordinate of the boundary of the A_1 isotope at a distance $\Delta\rho$, which is equal to the distance between the maxima of the isotopes responsible for A_1 and A_2 , proceeding toward longer wavelengths ($v = b/A_1$). Twenty parallel determinations showed that the systematic error could be neglected. The confidence limit ($P = 0.95$) for a single determination was ± 0.3 at percent for samples containing 47.47 to 98.2 at percent ^{151}Eu . Figures 3; references 6 (Russian).

UDC 543.258:546.18

Determination of Silicon by Controlled-Potential Coulometry

18410059d Moscow ZHURNAL ANALITICHESKOY KHMII in Russian Vol 43 No 8, Aug 88 (manuscript received 21 May 87) pp 1440-1442

[Article by L. B. Oganesyanyan, M. B. Ogareva, N. F. Konkova, G. G. Svirshchevsakaya, and V. B. Lisovskiy, Moscow Institute of Chemical Technology imeni D. I. Mendeleev]

[Abstract] Studies were conducted on the electrochemical behavior of acetone solutions of molybdosilicic acid on a platinum electrode with a view toward the development of a coulometric method for Si determination by means of controlled potential parameters. The result demonstrated that the optimum conditions consisted of a 25 percent acetone solution and a platinum electrode potential of 0.02 V for the determination of Si(IV). The current was directly proportional to the concentration of Si(IV) in the 7×10^{-5} to 3×10^{-3} M interval, with the reduction of the acid attributed to a single electron transfer at 0.375 V (first reduction wave) and to three electrons at 0.20 V (second wave). Analysis of samples containing Si in a concentration of 4 percent yielded values of 3.78 \pm 0.20 percent ($n = 5$, $P = 0.95$, $s_r = 0.052$). Figures 1; tables 1; references 15: 5 Russian, 10 Western.

UDC 535.343+543.253:546.882.5

Use of Mineral Acids in Aqueous Organic Solvents for Direct Polarographic Determination of Niobium in Steel and Nickel Alloys

18410059e Moscow ZHURNAL ANALITICHESKOY KHMII in Russian Vol 43 No 8, Aug 88 (manuscript received 5 Feb 87) pp 1453-1457

[Article by D. I. Kurbatov and M. Yu. Yanchenko, Institute of Chemistry, Ural Department, USSR Academy of Sciences, Sverdlovsk]

[Abstract] The electrical reduction of Nb(V) in aqueous organic solvents was analyzed to devise a polarographic method for direct determination of Nb in metallurgical technology and avoid the need for Nb separation prior to analysis. The studies were conducted with PU-1 and PO-5122 polarographs by employing systems in which the water component in $\text{H}_2\text{SO}_4\text{-HCl-H}_2\text{O}$ was replaced by DMF, ethanol, ethylene glycol, or glycerol. The results with ethylene glycol were used in recovery studies involving steel and nickel alloys. The data showed that with an Nb content of 0.51 to 2.08 percent the s_r did not exceed 0.03. Furthermore, even 30- to greater than 100-fold excesses of Cr, Ni, Mn, Fe, W, Ti, or Mo failed to interfere with the results. Figures 2; tables 4; references 15: 7 Russian, 8 Western.

UDC 543.420.62:541.183.1:546.791.6

**Determination of Trace Quantities of Uranium(VI)
by Solid-Phase Spectrophotometry**

*18410059f Moscow ZHURNAL ANALITICHESKOY
KHIMII in Russian Vol 43 No 8, Aug 88 (manuscript
received 4 May 87) pp 1461-1465*

[Article by G. D. Brykina, G. F. Agapova, V. F. Kalinina,
and L. S. Krysina. Moscow State University; All-Union
Scientific Research Institute of Mineral Raw Materials,
Moscow]

[Abstract] A sensitive spectrophotometric method was
developed to analyze uranium (VI) in mineralogical

samples, the method precluded the need for a preliminary separation step. The solid-phase spectrophotometry was attained by means of a system using the anion exchange resin AB-17x8-C1, modified by reaction with 2-(2-thiazolylazo)-5-diethyl-m-aminophenol (TAAP). Cursory technical details are presented for the preparation of the solid-phase carrier along with conditions that favor optimum sensitivity. The method is based on the fact that TAAP has maximum absorption at 520 nm and the TAAP-U(VI) complex has maximum absorption at 590 nm in solution. In the solid-phase situation the complex absorbs at 600 nm at pH 6.0. Recovery studies conducted with several different samples yielded a sensitivity better than 10^{-5} percent U(VI), with $s_r = 0.2$. Figures 2; tables 2; references 12: 8 Russian, 4 Western.

UDC 66.074.37

Liquid-Phase Catalytic Scrubbing of Gases To Remove Sulfur Dioxide

18410040a Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 61 No 7 Jul 88 (manuscript received 17 Dec 86) pp 1481-1485

[Article by V. A. Fomin, N. R. Izmaylova, T. I. Komleva, and A. M. Mazgarov, All-Union Scientific Research Institute of Hydrocarbon Raw Materials]

[Abstract] This article describes a liquid-phase catalytic method of scrubbing gases to remove sulfur dioxide in a solution of tributylphosphate. The influence of various parameters on the purification of a model gas mixture was studied under static conditions in a laboratory installation by passing a gas mixture consisting of nitrogen, hydrogen sulfide, and sulfur dioxide through a bubbler reactor filled with a solution of tributylphosphate and a catalyst. The gas feed rate was kept constant at 89.4 liters per hour, while the catalyst concentration, water content, sulfur dioxide concentration, and $H_2S:SO_2$ ratio were varied. The hydrogen sulfide and sulfur dioxide combined in the reaction to produce crystalline sulfur and water in the presence of the higher dialkylaminopropionitrile catalyst. The catalyst was found to be highly active and quite stable, resulting in the virtually complete removal of the sulfur dioxide. An author's certificate has been granted to protect the new method of gas purification. Figures 4, references 10: 6 Russian, 4 Western.

Influence of Composition of Spinning Solutions Used To Form Biological Catalyst Fibers on Their Rheologic Properties

18410040h Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 61 No 7 Jul 88 (manuscript received 13 Sep 86) pp 1671-1672

[Article by S. A. Galkin, N. R. Killdeyeva, A. D. Virnik, and L. S. Galbraykh, Moscow Textile Institute]

[Abstract] In order to determine the relationship between the properties of biological catalyst fibers containing penicillin amidase and the structure of the spinning compositions used to form the fibers, the rheologic properties of

the spinning compositions were studied. It was found that increasing the concentration of protein in the aqueous-phase, increasing the quantity of the aqueous phase, and decreasing the mean aqueous phase particle radius while maintaining a constant volume of aqueous phase can significantly increase the viscosity of the system. This points to the predominant role played by the interaction among dispersed phase particles in forming the structure of the spinning compositions studied. An increase in spinning composition viscosity causes a relative decrease in stability and an increase in activity of the biocatalytic fibers. Figure 1, references 3: Russian.

UDC 66.097.3.022.4

Modification of Hydrorefining Catalysts

18410055b Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 61 No 8 Aug 88 (manuscript received 24 Apr 85) pp 1843-1849

[Article by I. M. Kolesnikov and N. N. Belov, Moscow Institute of Petroleum and Gas imeni I. M. Gubkin]

[Abstract] The authors have developed a theory of catalysis by polyhedrons and thermodynamic methods for selecting the structure and composition of catalysts that are optimal from the standpoint of their catalytic properties. This allows computation of the optimal structure of a catalyst and its catalytic centers in advance by relating the chemical composition of a catalyst to the optimal content of catalytic centers on its surface. Thermodynamic computation of the optimal Co:Mo ratio in the composition of an Al-Co-Mo-O catalyst is undertaken. Hydrorefining catalysts were synthesized by the method of mixing and by successive impregnation of the carrier. Catalysts were treated with salts of Co or Mo, and the activity of the modified catalysts was compared with that of the untreated catalysts. The catalysts produced by mixing and then treatment in ammonium paramolybdate and cobalt nitrate had higher activity only following surface modification with Mo ions in the $[MoO_4]$ tetrahedron. Catalysts produced by treating aluminum γ oxide with aqueous solutions of molybdenum and cobalt salts had the optimum number of active tetrahedron sets on their surfaces. References 5: 2 Russian, 3 Western.

UDC 532.71.62-278

Structural Changes in Reverse-Osmotic Cellulose Acetate Membranes Upon Storage

18410060a Moscow *KOLLOIDNYY ZHURNAL*
in Russian Vol 50 No 5 Sep-Oct 88 (manuscript received
13 Aug 86) pp 835-842

[Article by I. D. Atamanenko, M. T. Bryk, and Ye. A. Tsapyuk, Institute of Colloid Chemistry and Water Chemistry, Ukrainian Academy of Sciences, Kiev]

[Abstract] A study is made of changes in the molecular, supermolecular, and macroscopic structure of reverse-osmotic cellulose acetate membranes upon storage in water at room temperature for over 2 years. The hydrolytic stability of the membranes in water at pH 6-7 was measured by the spectral method determining the content of acetate groups in the polymer. The degree of substitution and acetyl number were determined. A sorption method was used to investigate the structural characteristics of the membranes. The effect of the changes occurring in the membranes upon storage on their throughput and retention was studied. The separation characteristics were found to change significantly, with retention of NaCl increasing slightly along with throughput. The fraction of penetrating pores increased due to merging of dead-end and closed pores. Polymer chain flexibility decreased, as did total pore volume, due to relaxation of internal stresses and restructuring of the supermolecular organization: compacting the polymer and decreasing pore volume. Figures 4, references 12: Russian.

UDC 541.182:578.083.2

Aggregation of A1 Influenza Viruses in NaCl Solutions

18410060b Moscow *KOLLOIDNYY ZHURNAL*
in Russian Vol 50 No 5 Sep-Oct 88 (manuscript received
25 Jun 86) pp 848-854

[Article by Ye. V. Golikova, L. M. Molodkina, D. G. Selentev, V. M. Kolikov, and Yu. M. Chernoberezhskiy, Leningrad Polytechnical Institute, Leningrad University]

[Abstract] Results are presented from a study of dispersions of A/Leningrad/54/1 influenza virus in NaCl solutions. The stability and coagulation of the dispersions were studied by ultramicroscopy based on direct counting of the number of particles in the system. The data indicate that the aggregation resistance of the virus results from ion-electrostatic and structural forces of repulsion. Increasing the electrolyte concentration significantly decreases these forces. The aggregation of

charged and uncharged virus particles is reversible, due largely to the stabilizing effect of the virion hydrate shells. Figures 4, references 35: 21 Russian, 14 Western.

UDC 678.0.21.6:535.36

Study of Latex Coagulation by Dynamic Light Scattering

18410060c Moscow *KOLLOIDNYY ZHURNAL*
in Russian Vol 50 No 5 Sep-Oct 88 (manuscript received
15 Jul 86) pp 864-872

[Article by V. V. Klyubin, L. A. Kruglova, and V. N. Sokolov, All-Union Scientific Research Institute of Synthetic Rubber imeni S. V. Lebedev]

[Abstract] The dynamic light-scattering method was used to study the process of coagulation of monodispersed polystyrene latexes. The capabilities of the method were analyzed, and the characteristics in question were compared with quantities determined by turbidity measurement. Dynamic light scattering can be used to monitor changes in particle size distribution during coagulation. The influence of latex concentration on the coagulation rate was studied with various KVI concentrations. It was found that more concentrated latexes coagulated more rapidly. The maximum coagulation rate increased in proportion to the latex concentration. Figures 5, references 21: 10 Russian, 11 Western.

UDC 661.632.1

Thermodynamic Analysis of Behavior of Arsenic in Process of Producing Phosphorus

18410055f Leningrad *ZHURNAL PRIKLADNOY KHIMII*
in Russian Vol 61 No 8 Aug 88 (manuscript
received 24 Feb 88) pp 1907-1909

[Article by E. E. Shpayzer, A. P. Melnik, V. A. Yershov, M. P. Tyunni, and M. R. Konevskiy]

[Abstract] The method of thermodynamic analysis, based on the principle of the maximum entropy of an isolated system at equilibrium, was used to study the behavior of arsenic in the complex multicomponent phosphate-silicate system used in the electrothermic production of phosphorus. The essence of the method lies in the combined use of a of LaGrange equation system consisting of expressions for the entropy of the gas phase, condensed solutions, and individual condensed phases and state equations for ideal gases and expressions for full internal energy, material balance, normalization, and electroneutrality of the isolated system. Computer solution of the equations indicates that, in the production of phosphorus from natural phosphates, arsenic is reduced at lower temperatures than is phosphorus. Dearsenization of the phosphate raw material is thermodynamically favored in the process of

agglomeration of the crushed phosphorite. Ferrophosphorus is present in one of the condensed phases of the multicomponent reacting system during agglomeration of crushed phosphorite. Figure 1, references 10: Russian.

UDC 678.01.046:678.023.3

**Interaction of Polymers With Mineral Fillers
During Joint Dispersion**

18410060d Moscow KOLLOIDNYY ZHURNAL
in Russian Vol 50 No 5 Sep-Oct 88 (manuscript received
26 Aug 86) pp 873-879

[Article by V. A. Kuznetsov, T. A. Khasanova, D. M. Sakov, A. G. Lipson, and S. N. Talstaya, Institute of Physical Chemistry, USSR Academy of Sciences, Moscow]

[Abstract] A study examined the influence of the nature of the polymer modifier on mechanochemical grafting of polymers as filler-polymer systems are dispersed and the mechanism of the process. The active state of the freshly formed surface of the polymer particles as they are broken and the active state of the freshly formed surface of mineral filler particles resulting from the electrophysical processes accompanying breakdown were both considered. Modifiers included a number of powder polymers with and without active functional groups. The presence or absence of functional groups was found to have a significant influence on the effectiveness of mechanochemical grafting of the polymers onto the filler surfaces. A possible mechanism is suggested for the process, which includes radical and ionic mechanisms. The processes of irreversible interaction of nonfunctional and carboxyl-containing polymers is found to differ significantly. Functional groups increase the effectiveness of polymer grafting. Figures 3, references 17: 14 Russian, 3 Western.

UDC 541.18.04:614.77

**Relationship of Colloid-Chemical and Hygienic
Characteristics of Surfactants Contaminating
Bodies of Water**

18410060e Moscow KOLLOIDNYY ZHURNAL
in Russian Vol 50 No 5 Sep-Oct 88 (manuscript received
11 Sep 86) pp 985-988

[Article by V. V. Bocharov and Yu. F. Peregudin, All-Union Surfactants Scientific Research and Planning Institute, Shebekino]

[Abstract] The purpose of this work was to develop a physicochemical method of determining the limiting

concentrations of surfactants in reservoirs and biological purification systems. The relationship between the concentration at which a densely packed adsorption monolayer of surfactant molecules is formed at the water-air interface and the maximum permissible concentration is investigated. Experiments were also performed on the biological decomposition of surfactants by adapted active silt in aeration and settling tank models. Surfactants were found to cause degradation of good forms of indicator microorganisms and deterioration of purification characteristics. The toxicity parameters of the surfactants were found to be related to the concentration at which maximum adsorption at the water-air interface is achieved, with the appearance of micelles in the volume of the solution. It is recommended that the biological decomposition capability of surfactants be determined at volumes producing equal effective loads on the active silt. Figure 1, references 8: 7 Russian, 1 Western.

UDC 678.01:537.311

**Mechanism of Conductivity of Nickel
Powder-Filled Polymer Compositions**

18410060f Moscow KOLLOIDNYY ZHURNAL
in Russian Vol 50 No 5 Sep-Oct 88 (manuscript received
14 Jul 86) pp 1003-1006

[Article by G. V. Kozlov and T. D. Pryamova, Institute of Physical Chemistry, USSR Academy of Sciences, Moscow]

[Abstract] A special study was performed to refine the concept of "direct contact" of nickel particles in conductive polymer compositions and the mechanism of conductivity of these compositions. The electrical contact between particles was modeled by two nickel electrodes (one needle shaped, the other a plate) and by measurement of the contact resistance as a function of compressive force between the electrodes. It is found that the conductivity is strictly metallic in nature and results from the formation of metallic conductivity bridges between filler particles. The dropping R-U characteristic of the compositions may result not only from the tunnel mechanism of conductivity but also from welding of contacting particles in the compositions. Figures 3, references 6: 4 Russian, 2 Western.

UDC 541.095

Detonation—Solid-Phase Chemical Reaction

18410054b Moscow DOKLADY AKADEMII NAUK
SSSR in Russian Vol 302 No 3 Sep 88 (manuscript
received 29 Jul 88) pp 630-634

[Article by Academician N. S. Yenikolopyan, Institute of
Synthetic Polymer Materials, USSR Academy of Sci-
ences, Moscow]

[Abstract] Experimental results from a study of solid-
phase chemical reactions have revealed that it is possible
to excite a detonation wave in solids without a gas phase
being present. What is more important, it is possible to
do so at low temperatures. Experiments were performed

at room temperature by using Bridgman anvils at 10-20
kbar. The study showed that all types of chemical reac-
tions characteristic for organic and inorganic substances
occur at a certain critical pressure, which increases with
decreasing thickness. Reactions occur at speeds much
higher than in the liquid phase and are independent of
temperature. Metallothermic reactions in which the
reaction products are also solid were studied and
revealed the formation and propagation of powerful
detonation waves in solids at room temperatures without
the formation of gaseous products. The phenomenon of
solid-phase detonation may relate directly to processes
occurring deep in the earth, including mineral forma-
tion, earthquake generation, volcanic activity, etc. Fig-
ures 3, references 6: Russian.

UDC 669.337

Electrocrystallization of Copper in Sulfate Electrolytes Under Nonsteady Current Conditions

18410040b Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 61 No 7 Jul 88 (manuscript received 19 Jul 87) pp 1485-1488

[Article by I. V. Zauzolkov, V. V. Puzakov, V. L. Rudenko, A. I. Barg, and O. M. Zotkov, Urals Copper Industry Scientific Research and Planning Institute]

[Abstract] Experiments were conducted in an electrochemical cell with intensive agitation of the electrolyte, which was heated to 60°C and contained the following: 40-45 g/l copper (in the form of Cu^{2+}), 25 g/l nickel (in the form of Ni^{2+}), and 130-140 g/l sulfuric acid. The cathodic polarization was measured by a potentiometer, and the polarization-time variation was measured during eight periods of pulsed or reversed current. The reversed and pulsed currents were found to influence the cathodic polarization. The pauses in the pulsed current mode decrease the concentration polarization; the reversed current increases the cathodic depolarization in direct proportion to the reverse current and time. Non-steady currents decrease the grain size of the precipitate of the copper crystallizing from the electrolyte. Dissolution of the cathodic sediment during current reversal and surface equalization during current pauses further reduce grain size. When surfactants are added, fine crystalline cathodic copper deposits are formed by increasing the copper segregation overvoltage and creating a smoothing effect at the sediment-electrolyte interface. Figures 3, references 5: Russian.

UDC 541.13:620.193

Laser Activation of Nickel Electrode

18410076a Moscow ELEKTROKHIMIYA in Russian Vol 24 No 9, Sep 88 (manuscript received 13 Jan 87) pp 1176-1180

[Article by I. O. Yefimov, A. G. Krivenko, and V. A. Benderskiy, Institute of Power Generation Problems in Chemical Physics, USSR Academy of Sciences, Moscow]

[Abstract] A study was conducted on the kinetics of hydrogen evolution and nickel dissolution after treating a nickel electrode with nanosecond laser pulses, with intensities from 10 to 100 MW/cm^2 . The 530-nm secondary harmonic of a neodymium laser was used. Metal evaporation did not occur below 100 MW/cm^2 laser intensity. Laser irradiation accelerated nickel dissolution by a factor of 10^2 to 10^3 . The maximum current was achieved at 0.2 V above the corrosion potential, independent of preliminary passivation or solution composition. The impulse current was the same in acidic, neutral, or basic solution. In basic solution, oxygen evolution was intensified after laser irradiation. Nickel dissolution and hydrogen evolution currents were 1 A/cm^2 , independent of preliminary passivation. In the

corrosion potential area hydrogen evolution was observed at times below 10^{-4} seconds and metal dissolution at times above 10^{-4} seconds. Local copper deposition occurred when cathode overvoltage was reduced. Electrode surface heating was calculated not to exceed 6°. The data indicate that the acceleration of electrode processes observed is connected with relaxation over time of plastic deformation in the surface layer of the metal. Figures 5; references 12: 6 Russian, 6 Western.

UDC 620.193

Laser Activation of Metallic Electrodes

18410076b Moscow ELEKTROKHIMIYA in Russian Vol 24 No 9, Sep 88 (manuscript received 7 Dec 87) pp 1181-1186

[Article by I. O. Yefimov, A. G. Krivenko, and V. A. Benderskiy, Institute of Energetic Problems in Chemical Physics, USSR Academy of Sciences, Moscow]

[Abstract] Laser activation of anode dissolution was studied in Pb, Zn, Al, Ni, Ti, W, and Ta electrodes after nanosecond laser pulsed irradiation with a peak power up to 60 MW/cm^2 . All electrodes exhibited similar current rises after irradiation and subsequent current drops that were linearly proportional to the inverse time. The time of current drop from the maximum to 0.1 Amp/cm^2 ranged from 0.025 msec for Ta to 1.2 milliseconds for Pb. The irradiation power was below what caused metal evaporation. The metal dissolution rate was linearly proportional to the radiation power. The power yield ranged from 7×10^{-6} cal/J for Ta to 4×10^{-3} for Pb. At intensities above 60 MW/cm^2 , interrupted current signals were observed for both anodic (metal dissolution) and cathodic (hydrogen evolution) potentials. These interruptions were connected with bubble formation at the irradiated surface. For all electrodes, relaxation times greatly exceeded cooling times, with identical kinetic curves for passivated and active electrodes. This appears to be connected with radiation rendering the metal amorphous and causing the development of stress compression. The laser irradiation lowers the activation energy of this process while conserving the charge retardation mechanism. Figures 7; references 13: 9 Russian, 4 Western.

UDC 541.138.3

Cathodic Polarization of Solid Germanium in Sodium-Containing Melts

18410076a Moscow ELEKTROKHIMIYA in Russian Vol 24 No 9, Sep 88 (manuscript received 6 Aug 87) pp 1251-1252

[Article by Ye. B. Klebanov, A. G. Morachevskiy, O. N. Gorobetz, and I. I. Shibalovskaya, Leningrad Polytechnical Institute imeni M. M. Kalinin]

[Abstract] The thermodynamics of introducing fused electrolyte sodium into a solid germanium cathode were studied. Pulse galvanostatic polarization curves at 823°

were recorded in argon. The sodium separation zone with Ge melt formation was from 0.04 to 2.5 A/cm² current density, with electrode potential shift from -3.070 V to -3.125 V. The polarization curves had two vertical portions, one at each potential, independent of electrolyte composition. The -3.070 V area represents Ge + GeNa; the -3.125 V area represents GeNa + GeNa₃. These potentials show good agreement with the horizontal portions of the separation curves. The sodium separation potential was found to be -3.400 V, leading to calculated Gibbs free energy changes of -31.8 kJ/mole and -84.9 kJ/mole for GeNa and GeNa₃, respectively. Figures 1; references 4: 3 Russian, 1 Western.

UDC 541.138.3

Selective Ion Emission From Solutions

18410076d Moscow ELEKTROKHIMIYA in Russian
Vol 24 No 9, Sep 88 (manuscript received 27 Feb 86,
after revision 3 Feb 88) pp 1251-1255

[Article by A. A. Kazarov, E. A. Arzumanyants, and N. K. Revazyan, Severo-Ostinskiy State University imeni K. L. Khetagurov, Ordzhonikidze]

[Abstract] Selective ion fractionation from solutions was studied at atmospheric pressure and in a rotary evaporation apparatus. The solutions were carefully purified to remove all surface-active organic impurities by using specially purified activated carbon. For LiCl in water, the coefficient of fractionation was about 1.5, independent of the logarithm of initial electrolyte concentration, while the concentration of both ions in the condensate increased slightly, linearly, from 0.2 to 0.3 mg/L for Cl⁻ and from 0.025 to 0.075 mg/L for Li⁺. The initial electrolyte concentration was between 0.05 M and 5 M. For RbNO₃, K₂SO₄, CSNO₃, Na₂SO₄, and LiCl in dimethyl formamide, the fractionation coefficients were 4.4, 0.8, 2.0, 1.38, and 0.37, respectively. This ion enrichment of the condensate is caused by the transfer of solvated ions into the vapor phase. This is influenced by the properties of the solution surface, ion solvation energy, and solvated ion surface activity. The generation of natural systems involving charge nonequilibrium during evaporation and condensation could play an important role in atmospheric pollution and world hydrochemistry. Figures 1; references 11: 10 Russian, 1 Western.

UDC 541.138.3

Electrochemical Reduction of Nitric Acid at Brass

18410076e Moscow ELEKTROKHIMIYA in Russian
Vol 24 No 9, Sep 88 (manuscript received 28 Feb 86,
after revision 3 Feb 88) pp 1255-1259

[Article by V. I. Kichigin, A. V. Pevneva, and I. M. Gimasheva, Perm State University imeni A. M. Gorki]

[Abstract] The mechanism of the cathodic processes that occur at a brass wire electrode was studied by using analysis of the frequency characteristics of impedance

and polarization curves. At cathodic potentials of -0.1 to -0.2 V, the resistances determined from the capacitance of the double layer and from charge transfer were equal, indicating that the electrode electrochemical reactions were not reversible. At potentials near 0.1 V, the data indicate the presence of relaxation processes with at least three successive stages of differing time characteristics occurring. Multistage processes also occur at more positive potentials. At the more positive potentials, the rate-limiting steps proposed are the reaction of HNO₂ with HNO₃ and the charge transfer reaction of HNO₂ with a hydrogen ion and an electron. Electron transfer is proposed to be rate limiting at more negative potentials. Kinetic calculations exclude mechanisms involving the participation of adsorbed molecular hydrogen. Figures 2; references 11: 6 Russian, 5 Western.

UDC 621.357.7:669.745:5776

Electrodeposition of Manganese-Zinc-Selenium Alloy

18410076f Moscow ELEKTROKHIMIYA in Russian
Vol 24 No 9, Sep 88 (manuscript received
22 May 87) pp 1262-1264

[Article by A. A. Shulchyus, G. I. Buynyavichene, and B. B. Stulpinas, Kaunaskiy Polytechnical Institute imeni A. Sneckkus]

[Abstract] The influence of ammonium selenate in a citrate electrolyte on the electrodeposition of Mn-Zn alloys was studied. Adding ammonium selenate to a zinc sulfate/sodium citrate electrolyte depolarized the cathodic processes by 50-180 mV, depending on the selenate concentration. For a manganese sulfate/sodium citrate electrolyte, selenate increased the polarization slightly. For electrolyte containing both Mn and Zn, selenate acted as a depolarizer at low current densities, whereas at current densities of 2-3 A/dm² selenate increased the polarization 50-100 mV. Increasing selenate concentrations decreased the polarization. The maximum alloy yield and manganese concentrations were obtained at 0.5 g/L selenate. At 20 A/dm², selenate increased the yield from 22 percent to 75 percent. Zinc enrichment occurred only at 2-3 A/dm²; at higher current densities selenate increased the manganese concentration in the alloy. This may be connected with the retardation of manganese solubility by the products of selenate reduction. The selenium concentration in the alloys ranged from 0.035 to 0.17 percent. Figures 4; references 8: 6 Russian, 2 Western.

UDC 541.183:547

Adsorption of Organic Substances on Silver

18410076g Moscow ELEKTROKHIMIYA in Russian
Vol 24 No 9, Sep 88 (manuscript received
29 Nov 87) pp 1273-1275

[Article by Ye. A. Nechayev, V. P. Kuprin, and T. N. Avdiyenko, Dneprovsk Chemical Technology Institute imeni T. E. Dzerzhinskiy]

[Abstract] The adsorption of various organic compounds with ionization potentials from 7 to 11 eV on silver

powder was studied spectrophotometrically. At 10^{-3} M no adsorption of compounds with ionization potentials of 7-9.5 eV was seen. In 0.1 M NaClO_4 , adsorption was noted for nitrobenzoic acid and dinitrobenzoic acid. n-Nitrobenzaldehyde and dinitrobenzoic acid were adsorbed in 0.1 M AgClO_4 , whereas dinitrotoluene and picric acid were slightly adsorbed. The resonance potential of silver, as calculated from the data, was 8.9 eV. For dinitrobenzoic acid independent of background electrolyte, the second maximum in the absorption-versus-ionization potential curve is connected with the presence

of oxidized areas on the silver surface. The free energy of adsorption, which was calculated from the adsorption isotherms by using the Langmuir equation, was 31.8 kJ/mole for nitrobenzoic acid in NaClO_4 and 34.6 kJ/mole for dinitrobenzoic acid in NaClO_4 . These values are similar to those found for the compounds maximally adsorbed on mercury and bismuth, and greater than those for lead and tin. The resultant sequence corresponds to a number of metals from the standpoint of the degree of the increase in their hydrophilicity. Figures 3; references 13: 11 Russian, 2 Western.

UDC 628.3:543.56:66.067.38

Ultrafiltration Extraction of Organic Pollutants From Printing Plate Production Wastewater

18410040g Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 61 No 7 Jul 88 (manuscript received 22 Oct 87) pp 1615-1617

[Article by K. B. Grekov, N. A. Mortikova, and Ye. G. Rizo, Institute of Motion Picture Engineering, Remstroyproekt Central Planning and Design Bureau]

[Abstract] Membrane fractionation was used to meet the need for local purification of wastewaters from the development of photoresists on printing plates. The solutions were filtered through paper filters, microfiltration membranes with pore sizes of 0.2, 0.5 and 1.0 μm , and acetate-cellulose ultrafiltration membranes plus a polyamide membrane. Settling and paper filtration did not change the characteristics of the solutions. Ultrafiltration purified the solutions sufficiently to allow the filtrates to be biologically purified. The polyamide membrane was found to be preferable due to its greater chemical stability. References 7: Russian.

UDC 628.54:547.673.1

Determination of Anthraquinone in Wastewaters From Paper and Pulp Production

18410051E Riga KHIMIYA DREVESINY in Russian No 4 Jul-Aug 88 (manuscript received 16 Jun 87) pp 62-63

[Article by Ye. S. Burlak, V. N. Piyalkin, and D. B. Bolotin, All-Union Cellulose and Paper Industry Scientific Production Association]

[Abstract] Anthraquinone was determined in wastewaters by using gas-liquid chromatography. The method developed for gas-chromatographic determination of anthraquinone in wastewaters by using an electron-capture detector has acceptable accuracy and reproducibility. It is now being used for monitoring purposes in production. With slight modifications, the method could also be used to analyze alkali and cellulose. Figures 2, references 8: 4 Russian, 4 Western.

UDC (546.3:663.7):551.464

Extraction of Heavy Metals From Natural Waters by Surface Petroleum Films

18410055c Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 61 No 8 Aug 88 (manuscript received 25 Jun 86) pp 1867-1871

[Article by N. N. Osipov and A. K. Charykov, Leningrad State University]

[Abstract] An experimental study examined the distribution of iron, copper, lead, and cadmium between model natural water solutions and surface petroleum films. The

influence of pH and mineralization of the water on the process is studied. The rate of saturation of the organic phase with each metal was found to be constant for all petroleum products tested. Saturation with copper took the longest time, with iron taking the shortest time, and lead and cadmium occupying an intermediate position. The influence of pH on the distribution of metals indicates that the mechanism of transition of the metals to the organic phase is at least partially a cation-exchange mechanism. The concentration of heavy metals by surface films makes the effects of petroleum contamination worse for natural bodies of water. Figures 4, references 14: 13 Russian, 1 Western.

UDC [630*867.7.6:661.731-967.1]:628.51

Determination of Acetic Acid in Gas Effluents of Wood Chemical Plants

18410057b Moscow GIDROLIZNAYA I LESOKHIMICHESKAYA PROMYSHLENNOST in Russian No 9, Sep-Oct 88 pp 9-11

[Article by I. Yu. Dmitriyeva, engineer, and V. F. Korytseva, senior scientific associate, TsNILKhI [expansion unknown]]

[Abstract] Trials were conducted with gas-liquid chromatography (GLC) to determine acetic acid in gas effluents so as to evaluate the method's suitability for environmental monitoring at wood chemistry plants. The approach most suitable for the purpose intended consisted of the use of 20 percent polyethylene glycol adipinate on polysorb-1 and detection by flame ionization. In its final version, the GLC was suitable for acetic acid determinations in the range of 0.4 to 1.5 mg/m^3 , with s_r less than 0.16 and a relative error below 1 percent. Studies on the gas effluents from the Dmitriyev and Syavskiy wood chemistry plants showed that the acetic acid concentrations were within the range of 1.29 to 1.36 g/m^3 and within 0.03 to 0.007 g/m^3 in the work areas. Figures 4; tables 1; references 3: 2 Russian, 1 Western.

UDC 504.064:543.3

Chromatographic-Mass Spectrometric Analysis of Water Samples

18410057c Moscow GIDROLIZNAYA I LESOKHIMICHESKAYA PROMYSHLENNOST in Russian No 9, Sep-Oct 88 pp 9-11

[Article by M. T. Dmitriyev, doctor of chemical sciences, A. G. Malysheva, candidate of biological sciences, and Ye. G. Ratyannikov, candidate of chemical sciences, Scientific Research Institute of General and Communal Hygiene imeni A. N. Sysin]

[Abstract] A combined chromatographic-mass spectrometric method was devised to analyze water samples for organic pollutants. The method demonstrated that, without mass spectrometric data, analysis of a sample containing multiple organics is virtually impossible. The

system utilized in this study relied on an LKB-2901 (Sweden) chromat-mass spectrometer coupled with an LKB-2130 data processing system based on a PDP-11/34 computer (United States). The organics were recovered by gas extraction by using highly purified helium. The extraction of chloroform was on the order of 98.2 percent; for other organic compounds, the extraction rate ranged from a low of 30 percent to a high of 100

percent. The analytical accuracy was improved by 1.5 to 2.0 percent with thermostatted water samples, and heating of the samples was necessary for extraction of compounds with molecular masses exceeding 300 to 400 D. The lower end of the detectable concentration of an organic compound was in the 0.1 to 1 $\mu\text{g/liter}$ range, or 10^{-8} to 10^{-7} percent. Figures 1; tables 2; references 6: 3 Russian, 3 Western.

UDC 661.632.72

**Influence of Raw Material Composition on
Processes in Production of Fused Phosphorus-
Magnesium Fertilizers**

*18410055e Leningrad ZHURNAL PRIKLADNOY
KHIMII in Russian Vol 61 No 8 Aug 88 (manuscript
received 14 Jul 87) pp 1881-1884*

[Article by L. P. Lebedeva, V. F. Lagunova, and P. B. Gramov, Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials]

[Abstract] X-ray and crystal optics studies of cooled roasted charges containing about 20 percent P_2O_5 were performed to identify processes occurring when the charges are heated. Mixtures of apatite and calcite (9:1), forsterite and calcite (9:1), and pure forsterite were prepared and studied as well. It was found that increasing the content of calcite in the raw material increases the melting point without reducing the quality of the fertilizers obtained. The quantity of calcite in the raw material must be limited to allow the melting process to be conducted at 1,400-1,450°C. With 20 percent P_2O_5 , the ratio of forsterite to calcite should be at least 2. Figures 3, references 10: 9 Russian, 1 Western.

UDC 546.33.284-145

Modifying Liquid Glass With Inorganic Polymers

18410040c Leningrad ZHURNAL PRIKLADNOY
KHIMII in Russian Vol 61 No 7 Jul 88 (manuscript
received 5 Jan 86) pp 1493-1497

[Article by V. V. Shevchuk, D. M. Kukuy, N. D. Mylnikova, and V. A. Yesepkin, Institute of General and Inorganic Chemistry, Bellsorussian Academy of Sciences]

[Abstract] Water-soluble inorganic sodium polyphosphates, which are mixtures of linear polymer homologues with cyclic and simple phosphates, are promising as modifiers to regulate the properties of sodium silicate solutions used as binders in various areas of technology. The properties of silicate solutions produced in this manner were studied by using physicochemical test methods; determining the viscosity and contact wetting angle; conducting a physicochemical analysis based on IR spectroscopy, differential-thermal analysis, and x-ray-structural analysis; determining the change in the temperature coefficient of linear expansion; and using electron microscopy. The studies indicated that the mechanism of action of sodium polyphosphates on polymer sodium silicate solutions is as follows: a system of inorganic polymers is formed that has a high degree of homogeneity and in which the polymers are interconnected by physical interaction forces at the molecular level. The phosphate polymer grid structures the silicate binder, thereby strengthening it. This binder material can be considered a compound formed of polymers with mutually penetrating lattices. Heat treatment of the composition causes a chemical reaction of the polymers that results from isomorphic replacement of the silicate ions by phosphate ions with the liberation of free quartz and the formation of refractory silicophosphates. The modified silicate binder was introduced at two casting shops in 1985-1986, where it had an economic effect of over 100,000 rubles per year. Figures 2, references 8: Russian.

UDC 666.9.01:541.18

Influence of Mechanical Processing of Ceramic Hydrosuspensions on Their Content of Hydration Products

18410040d Leningrad ZHURNAL PRIKLADNOY
KHIMII in Russian Vol 61 No 7 Jul 88 (manuscript
received 28 Oct 86) pp 1506-1511

[Article by O. M. Rozental and V. M. Goldman, Urals Scientific Research Chemical Institute]

[Abstract] The purpose of this work was to determine the source of stimulation of the hydration process in the dispersed material of a hydrosuspension upon mechanical treatment in a common drum mill and to analyze the kinetics of this process. It is suggested that impact loads experienced by the dispersed-phase particles in the area

of the formation and disappearance of suspension-air-grinding body interfaces stimulate the process of the hydration of the powdered ceramic material. These loads have a pressure of at least 10^8 Pa, which is comparable to the loading of particles in high-energy planetary mills. The system suggested can describe the S-shaped experimental hydration kinetic curves produced. It was discovered that, as the degree of sintering of MgO powder is increased by heating to 750-2,250°C, the duration of its wet mechanical processing increases from tens to hundreds of hours because effective hydration of the material requires an increase in the number of impact loadings per particle of dispersed phase from an average of one to five. Figures 3, references 11: Russian.

UDC 541.11+546.65:546.264

Higher Oxides of Praseodymium and Neodymium

18410047a Moscow ZHURNAL
NEORGANICHESKOY KHIMII in Russian
Vol 33 No 9, Sep 88 (manuscript received
16 Jun 86) pp 2190-2195

[Article by V. D. Savin, A. V. Yelyutin, N. P. Mikhaylova, and Z. V. Yeremenko]

[Abstract] The procurement of previously unknown oxides of praseodymium and neodymium (Pr_2O_5 , Nd_2O_5 , and Nd_6O_{11}) in pure form for the first time was described and discussed. The metals are stable in temperature ranges up to 360°, 300°, and 520°C respectively. Their oxygen, CO_2 , and H_2O content and their diffractometric and basic physicochemical characteristics were determined. Standard oxides of the metals Pr_2O_3 and Nd_2O_3 are unstable and, during storage in air, pass into higher oxides with a combination of excess oxygen and oxygen-containing admixtures. The mechanisms of their thermal dissociation with temperature increase were established. Figures 2; references 3: 2 Russian; 1 Western.

UDC 546.34.713'714

Synthesis of Lithium-Manganese Spinel for Inorganic Ion Exchange Materials

18410047b Moscow ZHURNAL
NEORGANICHESKOY KHIMII in Russian
Vol 33 No 9, Sep 88 (manuscript received
24 Feb 87) pp 2196-2199

[Article by G. V. Leonteva, Turkmen State University imeni A. M. Gorki]

[Abstract] Peculiarities of the synthesis of lithium-manganese spinels were described and discussed. Manganese hydroxides (III, IV) with bernebsite or spinel structures were synthesized by reacting them with soluble reagents. Saturating them with Li^+ ions followed by heating at 105-600°C led to the formation or improvement of their spinel phase structure. Three samples of starting materials were prepared. Heating the samples at 500-600°C

formed a spinel phase that approaches $\text{Li}[\text{Mn}^{3+}\text{Mn}^{4+}]\text{O}_4$ in composition. The reversibility of the exchange of the Li^+ and H^+ in the compound was confirmed by completely substituting the Li^+ ions by H^+ ions while processing the materials with HNO_3 (0.1-0.5 mole/dm³). This produced partial amorphization of the spinel structure and decreased parameter a to 0.005-0.008 nm. Subsequent sorption of Li^+ ions reduced the material's crystallinity a parameter significantly. The slight increase in mean degree of oxidation of manganese (by 0.03-0.08) was attributed to disproportionation of part of the Mn^{3+} ions in the material with subsequent washing out of Mn^{2+} ions in the solution. Ion-exchange materials obtained from the three samples differed only slightly. Figures 3; references 8: 4 Russian; 4 Western.

UDC 546.91:541.49+54-165

Interaction of Metallic Palladium With Chlorocomplexes of Platinum in Aqueous Solutions

18410047c Moscow ZHURNAL
NEORGANICHESKOY KHIMII in Russian
Vol 33 No 9, Sep 88 (manuscript received
21 Jul 87) pp 2328-2332

[Article by N. L. Kovalenko, L. I. Kochubeyeva, N. V. Grizan, V. G. Chumakov, and G. A. Moiseyeva, Institute of Chemistry and Chemical Technology, Siberian Department, USSR Academy of Sciences, Krasnoyarsk]

[Abstract] The temperature range in which PtCl_4^{2-} and PtCl_6^{2-} are reduced by metallic palladium was determined, and the mechanisms of reduction involved were studied by examining the interaction of palladium black with hydrochloric solutions of K_2PtCl_4 and K_2PtCl_6 at 150 and 180°C. Palladium reduced platinum (II) and (IV) with the formation of a continuous series of solid solutions of Pt-Pd. The completeness with which the platinum was reduced depended on the molar ratio of palladium to platinum. Incomplete reduction of platinum (II) was accompanied by the appearance of platinum (IV) in the solution, which was attributed to a disproportionation reaction. Analysis of the characteristics of the solid phase and composition of the solution as a function of temperature, time, and starting composition was discussed. Figures 3; references 12: 11 Russian; 1 Western.

UDC 546.19'23+683'24

Chemical Interaction and Vitrification in $\text{As}_2\text{Se}_3\text{-Ti}_2\text{Te}$

18410047d Moscow ZHURNAL
NEORGANICHESKOY KHIMII in Russian
(manuscript received 14 Jul 87) Vol 33 No 9, Sep 88
pp 2376-2378

[Article by I. I. Aliyev, O. M. Aliyev, G. P. Rustamov, and T. M. Ilyasov, Azerbaijan University imeni S. M. Kirov, Institute of Inorganic and Physical Chemistry, AzSSR Academy of Sciences]

[Abstract] A study examined the interaction of components in an $\text{As}_2\text{Se}_3\text{-Ti}_2\text{Te}$ system by differential thermal

analysis, roentgenographic analysis, microstructural analysis, and measurement of microhardness and density. It was discovered that the section is a quasibinary cross section of a ternary, mutual $\text{As}_2\text{Te-Ti}_2\text{Te-Te}$ system. A new chemical compound having the composition $\text{Ti}_2\text{As}_2\text{Se}_3\text{Te}$, which melts congruently at 415°C, formed in the system. The data obtained made it possible to construct a phase diagram that gives a complete picture of the nature of the chemical interaction between the compounds. Figures 2; references 7: 6 Russian; 1 Western.

UDC 541.123.3+621.315.592

Interaction in $\text{Cu}_2\text{Ge(Sn)Se}_3\text{-HgSe}$ Systems

18410047e Moscow ZHURNAL
NEORGANICHESKOY KHIMII in Russian
Vol 33 No 9, Sep 88 (manuscript received
30 Jul 87) pp 2379-2384

[Article by S. A. Mkrtychyan, E. G. Zhukov, K. Dvletov, A. G. Melikdzhanyan, and S. Nuryev, Physicotechnical Institute, TSSR Academy of Sciences, and Institute of General and Inorganic Chemistry imeni N. S. Kurnakov, USSR Academy of Sciences]

[Abstract] This article describes and discusses a study of the interaction occurring in $\text{Cu}_2\text{Ge(Sn)Se}_3\text{-HgSe}$ systems and a study of the electrophysical characteristics of the phases formed. Phase diagrams of the compounds were constructed. Physicochemical analysis showed the formation of quaternary compounds $\text{Cu}_2\text{HgGeSe}_4$ and $\text{Cu}_2\text{HgSnSe}_4$ in the systems studied. The compounds melted congruently at 1010 and 970 plus or minus 5 K, respectively. At room temperature, 9 molecular percent of Cu_2GeSe_3 and 15 molecular percent of Cu_2SnSe_3 was dissolved in HgSe. The solubility of the mercury selenide was 15 molecular percent in Cu_2Se and 17 molecular percent in Cu_2SnSe_3 . The electrophysical characteristics of the solid solutions were discussed. Figures 5; references 16: 11 Russian; 5 Western.

UDC 543.5.12.012

Physicochemical Analysis of Binary Liquid Systems $\text{A}^{\text{IV}}\text{-Te(A}^{\text{IV}}\text{-Ge, Sn, Pb)}$ Based on Experimental Study of Density

18410047f Moscow ZHURNAL NEORGANICHESKOY
KHIMII in Russian Vol 33 No 9, Sep 88 (manuscript
received 14 Oct 87) pp 2388-2393

[Article by V. M. Glazov, L. M. Pavlova, and A. V. Shishkin, Moscow Institute of Electronic Technology]

[Abstract] The results of an experimental study of the density of melts in $\text{A}^{\text{IV}}\text{-Te}$ systems were presented and discussed. The data obtained were processed together on a computer and compared with all available experimental data dealing with this subject. Using the results made it possible to construct and analyze the density isotherms and the concentration dependence of the coefficient of

volumetric expansion. Conclusions concerning the molecular structure of the melts in the systems studied were formulated and discussed. The possibility of the existence in the melts of Pb-Te and Sn-Te systems of associates of monotellurides was confirmed. The formation of ditelluride associates in the Ge-Te system, in addition to germanium monotelluride associates, was assumed to be possible. The studies indicated an irregular sequence of change in the degree of thermal resistance in the series of compounds PbTe yields SnTe, which yields GeTe. Figures 3; references 21: 20 Russian; 1 Western.

UDC 546.654'21'151+546.34'151:541.123.2

Study of Interaction of Lanthanum Oxiodide With Sodium Iodide, Potassium Iodide, and Rubidium Iodide

18410047g Moscow ZHURNAL
NEORGANICHESKOY KHIMII in Russian
Vol 33 No 9, Sep 88 (manuscript received
28 Oct 87) pp 2394-2399

[Article by A. L. Tupoleva, A. G. Dudareva, A. K. Molodkin, and A. I. Yezhov, University of Friendship of Peoples imeni P. Lumumba]

[Abstract] A study examined LaOI-MI systems, in which M represents Na, K, Rb. The study entailed the following methods: differential thermal analysis, roentgenophase analysis, and crystal-optical analysis. The components formed compounds among themselves. These compounds had the composition $2MxLaOI$ ($M=Na, K, Rb$) and $2RbIx3LaOI$. The compound $2KixLaOI$ melted incongruently at $260^{\circ}C$ and underwent polymorphic transformation at $260^{\circ}C$. The other compounds exist in solid phase and decomposed in the $300-340^{\circ}C$ range. Compounds $2NaIxLaOI$ and $2RbIx3LaOI$ displayed polymorphism at $260^{\circ}C$ and $240^{\circ}C$ respectively. All systems had regions of organic solid solutions based on the starting components. An x-ray phase analysis and the crystal-optical characteristics of the compounds and phases were presented and discussed. Figures 3; reference 1 (Russian).

UDC 543.42:546.882

Raman Spectra of Solid Solutions Based on $Sr_6Nb_2O_{11}$ in System La_2O_3 - SrO - Nb_2O_5

18410047h Moscow ZHURNAL
NEORGANICHESKOY KHIMII in Russian
Vol 33 No 9, Sep 88 (manuscript received
5 Oct 87) pp 2432-2434

[Article by O. Ye. Averkova, V. V. Fomichev, and V. P. Sirotnikin, Moscow Institute of Radio Engineering, Electronics, and Automation, Moscow Institute of Precision Chemical Technology imeni M. V. Lomonosov]

[Abstract] A Raman spectroscopic study of samples of solid solutions forming in an SrO - La_2O_3 - Nb_2O_5 system based on $Sr_6Nb_2O_{11}$ showed that the Raman spectra of

solid solutions with cubic and tetragonal lattice cells have great similarity in the region of achievable vibration frequencies. Figure 1; references 5: 2 Russian; 3 Western.

UDC 541.123.5

Mutual System Consisting of Calcium, Strontium, and Barium Fluorides and Chlorides

18410047i Moscow ZHURNAL NEORGANICHESKOY
KHIMII in Russian Vol 33 No 9, Sep 88 (manuscript
received 18 Mar 87) pp 2434-2437

[Article by G. A. Bukhalova, N. N. Mirsoyanova, Ye. S. Yagubyan]

[Abstract] A simplicial breakdown of a prism with the composition of a quaternary mutual Ca, Sr, Ba[$\{F\}$], Cl system was presented, and a singular star of the system was constructed. The surface of liquidus of three tetrahedron-forming cross sections was studied by the visual-polythermal, thermographic, and roentgenographic methods. The system was confirmed to be isomorphous, with complete interaction of components equal to zero. The system's low-melting regions were determined. Figures 3; references 4: 3 Russian; 1 Western.

UDC 539.213:546.284

Spectroscopic Properties of Two-Coordination Silicon Atoms in Vitreous Silicon Dioxide

18410053 Leningrad FIZIKA I KHIMIYA STEKLA
in Russian Vol 14 No 4 Jul-Aug 88 (manuscript received
20 Jun 86) pp 481-489

[Article by L. N. Skuya, A. N. Streletskiy, and A. B. Pakovich, Solid-State Physics Scientific Research Institute; Latvian State University, Riga; Institute of Chemical Physics, USSR Academy of Sciences, Moscow]

[Abstract] A detailed study is presented of the spectroscopic properties of diamagnetic centers that cause absorption in the B_2 band of vitreous silicon. The properties of the surface and body defects are found to be similar, and it is demonstrated that the model of two-coordination silicon atoms is the only one that satisfactorily explains all the experimental data. A previously unknown band of photoluminescence at 2.65 eV is observed in vitreous SiO_2 that has been irradiated or has an oxygen deficit. This band corresponds to triplet excitation of the center. Luminescence centers with similar characteristics are found on the surface of mechanically activated SiO_2 . The kinetic characteristics are studied, and it is estimated that the strength of the oscillator in the 5.03 eV absorption band is over 0.13.

Photoluminescence polarization measurements indicate that the center has C_{2v} symmetry. Figures 5, references 33: 18 Russian, 15 Western.

UDC 539.2:335.37

Subthreshold Defect Formation in Quartz Glasses Exposed to Ionizing Radiation

18410053b Leningrad FIZIKA I KHIMIYA STEKLA in Russian Vol 14 No 4 Jul-Aug 88 (manuscript received 9 Jun 87) pp 494-500

[Article by G. B. Blinkova, Sh. A. Vakhidov, A. Kh. Islamov, I. Nuritdinov, and Kh. A. Khaydarova, Institute of Nuclear Physics, Uzbek Academy of Sciences, Tashkent]

[Abstract] A study examined the influence of ^{60}Co γ rays at 10^3 - $5 \cdot 10^{10}$ rad and xenon discharge plasma on the optical, IR, and EPR characteristics of commercial glasses as well as in quartz tubes produced by electromelting in a vacuum and in an atmosphere of hydrogen. This was done to determine the reasons for easy defect formation in the quartz shells of gas-discharge tubes. E'-center defects were found in all glass specimens after irradiation. Anionic vacancies and interstitial oxygen ions were also formed in the quartz specimens. All defect centers induced by γ radiation were also created by the xenon discharge plasma, with somewhat different spectral characteristics. The significant disordering of the glass lattice in quartz tubes in comparison to commercial glass yields a large set of weakly coupled atomic states in which the radiation defect formation energy is lower than in the ordered ideal lattice. The breakdown in electron excitation near these states causes effective generation of E'-center defects, non-bridge oxygen atoms, anion vacancies, and interstitial oxygen atoms. Figures 4, references 26: 21 Russian, 5 Western.

UDC 666.113.32

Glass Formation System CuI-Cu₂Se-As₂Se₃

18410053d Leningrad FIZIKA I KHIMIYA STEKLA in Russian Vol 14 No 4 Jul-Aug 88 (manuscript received 14 Nov 86) pp 514-517

[Article by S. B. Rozenkov, A. M. Bolotov, Ye. A. Bychkov, and Yu. G. Vlasov, Leningrad State University imeni A. A. Zhdanov]

[Abstract] A study examined glass formation, the composition of crystalline phases, and the thermal properties of glasses in the system CuI-Cu₂Se-As₂Se₃. Glasses were synthesized by vacuum melting in quartz ampules at not over 0.1 Pa, heating the ampules to 300-400°C for 3-4 hours and 800°C for 8-10 hours, and then quenching in water. Crystalline inclusions were detected and identified by x-ray phase analysis. The homogeneity of the specimens was verified by low-angle x-ray scattering. The maximum concentration of copper iodide in the

glasses was found to be 50 mol. percent in the CuI-As₂Se₃ binary cross section. The main crystallization product was γ -CuI. Increasing the concentration of Cu₂Se causes the appearance of conservative tetrahedral fragments and increases T_g and the crystallization capacity of the glasses. The addition of CuI acts as a glass depolymerizer, decreasing the glass formation temperature as well as the crystallization capacity of the glasses. Figures 4, references 12: 6 Russian, 6 Western.

UDC 666.192:535.349

Variation in Absorption of Quartz Glasses With Titanosilicate Coating as a Function of Temperature

18410053i Leningrad FIZIKA I KHIMIYA STEKLA in Russian Vol 14 No 4 Jul-Aug 88 (manuscript received 14 May 87) pp 614-615

[Article by I. V. Dreval, S. S. Pivovarov, and V. S. Khotimchenko, State Scientific Research Institute of Quartz Glass, Leningrad]

[Abstract] A study examined the temperature-dependent variation of the absorption of quartz glass with a titanium silicate coating. Transmission spectra were measured by a computing spectroscope on specimens heated by radiation from a CO₂ laser. Absorption spectra were measured in the 200-400 nm range. The temperature change in absorption was found to result almost completely from the layer of titanium silicate glass. This indicates that the spectral properties of light filters made of this material must be adjusted to make an allowance for the temperature variation of absorption. Figures 2, references 6: 5 Russian, 1 Western.

UDC 666.11.01

Change in Index of Refraction Upon Ion Exchange Mutual Diffusion in Alkaline Silicate Glasses Containing Niobium and Tantalum Oxides

18410053j Leningrad FIZIKA I KHIMIYA STEKLA in Russian Vol 14 No 4 Jul-Aug 88 (manuscript received 10 Sep 87) pp 626-627

[Article by V. Ya. Livshits, Ye. A. Marchuk, G. O. Karapetyan, and Yu. G. Korolev, Leningrad Technological Institute of the Cellulose and Paper Industry]

[Abstract] A study examined the possibility of changing the index of refraction of glasses in the system $R_2O-R_2O_5-SiO_2$ (where $R_2O=Li_2O+Na_2O$, while $R_2O_5=Nb_2O_5$ and Ta_2O_5) by ion exchange from lithium and sodium salt melts. It was found that decreasing the Nb₂O₅ content from 19 to 15 mol. percent and introducing Ta₂O₅ as a supplementary component at 3 mol. percent results in a decrease in the absolute value of the index of refraction from 14 to $12 \cdot 10^{-4}$ (mol. percent)⁻¹. The change the refraction index that occurs during the

lithium (glass)—sodium (melt) exchange reaches $500 \cdot 10^4$. The results indicate that alkaline silicate glasses with Nb_2O_5 and Ta_2O_5 can be used as effective initial ion exchange matrices for gradient optical glasses. Reference 1: Russian.

UDC

[666.01:548.5+666.11.01:532.13]:[666.123.32+666.123.35]

Estimating Maximum Linear Crystal Growth Rate In Sodium-Silicate System. Report 1

18410052a Alma-Ata IZVESTIYA AKADEMII NAUK KAZAKHSKOY SSR: SERIYA KHIMICHESKAYA in Russian No 5 Sep-Oct 88 (manuscript received 20 Jul 87) pp 5-10

[Article by L. N. Sheludyakov and T. A. Dyshlova, Institute of Chemical Sciences, Kazakh Academy of Sciences, Alma-Ata]

[Abstract] A study was conducted to determine the applicability of available methods for computing the maximum crystallization rate of glasses (supercooled melts) in the binary system $\text{Na}_2\text{O-SiO}_2$, which is a part of the more complex multicomponent systems used in practice. Studies were performed on glasses containing an alkaline oxide as the modifying agent. The maximum linear crystal growth rate in the system is estimated. Systematic deviations of the values of the maximum growth rate calculated from experimental data are noted for compositions in the phase field of cristobalite. They exceed the permissible level of error significantly. These deviations probably result from the influence of factors not considered by the authors in computing the crystallization parameters or are caused by changes in the constants used in the equation due to a complication of the anionic structure of the melts. Figures 2, references 17: 14 Russian, 3 Western.

UDC

[666.01:548.5+666.11.01:532.13]:[666.123.32+666.123.35]

Estimating Maximum Crystallization Rate in Systems $\text{Na}_2\text{O-SiO}_2$ and $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$. Report 2.

18410052b Alma-Ata IZVESTIYA AKADEMII NAUK KAZAKHSKOY SSR: SERIYA KHIMICHESKAYA in Russian No 5 Sep-Oct 88 (manuscript received 20 Jan 86) pp 10-16

[Article by T. A. Dyshlova and L. N. Sheludyakov, Institute of Chemical Sciences, Kazakh Academy of Sciences, Alma-Ata]

[Abstract] Studies of the crystallization capacity of sodium-silicate glasses containing up to 45 molecular

percent of sodium oxide have shown a systematic and significant deviation in the experimental values of the maximum linear growth rate from the calculated values. This article compares the values of viscous flow and crystallization activation energy over a broad range of compositions. It is found that the deviation in the maximum linear growth rate results from an inconsistency of assumptions concerning the equality of viscous flow and crystallization activation energy used to derive the equations of the kinetic theory of crystal growth. An equation is suggested that can be used to refine the estimate of the crystallization capacity in the system for compositions with an anion structure coefficient of less than 2.35. Considering the error in $\log C$ at low values of the coefficient results in a 1.7-fold decrease in the error of estimating the maximum crystallization rate. Figures 5, references 10: 4 Russian, 6 Western.

UDC 537.312.62+546.562+536.421.1

Phase Transformation Of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\sigma}$ at 1,000-1,300°C

18410054a Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 302 No 3 Sep 88 (manuscript received 31 May 88) pp 626-630

[Article by R. G. Grebenshchikov, G. A. Mikirticheva, O. G. Chigareva and D. P. Romanov, Institute of Silicate Chemistry imeni I. V. Grebenshchikov, USSR Academy of Sciences, Leningrad]

[Abstract] A study examined the phase transformations occurring upon the melting of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\sigma}$ in air by annealing and quenching in the 950-1,300°C interval with holding times of 10 minutes to 24 hours. The compound was produced by ceramic technology at 920°C from a mixture of the initial components Y_2O_3 , $\text{Ba}(\text{NO}_3)_2$, and CuO . The process of incongruent melting of the compound, accompanied by partial reduction of copper to the univalent state, is complicated by a number of chemical transformations. At 1,260°C, full melting of the products of thermal decomposition of the compound occurs. The mechanism of the compound's decomposition occurs in the same sequence as its formation in solid-phase synthesis, with a number of intermediate reactions involving the blue phase and BaCuO_2 . The chemical interaction of Y_2BaCuO_5 with a melt rich in CuO (Cu_2O), which causes crystallization of YCu_2O_5 , is established for the first time and must be considered in studies of the phase relationships in the ternary system $\text{Y}_2\text{O}_3\text{-BaO-CuO}$ (Cu_2O). Figures 2, references 15: 3 Russian, 12 Western.

UDC 547.1'13

Synthesis of Triphenylbismuth Diacylates

18410046n Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 9 Sep 88 (manuscript
received 6 Oct 87) pp 2170-2171

[Article by V. A. Dodonov, A. V. Gushchin, and M. B. Yezhova, Gorkiy State University imeni N. I. Lobachevskiy]

[Abstract] It has been suggested that the reaction of triphenylbismuth with tert-butylhydroperoxide and carboxylic acid anhydrides produces triphenylbismuth diacylates. In the case of a reagents' reaction with acetic anhydride, the reaction was performed at room temperature in ether with equal quantities of the reagents. The reaction yielded tert-butyl alcohol and crystalline triphenyl bismuth diacetate. It had a melting point of 184°C and a 65 percent yield after 90 hours. References 6: 3 Russian, 3 Western.[]

UDC 547.279.8+546.265.8

New Direction of Dimethyldiselenide Thermolysis

18410046o Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 9 Sep 88 (manuscript
received 23 Feb 88) pp 2171-2172

[Article by L. A. Ostroukhova, N. A. Korchevin, E. N. Deryagina, and M. G. Voronkov, Irkutsk Institute of Organic Chemistry, Siberian Division, USSR Academy of Sciences]

[Abstract] The main liquid product of the thermolysis of dimethyldiselenide at 470°C and atmospheric pressure in a current of nitrogen is carbon diselenide. A reaction mechanism is suggested that includes the initial breaking of the C-Se bond of the dimethyldiselenide. The intermediate product of the reaction is diselenairane. Zinc dimethyldiselenocarbamate is formed when CSe₂ is reacted with diethylamine, alkali, and then zinc chloride. Selenophene is formed in addition to carbon diselenide. The selenophene is apparently the product of the condensation of vinylselenol. In the presence of acetylene, dimethylselenide is converted to selenophene with a yield of 95 percent. References 4: 2 Russian, 2 Western.

UDC 547.41:547.341

Synthesis of Vinyl Phenyl Phosphinic Acid Derivatives

18410046a Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 9 Sep 88 (manuscript
received 7 Jan 87) pp 1962-1967

[Article by T. A. Mastryukova, N. V. Mashchenko, I. L. Odinets, and M. I. Kabachnik, Institute of Heteroorganic Compounds imeni A. N. Nesmeyanov, USSR Academy of Sciences, Moscow]

[Abstract] An attempt was made to develop a simple method for synthesizing O-ethylvinylphenyl phosphinate from phenyldichlorophosphine. Particular attention was paid to the individuality and purity of the substances produced. Analysis of the ^1H and ^{31}P NMR spectra of the compound's intermediate synthesis products indicates that the method developed has a high yield. References 13: 7 Russian, 6 Western.

UDC 547.241+547.26'118

Imide-Amide Regrouping of β -Chloroethyl Esters of Phosphorus Acid N-Phenyl Imides

18410046b Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 9 Sep 88 (manuscript
received 18 May 87) pp 1967-1973

[Article by T. A. Mastryukova, N. V. Mashchenko, I. L. Odinets, P. V. Petrovskiy, and M. I. Kabachnik, Institute of Heteroorganic Compounds imeni A. N. Nesmeyanov, USSR Academy of Sciences, Moscow]

[Abstract] While studying the reaction of β -chloroethyl esters of alkyl- and arylphosphonous and phosphorous acids with phenyl azide, the authors observed that the noncatalytic regrouping of the N-phenyl imides of these acids into the corresponding N-phenyl-N- β -chloroethyl amides occurred in an unusually easy manner. The regrouping was studied in more detail by investigating the kinetics of the regrouping of imides into amides at 20-100°C. The imide esters formed are easily hydrolyzed to form the corresponding phenyl acid amides. The great facility of imide-amide regrouping results from the presence of the β -chloroethyl ester group. Regrouping is a first-order reaction. Its probable mechanism is suggested. Figure 1, references 14: 12 Russian, 2 Western.

UDC 547.1:541+547.538.141

Phosphinotricine and Its Analogues (I. Synthesis and Equilibrium CH-Acidity of N-Benzylidene Amino Alkyl (Aralkyl) Carboxylic Acid Esters)

18410046c Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 9 Sep 88 (manuscript
received 15 Feb 88) pp 1973-1979

[Article by N. V. Mashchenko, A. G. Matveyeva, I. L. Odinets, Ye. I. Matrosov, E. S. Petrov, M. I. Terekhova, A. K. Matveyev, T. A. Mastryukova, and M. I. Kabachnik, Institute of Heteroorganic Compounds imeni A. N. Nesmeyanov, USSR Academy of Sciences, Moscow]

[Abstract] A number of Schiff bases produced from parasubstituted benzaldehydes and α -amino acid esters

were synthesized, and their CH acidity was studied in dimethyl sulfoxide. The composition and structure of the substances obtained were confirmed by elemental analysis and spectral studies. The equilibrium CH acidity of the esters was determined by an indicator method in DMSO. The constants $\sigma^*(\text{CH})$ and $\sigma^*(\text{CH}_2)$ were computed for several benzylidene-amide groups. References 23: 10 Russian, 13 Western.

UDC 541.623+547.341+547.544.3

Prototropic Phosphoryl-Oxylide Tautomerism. III. Influence of Substituents at Phosphorus Atom on Position of Tautomer Equilibrium in Tosyl-Substituted (Phosphoryl Methyl) Triphenyl Phosphonium Salts

18410046d Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 9 Sep 88 (manuscript
received 2 Mar 87) pp 1980-1986

[Article by O. V. Bykhovskaya, I. M. Aladzheva, P. V. Petrovskiy, T. A. Mastryukova, and M. I. Kabachnik, Institute of Heteroorganic Compounds imeni A. N. Nesmeyanov, USSR Academy of Sciences, Moscow]

[Abstract] A study examined of the influence of the type of substituent in the phosphoryl group on the position of tautomer equilibrium in phosphoryl-oxylide systems. A number of tosyl-substituted (phosphoryl methyl) triphenyl phosphonium salts were synthesized, and their behavior in solutions was studied for this purpose. The structure of the tosyl-substituted (phosphoryl methyl) triphenyl phosphonium salts in the crystalline state was found to be significantly determined by the ability of the anion to form hydrogen bonds with the oxylide hydroxyl group. The studies established that the nature of the substituents at the phosphoryl phosphorus atom in (phosphoryl methyl) triphenyl phosphonium salts has a significant influence on the position of the phosphoryl-oxylide tautomer equilibrium. It was also established that the electron influence of the substituents and steric factors are important. Electronegative substituents shift the equilibrium in the direction of the CH form. Figure 1, references 11: 7 Russian, 4 Western.

UDC 541.623-543.422.25+547.241+548.737

Prototropic Phosphoryl-Oxylide Tautomerism. IV. Synthesis and Structure of Phosphoryl-Substituted (Carboethoxymethyl) Triphenyl Phosphonium Salts

18410046e Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 9 Sep 88 (manuscript
received 12 Aug 87) pp 1987-1997

[Article by I. V. Leonteva, I. M. Aladzheva, T. A. Mastryukova, P. V. Petrovskiy, V. V. Negrebetskiy, M. Yu. Antipin, Yu. T. Struchkov, and M. I. Kabachnik, Institute of Heteroorganic Compounds imeni A. N. Nesmeyanov, USSR Academy of Sciences, Moscow]

[Abstract] A detailed study is presented of a number of phosphoryl-substituted (carboethoxymethyl) triphenyl phosphonium salts. It was found that in the crystalline

state they exist in the oxyilide form, phosphoryl form, or BHB⁺ complex, depending on the nature of the anion. X-ray structural analysis was used to determine the structure of the complex solved in which the cation has a dimer structure with a strong H bond stabilizing the OH-ilide form. A tautomer equilibrium occurs in solutions of the salts. Its position depends on the substituents at the phosphorus atom, the anion, the solvent, and the temperature. Formation of H bonds with the anion and solvent and the presence of phenyl substituents in the phosphoryl group tend to stabilize the OH (B) form. Figures 2, references 18: 14 Russian, 4 Western.

UDC 541.623+547.421+543.422.25+548.737

Prototropic Phosphoryl-Oxyilide Tautomerism. V. Influence of Substituents at Carbon Atom on Structure and Tautomer Equilibrium of

(Phosphorylmethyl) Triphenyl Phosphonium Salts
18410046f Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 9 Sep 88 (manuscript
received 6 Apr 88) pp 1998-2011

[Article by O. V. Bykhovskaya, I. V. Leontyeva, I. M. Aladzheva, P. V. Petrovskiy, M. Yu. Antipin, Yu. T. Struchkov, T. A. Mastryukova, and M. I. Kabachnik, Institute of Heteroorganic Compounds imeni A. N. Nesmeyanov, USSR Academy of Sciences, Moscow]

[Abstract] A study examined the influence of groups that are attached to the central carbon atom and that differ in their acidifying effect on the position of the prototropic tautomer phosphoryl-oxyilide equilibrium. In addition to the previously studied tosyl and carboethoxy derivatives, triphenylphosphonium and diethylcarbomoyl derivatives were synthesized and studied. It was found that, depending on the nature of the electron-acceptor substituent, the salts produced exist in the crystalline state in the oxyilide form, in the phosphoryl CH form, or as BHB⁺ complexes. X-ray structural analysis is used to determine the structure of the perchlorate, which is stabilized by a strong hydrogen bond between the cation and water molecule. The substituent at the carbon atom in the salts synthesized has a decisive influence on prototropic phosphoryl-oxyilide tautomer equilibrium, shifting it in the direction of the oxyilide OH form as the electron-acceptor properties of the substituent increase. Figure 1, references 18: 12 Russian, 6 Western.

UDC 547.241

N- and C-Phosphoro (III)-Substituted Azomethine Derivatives and Their Regrouping

18410046g Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 9 Sep 88 (manuscript
received 27 Apr 87) pp 2031-2038

[Article by Z. S. Novikova, M. M. Kabachnik, and I. F. Lutsenko, Moscow State University imeni M. V. Lomonosov]

[Abstract] In order to synthesize isomer N- and C-phosphoro (III)-substituted azomethine derivatives, the authors studied the reaction of trivalent phosphorus acid

halides with a number of azomethines of various structures containing primary, secondary, or tertiary α -carbon atoms as well as a tert-butyl group at the nitrogen atom. Halogen phosphites and phosphines were reacted with the azomethines. It was found that dialkyl and tetraethyl diamidochlorophosphites react with azomethines containing primary or secondary α -carbon atoms in the presence of triethylamine to form N-phosphoro (III)-substituted enamines (III). Regrouping of N-phosphoro-substituted enamines containing alkyl groups at the phosphorus atom was observed and yielded C-phosphoro (III)-substituted azomethines. References 8: Russian.

UDC 542.91+547.1'118+548.737

Some Dichloranhydrides of α -Hydroxyalkylphosphonic Acids. Synthesis, Spectral Characteristics, and X-ray Structural Analysis

18410046h Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 9 Sep 88 (manuscript
received 14 Mar 88) pp 2038-2044

[Article by N. A. Kardanov, A. M. Timofeyev, N. N. Godovikov, A. N. Chernega, M. Yu. Antipin, Yu. T. Struchkov, and M. I. Kabachnik, Institute of Heteroorganic Compounds imeni A. N. Nesmeyanov, USSR Academy of Sciences, Moscow]

[Abstract] A study examined the reaction of phosphorus trichloride with certain carbonyl compounds in the presence of acetic acid or water. NMR studies indicate that phosphorous acid and its chlorides accumulate in a solution of phosphorous trichloride in propionic acid at -20°C. The addition of carbonyl compounds yields intensive singlet signals that are characteristic for dichlorophosphonates. In the reactions examined, these compounds may be a dichlorane of substituted α -hydroxymethyl phosphonic acids that are formed by complexing hydrophosphoryl halide to the carbonyl compound. Low-temperature synthesis by this method was performed and yielded a number of substituted hydroxymethyl phosphonic acid dichlorides. The latter are low-melting-point crystalline substances that melt with decomposition. Figures 2, references 7: 12 Russian, 5 Western.

UDC 547.26'118

Synthesis and Certain Properties of N-Phosphorylated 1,3,2-Oxazaphospholanes

18410046i Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 9 Sep 88 (manuscript
received 30 Apr 87) pp 2056-2060

[Article by A. K. Kuliyeu, V. V. Moskva, D. A. Akhmedzade, and M. A. Pudovik, Institute of Petrochemical Processes, Azerbaijan Academy of Sciences, Baku]

[Abstract] To develop simple methods of synthesizing the N-phosphorylated 1,3,2-oxazaphospholanes, the authors studied the reaction of ortho-aminophenol with

phosphorus trichloride and phosphorus oxychloride. The reaction yields phospholanes that are reactive intermediates for the synthesis of various N-phosphorylated derivatives. The reaction of 2-alkoxy-3-dialkoxyphosphite-4,5-benzo-1,3,2-oxazaphospholanes with sulfur and chloral occurs in stages with the initial participation of the more nucleophilic exocyclic phosphorus atom. The reaction of N-phosphorylated oxazaphospholanes with alkyl iodides with heating involves both the exocyclic and the endocyclic phosphorus atoms. References 3: Russian.

UDC 547.241

Variations in Reactions of Phosphorous and Phosphonous Acids With Chloral Hydrate

18410046j Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 9 Sep 88 (manuscript
received 28 Apr 87) pp 2063-2066

[Article by V. I. Krutikov, A. V. Naydenov, T. V. Palagina, V. B. Lebedev, and A. N. Lavrentev, Leningrad Technological Institute imeni Lensovet]

[Abstract] NMR studies of the reaction of phosphites and phenylphosphonites with chloral hydrate in a nonpolar solvent indicate that the reaction is a complex reaction involving the formation of several products including (1-hydroxy-2,2,2-trichloroethyl) phosphonates and (2,2-dichloroethyl) phosphates. Formation of the reaction products involves a donor-acceptor associate that is formed between the phosphites and chloral hydrate. References 5: Russian.

UDC 547.26'118

Cyclic Trimethylsilyl Phosphites and Phosphorous Acids in Reactions With Carbonyl and α -Dicarbonyl Compounds

18410046k Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 9 Sep 88 (manuscript
received 21 Jul 86) pp 2066-2080

[Article by V. V. Ovchinnikov, Yu. G. Safina, R. A. Cherkasov, F. Kh. Karatayeva, and A. N. Pudovik, Kazan State University imeni V. I. Ulyanov-Lenin]

[Abstract] This article reports the results of a study of the reactions of five- and six-membered cyclic phosphorous acids and their silyl esters with benzaldehyde, p-nitrobenzaldehyde, cyclical α -oxophosphonates, tetrachloro- and tetrabromo-o-quinones, and benzyl. The reaction of cyclic hydrophosphoro compounds with hexamethyl disilyl azane or the reaction of the corresponding chlorophosphites with N,N-bis(trimethylsilyl) acetamide yields (trimethylsilyl)cyclophosphites not previously described. The spatial structure of the trimethylsilyl esters is studied. The six-membered silyl phosphites are in the chair conformation with axial orientation of the exocyclic substituent.

Reaction of trimethylsilyl cyclophosphites with aromatic aldehydes and α -oxophosphonates forms phosphonate-structure adducts. Reaction with α -dicarbonyl compounds occurs by oxidative cycloattachment and forms spirophosphorane intermediates. The end products are formed by opening one of the rings of the pentacoordination phosphorus derivative intermediates formed. Trimethylsilylcyclophosphites are more reactive in interactions with carbonyl and dicarbonyl compounds than with cyclophosphorus acids. They are therefore more convenient initial compounds for the synthesis of polyfunctional organophosphorus compounds. Figure 1, references 36: 29 Russian, 7 Western.

UDC 536.653+541.11+541.571.9+547.458

Thermochemistry of Organophosphorus Compounds. III. Enthalpy of Dissolution, Vapor Formation, and Solvation of Three-Coordination Phosphorus Derivatives

18410046l Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 9 Sep 88 (manuscript
received 21 Jul 86) pp 2081-2098

[Article by V. V. Ovchinnikov, Yu. G. Safina, R. A. Cherkasov, and A. N. Pudovik, Kazan State University imeni V. I. Ulyanov-Lenin]

[Abstract] A new method for estimating the evaporation enthalpy of organic substances based on their molar refraction and heats of dissolution in hexane was used to determine the evaporation enthalpy of organophosphorus compounds with a three- and four-coordination phosphorus atom, i.e., triphenylphosphine, triethyl- and trimethylphosphites, phosphorus trichloride, and oxides of phosphorus. A good agreement with previously published values was achieved. The solvation enthalpy of P^{III} compounds in various solvents was determined, and solvability was found to be maximum in weakly associated chloroform. The enthalpies of specific interaction with chloroform were calculated and found to be additive for the various electron-donor fragments of molecules with chloroform and yielded a quantitative estimate of the intramolecular electron effects. Figure 1, references 52: 44 Russian, 8 Western.

UDC 547.241

Synthesis of Trialkoxymethylphosphonates

18410046m Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 58 No 9 Sep 88 (manuscript
received 7 Jul 87) pp 2168-2170

[Article by A. A. Pritshchenko, M. V. Livantsov, N. V. Vaganova, and I. F. Lutsenko, Moscow State University imeni M. V. Lomonosov]

[Abstract] This article suggests convenient methods of synthesizing O,O-dialkyl (trialkoxymethyl) phosphonates. The methods are based on the phosphorylation of trialkoxycarbenium ions that have been produced during the course of a catalytic process or specially produced. References 6: 5 Russian, 1 Western.

UDC 665.765.404.038.2:665.637.6:665.7.033.23

New High-Vacuum Oils

18410062a Moscow KHIMIYA I TEKHOLOGIYA
TOPLIV I MASEL in Russian No 9 Sep 88 pp 13-15

[Article by V. A. Potanina, V. P. Artemyeva, N. N. Kucheryavaya, S. N. Orlova, R. A. Shagiakhmetov, and V. I. Kurashov]

[Abstract] New oils, types VM-1S and VM-5S, have been created on the basis of viscous white oil from western Siberian crude. They are intended to replace type VM-1 and VM-5 oils, which are produced by the high-vacuum distillation of medical vaseline-type oil. The technology for producing viscous white oil includes the vacuum distillation of neutral oil, its purification with oleum, extraction of sulfoacids with 65 percent ethyl alcohol, and catalytic purification. The still residue is used to produce viscous white oil, and the head fraction is used for perfume oil. Tests of VM-1S and VM-5S oils in high-vacuum pumps indicate that they have good usage characteristics. References 3: 1 Russian, 2 Western.

UDC 621.892:665.76(088.8)

Increasing Carbon Deposition Prevention Properties of Oils for Two-Stroke Gasoline Engines

18410062b Moscow KHIMIYA I TEKHOLOGIYA
TOPLIV I MASEL in Russian No 9 Sep 88 pp 15-16

[Article by Ye. M. Meshcherin, M. Ye. Ostrovskaya, A. Ya. Levin, and S. V. Monin]

[Abstract] A special two-stroke test motor was used to evaluate the carbon deposition prevention properties of standard motor lubricating oils that have not been specifically designed for two-stroke motors. None of the standard oils tested met the usage requirements, which indicates that two-stroke motors should not be lubricated with ordinary lubricating oils. A new type of oil, M-12TP, which has an alkylphenolate B detergent additive, satisfies all the requirements for two-stroke oil, thus reducing the requirement for oil in the fuel-oil mixture of a chain saw by 50 percent and decreasing deposits and the exhaust gas smoke content. References 4: Russian.

UDC 665.767:621.3

Electric Insulating Saturating Liquid Based on Aromatic Acid Esters

18410062c Moscow KHIMIYA I TEKHOLOGIYA
TOPLIV I MASEL in Russian No 9 Sep 88 pp 17-18

[Article by V. V. Grigorev, G. V. Surovskaya, and K. V. Prokofev]

[Abstract] A study examined the possibility of improving the dielectric properties of dioctylphthalate by purifying it and introducing stabilizing additives to allow it to be

used as the basis for a dielectric liquid for condenser insulation. Bleaching clays are the best purifying agents, but percolation with A-4M adsorbents is better than simple mixing with earth is. The adsorbent can increase the resistivity to $6-7 \times 10^8$ ohms x meters and decrease dielectric losses as well as the acid number. The adsorbent is easily regenerated in industrial use. Use of the adsorbent has resulted in the production of a dioctylphthalate saturating liquid for paper and paper-film condensers, i.e., type EIM-5 oil. The new oil is superior to castor oil in its dielectric characteristics, acid number, and viscosity. References 6: 4 Russian, 2 Western.

UDC 547.391:66

Polymethacrylate Additives Based on -Olefins

18410062d Moscow KHIMIYA I TEKHOLOGIYA
TOPLIV I MASEL in Russian No 9 Sep 88 pp 18-20

[Article by S. I. Mekhtiyev, deceased, Yu. P. Ryskina, R. A. Polchayev, and N. M. Aliyeva]

[Abstract] The All-Union Olefins Scientific Research Institute has synthesized higher polymethacrylates from methacrylic acid through methacrylonitrile that is produced by the oxidative ammonolysis of isobutylene and higher C_8-C_{16} α -olefins, which are in turn produced by high-temperature oligomerization of ethylene in a search for new, more economical methods of producing polymethacrylate additives. Oils thickened with methacrylic acid additives and α -olefins have low viscosities at low temperatures. Their resistance to thermal oxidative and mechanical destruction is equal to that of commercial oils. References 4: Russian.

UDC 665.644.4

Production of B-91/115 Aviation Gasoline Basic Component on Metal-Zeolite Catalysts

18410062e Moscow KHIMIYA I TEKHOLOGIYA
TOPLIV I MASEL in Russian No 9 Sep 88 pp 20-22

[Article by V. Yu. Bortov, V. V. Shipikin, R. A. Zaynulin, I. N. Tolkacheva, and V. N. Mozhayko]

[Abstract] A technology has been developed for producing B-91/115 aviation gasoline from the head fraction of reforming catalysate. The fraction boiling up to 150°C is separated from the reformed product, hydrogenated, and hydroisomerized to convert the "excess" aromatic hydrocarbons to five-membered naphthenic hydrocarbons; this is followed by selective hydrocracking of normal paraffin hydrocarbons. The basic component of the aviation gasoline can also be produced by processing the straight-run fraction on a metal-zeolite catalyst for dehydrogenation of naphthenic, hydrogenation of aromatic, dehydrocyclization of paraffin, hydroisomerization of naphthenic, and isomerization and hydrocracking of m-paraffin hydrocarbons. The process significantly decreases the consumption of alkylbenzene

in the production of aviation gasoline. The 62-150°C straight-run gasoline fraction treated on the metal-zeolite catalyst utilizes temperatures, space velocities, pressures, etc., that can be implemented on existing catalytic reforming installations, thereby significantly improving their economic characteristics. Figures 5, references 3: Russian.

UDC 621.892.8:621.43

Estimating Pumpability of Motor Oils

18410062f Moscow *KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL* in Russian No 9 Sep 88 pp 31-32

[Article by M. G. Arslanov, V. L. Lashkhi, G. M. Veloshapkina, L. A. Demyanov, and G. I. Shor]

[Abstract] Pumpability refers to the time from the moment an engine is started until oil reaches a bearing or other part or until the required oil pressure is reached. This article suggests a method and equations for estimating the pumpability of oils by using standard laboratory viscosimeters and thus avoiding the influence of dilution of the oil on the fuel and design specifics of motors. It is concluded that pumpability can be estimated on the basis of viscosity. References 8: 2 Russian, 6 Western.

UDC 553.981/982.2:550.84(479.24+262.81)

Certain Features of Hydrocarbon Migration in South Caspian Oil and Gas-Bearing Basin

18410079a Baku *IZVESTIYA VYSSHIKH UCHEBNIKH ZAVEDENIY: NEFT I GAZ* in Russian No 6, Jun 88 (manuscript received 28 Mar 86) pp 14-17

[Article by A. A. Dzhevadov, O. G. Melikov, and N. R. Narimanov, Azerbaydzhan Institute of Petroleum and Chemistry imeni M. Azizbekov]

[Abstract] The fluid coefficient ratios for various hydrocarbons, the methane to aromatic ratio, the benzene to kerosene or ligroin ratio, the ratio of the fraction boiling below 200°C to that boiling at 200-300°C and the depression of the temperature achieved at the end of condensate boiling were used to analyze the migration of hydrocarbons in the South Caspian basin. Changes in all geochemical parameters that accompany the rise in submerged red layers indicate the direction of migratory processes. In the Gorandag-Okaremskiy zone the direction of migration and folding lines are oriented tangentially to the Balkhansk area. In the eastern portion of the South Caspian basin, in the Balkhansk area, migration proceeded from west to east, from the submerged section of the red sediments toward the rise in layers. Migration went from south-southwest to north in the Gorandag-Okaremskiy zone. Migration from deep layers to lateral zones was observed in several locations. The findings indicate that regular changes in gas condensate composition may be used to determine the migration direction. Low-lying condensates are enriched in aromatic and methane hydrocarbons, with high boiling compounds separating from the gas condensate. These phenomena lead to accumulation of petroleum deposits in

the lateral zones of the basin, with the most suitable tectonic structures (with gas condensate deposits) being located in the most submerged zones. Figures 1; references 4 (Russian).

UDC 665.664.22:665.666.55

Purifying Diesel Fuel Using Ammonium Hydroxide in Two-Section Reactor

18410079b Baku *IZVESTIYA VYSSHIKH UCHEBNIKH ZAVEDENIY: NEFT I GAZ* in Russian No 6, Jun 88 (manuscript received 3 May 87) pp 49-53

[Article by Ch. D. Murshudli, Kastilo Kh. Khose Del K., and B. K. Zeynolov, Azerbaydzhan Institute of Petroleum and Chemistry imeni M. Azizbekov]

[Abstract] The process of extracting petroleum acids from continuous-layer dispersed aqueous ammonium hydroxide in diesel fuel was studied by using a two-section cylindrical glass reactor containing perforated disks and heated electrically. The drops of diesel fuel come into contact with a dispersed layer of aqueous ammonium hydroxide as they rise through the reactor. As a result, the petroleum acids dissolve in the aqueous phase as ammonium salts. Experiments with different reagent heights demonstrated that the leaching reaction occurs more intensely in the initial zone of each reactor section. A contact zone height of 0.150 m and 3 mass percent aqueous ammonium hydroxide were used to reduce the diesel fuel's acidity from 183 to 34 mg KOH/100 mL. A final fuel acidity as low as 3.8 mg KOH/100 mL was achieved. The optimal working temperature range was 45-55°C, whereas the optimal aqueous ammonium hydroxide concentration was 3.5-4 mass percent. Dispersing the diesel fuel in a stationary reagent layer permits one to lower the reagent excess coefficient from 3 to 2 when compared with a process that disperses the reagent in a layer of diesel fuel. Figures 2; references 2 (Russian).

UDC 621.892.097.620.197:665.614

Biostability and Protective Properties of Film-Forming Petroleum Composites

18410079c Baku *IZVESTIYA VYSSHIKH UCHEBNIKH ZAVEDENIY: NEFT I GAZ* in Russian No 6, Jun 88 (manuscript received 27 Feb 87) pp 53-56

[Article by A. A. Gureyev, I. A. Timokhin, Ye. G. Topopova, and Yu. N. Shekhter, Moscow Institute of Oil and Gas imeni Academician I. M. Gubkin]

[Abstract] The biostability of film-forming petroleum composites, the effectiveness of added biocides, and the effect of the biocides on the protective properties of the modified composites were studied. Three aqueous emulsions, two wax and hydrocarbon solvent composites, and two bitumen with hydrocarbon solvent composites were tested. The addition of 0.5-1.5 percent of the organotin compounds Afotas or TBOO greatly increased composite bioresistance to molds, and it eliminated the slight

susceptibility of the composites to bacterial damage. The metabolic products of molds are very corrosive to steel. The organotin additives increased the protective properties of the composites. One wax and one emulsion composite film were found to protect steel from the corrosive effects of mold even without the organotin additives. References 6 (Russian).

UDC 622.692.4.052.6

Modeling Main Pipelines for Liquid Hydrocarbons

18410079d Baku IZVESTIYA VYSSHIKH UCHEBNIKH ZAVEDENIY: NEFT I GAZ in Russian No 6, Jun 88 (manuscript received 13 Mar 86) pp 76-78

[Article by A. Ye. Soshchenko, A. G. Orudzhev, M. M. Mekhtiyev, and D. R. Nazirova, Moscow Institute of Oil and Gas imeni Academician I. M. Gubkin]

[Abstract] A method is proposed for mathematically describing a pipeline system for transporting liquid

hydrocarbons as a dynamic control object. The method uses the mathematical method of linear and nonlinear identification via dispatcher "input-output" data. This method permits evaluation of hydrodynamic pressure, pumped product flow rate, and pipeline resistance. The basis of the method is a previously developed algorithm that is part of a package of applied programs. The program determines whether the parameter is linear or nonlinear and whether it is steady-state or non-steady-state. Applying the method to the pipelines of the Orenburg Gas Condensate Complex resulted in a model in the form of two transfer functions. The time constants and pure lag values were expressed in hours, and the model's error did not exceed 5 percent, which makes it adequate for modeling the process. The ratio of the transfer function values before and after the pump piston's idle stroke can be used to evaluate changes in hydraulic resistance. When the model was used to describe the nonsteady operating modes of a system containing a condenser pump, the deviation of the calculated values from observed data did not exceed 8.3 percent. References 2 (Russian).

UDC 678.5:54.138

Production of Polymer Coatings by Electrochemical Cross-Linking

18410040e Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 61 No 7 Jul 88 (manuscript received 29 Dec 86) pp 1568-1572

[Article by N. K. Fedorova, Ya. D. Zytner, V. A. Myshlennikova, and L. N. Mashlyakovskiy, Leningrad Institute of Technology imeni Lensovet]

[Abstract] This article reports the study of a system for forming electrochemical polymer coatings by electrochemical cross-linking. The system contains an epoxy (meth)acrylate oligomer, a polyelectrolyte, an electrically conducting additive, and an amide solvent. Polymer coatings were produced at room temperature in direct current on the surface of a flat anode of type St.3 steel after it had been degreased and dried. All experiments were performed in a single-section circular cell with a cylindrical aluminum counterelectrode. A comparison of the properties of coatings obtained from oligomer-polymer systems of various compositions with polyamide coatings produced by electroprecipitation with subsequent heat treatment at 300°C indicated that the electrochemical cross-linking method allows the composition of the polymer coating to be varied over broad limits. It was discovered that introducing 20 percent epoxy (meth)acrylate to the coating can decrease the heat treatment temperature. Coatings based on epoxy (meth)acrylates modified with small quantities of polyelectrolyte have superior electrical insulation and thermal stability properties. Figures 5, references 8: Russian.

UDC 539.612:678.01

Mass Spectrometric Study of Hydrolytic Destruction of Ethylene-Vinyl Acetate Copolymer On Metal Surface

18410040f Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 61 No 7 Jul 88 (manuscript received 16 Jul 87) pp 1582-1586

[Article by O. F. Pozdnyakov, K. V. Prasolov, A. D. Yakovlev, N. Z. Yevtyukov, and G. N. Garinova]

[Abstract] Mass spectrometry is used to study the processes of the formation and breakdown of adhesive joints between ethylene-vinyl acetate copolymers and oxidized metals in a vacuum and the mechanism of destruction of the polymer involving water adsorbed on the interface. The results obtained are compared with data on the influence of water on the long-term adhesive strength of the copolymer coatings. The mass spectra indicated that its thermal destruction in a vacuum begins at 570 K, the primary component being acetic acid. The kinetics of acetic acid formation are influenced by the degree and nature of adsorption of water. Water adsorbed on the substrate influences the transfer of the polymer, reducing it to one-third the amount on substrates not containing

water. Coatings produced at less than 440 K have little adhesive strength, which drops rapidly upon exposure to water. Coatings produced at 440 K have high and stable adhesion on all substrates. Water adsorbed on the interface and caused hydrolysis of the boundary copolymer layers, which significantly influences the adhesive strength of coatings. The reason for the increase in the strength of the coatings produced at higher temperatures is that physically absorbed water is virtually completely eliminated at 430 K. Figures 4, references 8: 7 Russian, 1 Western.

UDC 547.992.3

Inhibited Lignin Oxidation Under Conditions of Alkaline Delignification of Wood

18410051d Riga KHIMIYA DREVESINY in Russian No 4 Jul-Aug 88 (manuscript received 28 Apr 87; after revision 20 Jul 87) pp 56-61

[Article by E. I. Chupka and I. M. Luzhanskaya, Siberian Cellulose and Cardboard Scientific Research Institute]

[Abstract] A number of lignin oxidation inhibitors were tested individually and in compositions with anthraquinone-2-sulfoacid. The study focused on the kinetic mechanism of their action in damping chemiluminescence—something that had not been studied previously. The compounds vary in effectiveness: N,N-dimethyl-p-phenylene diamine and N,N-dimethylaniline have no inhibiting effect, but nitrosodimethylaniline, p-oxyneosol, naphthylenediamine, and phenidone are effective lignin oxidation inhibitors. Each component in the composition reaches a characteristic limiting level of chemiluminescence inhibition that is determined by the individual properties of the inhibitor. The inhibition of radical reactions in delignification indicates that oxidative reactions and intermediate products in an electron-excited state play a significant role in the process. Figures 5, references 13: Russian.

UDC 547.992.3

Influence of Various Bases on Solvolysis of Milled Wood Lignin

18410051f Riga KHIMIYA DREVESINY in Russian No 4 Jul-Aug 88 (manuscript received 30 Apr 87) pp 64-69

[Article by M. I. Yermakova, M. F. Kuryushina, and M. Ya. Zarubin, Leningrad Wood-Engineering Academy imeni S. M. Kirov]

[Abstract] A study examined the effect of "mild" and "strong" bases on the degree of destruction of milled wood lignin. This was done to determine their correlation with the results obtained in dimer models and to discover the influence of individual solvents. Studies were performed on pine milled wood lignin heated to 170°C for 2 hours in an autoclave with 5 percent aqueous NaOH that contained various mild and strong bases.

The studies showed that the same tendencies are retained with the various bases as in dimer lignin models. This was particularly true in the case of the mild bases. Introducing mild bases facilitates the destruction of the lignin preparations, with the intensity depending on the electronegativity of the anion or reagent molecule. Introducing organic solvents to the solutions has little influence on the destruction of milled wood lignin by stronger electrolytes, but it increases the reactivity of the mild electrolytes. References 17: 14 Russian, 3 Western.

UDC 634.0.813.11:634.0.844.2

Change in Birch Lignin Damaged by Fungus *Coriolus Hirsutus* 070

18410051g Riga KHIMIYA DREVESINY in Russian
No 4 Jul-Aug 88 (manuscript received
21 May 87) pp 74-79

[Article by N. R. Ozolinya, V. N. Sergeeva, S. V. Khokholko, and Ts. L. Abramovich, Institute of Wood Chemistry, Latvian Academy of Sciences]

[Abstract] There is interest in the lignin remaining after lignin-cellulose materials are treated with microorganisms. The quantity and properties of the residual lignin determine the practical application of materials of plant origin following treatment with destructive fungi. The authors studied milled beach lignin that had been damaged to varying degrees by the fungus *coriolus hirsutus* 070. It is found that the easily accessible parts of lignin and hemicellulose are attacked first, gradually breaking down the cell wall. Meanwhile, the extracellular components of the lignolytic system diffuse inward, splitting the accessible intramolecular bonds in the lignin macromolecule. This forms fragments of varying molecular mass, some of which are polymerized or condensed in situ to form compounds with a greater molecular mass than that of the initial lignin. At the same time, the fungi utilize the degraded structures. In heavily damaged wood, the remaining lignin is a highly condensed product. At over 20 percent destruction, the action of hydrolytic enzymes increases, and cellulose is broken down intensely. Figures 2, references 22: 9 Russian, 13 Western.

UDC 547.548.81:677.11

Influence of Flax Bast Substances on Hygroscopic Properties of Untreated Flax Cellulose

18410051h Riga KHIMIYA DREVESINY in Russian
No 4 Jul-Aug 88 (manuscript received 12 Aug 87; after
revision 30 Nov 87) pp 92-94

[Article by L. N. Kuleshova, N. V. Komarova, N. N. Osipova, N. G. Taraskina, and V. I. Khodyrev, Central Scientific Research Institute of Bast Fibers]

[Abstract] This article reports on an attempt to estimate the influence of flax cellulose accessories on hygroscopic properties. A number of solvents were used to extract

fatty, resinous, and other nonpolar substances, dyes, flavanoids, phenolic acids, tanning substances, phlobaphenes, monosaccharides, lower oligosaccharides, starches, pectins, inorganic salts, and hemicellulose. As the flax cellulose accessories were removed, the hygroscopic moisture decreased by a factor of 2 while the moisture extraction speed increased by more than a factor of 3. Removal of the extracted substances thus decreased the hygroscopic capacity of the fiber while increasing the moisture loss rate. Removing the pectins and hemicellulose proved to be particularly significant, as was confirmed by chemical analysis and NMR studies in the system water-flax cellulose. References 7: 6 Russian, 1 Western.

UDC 541

Polymer Spin Glasses

18410054c Moscow DOKLADY AKADEMII NAUK
SSSR in Russian Vol 302 No 3 Sep 88 (manuscript
received 9 Mar 88) pp 634-637

[Article by A. A. Ovchinnikov, corresponding member USSR Academy of Sciences, A. I. Tsapin, V. N. Spektor, G. A. Vinogradov, O. L. Lazareva, and A. N. Shchegolikhin, Chemical Physics Institute, USSR Academy of Sciences, Moscow]

[Abstract] A study examined polyBIPO spin glasses in the 6-300 K temperature interval by using a radiospectroscopic method that was developed to study biological spin glasses. Specimens of polyBIPO, the first polymer ferromagnetic with residual magnetism of 0.1-1.0 G, retained their magnetism up to 580-585 K. The magnetic properties of the material were determined by the organic matrix. States of the spin glass were identified in specimens by cooling of specimens in a magnetic field to below the freezing point determined in earlier works. The studies showed that, in a purely organic polyBIPO system, as the degree of polymerization increases the magnetic properties change and the system gradually changes its state from paramagnetic to superparamagnetic to spin glass to ferromagnetic. Figure 4, references 9: 5 Russian, 4 Western.

UDC 542.943:547.593.211:564.21-121

Change in Mechanism of Formation of Free Radicals During Oxidation of Cyclohexanol

18410055a Leningrad ZHURNAL PRIKLADNOY
KHIMII in Russian Vol 61 No 8 Aug 88 (manuscript
received 19 Jul 87) pp 1826-1831

[Article by R. V. Neginskaya and B. G. Freydin, Kuznets Basin Polytechnical Institute]

[Abstract] Changes in the mechanism of initiation in the process of cyclohexanol oxidation are studied by determining the variation in rate at which free radicals form as a function of hydrogen peroxide and cyclohexanone concentrations. Experiments were performed in the

kinetic area of oxygen absorption at 120°C. It was found that initiation occurs over a significant range of the process by decomposition of α , α -dioxycyclohexyl peroxide, which was identified in the oxidized alcohol by thin-layer chromatography. Introduction of 2-oxycyclohexanone to the cyclohexanol oxidized at 120°C resulted in the formation of a product of the addition of hydrogen peroxide to the ketoalcohol, which decomposes rapidly by an ionic mechanism. Figures 4, references 12: 11 Russian, 1 Western.

UDC 678.743.41-139.074.063.01:536.468+678.043

Influence of Vulcanization Agent Chemistry on Flame Resistance of SKF-32-Based Rubbers
18410056a Moscow KAUCHUK I REZINA in Russian No 9 Sep 88 pp 18-19

[Article by N. D. Sapuntsova, D. P. Trofimovich, F. A. Galil-Ogly, deceased, and A. S. Rozovskiy]

[Abstract] A study is made of the flame resistance of rubbers based on SKF-32 in oxygen. The specimens were vulcanized by γ -radiation, benzoyl peroxide, m-phenylene dimaleimide, copper salicylalimide and methox in one stage at 150°C, 60 minutes. It was found that peroxide- and radiation-vulcanized rubbers were more flammable than the initial raw rubber. Rubbers vulcanized with m-phenylene dimaleimide, methox, and salicylalimide are less flammable in oxygen. These latter agents are not only vulcanizing agents but also antipyrenes and can be used to produce rubbers that are flame resistant in oxygen. Figures 2, references 2: 1 Russian, 1 Western.

UDC 678.06:62-762; 678.4.019.391; 678.4.01:536.485

Change In Cold Resistance of Rubber Seals In the Process of Aging
18410056b Moscow KAUCHUK I REZINA in Russian No 9 Sep 88 pp 28-30

[Article by Ye. M. Ukhova and A. A. Sokolovskiy]

[Abstract] The purpose of this work was to obtain a set of data on the influence of aging on the low-temperature serviceability limit of seals made of various types of rubber. The specimens tested were circular sealing rings tested under an axial compression of 20-25 percent and aged in air or with a vacuum on one side under isothermal conditions. All seals showed a monotonic increase in residual deformation and a nonmonotonic variation in tensile strength with aging. Resistance to cold also changes nonmonotonically, which indicates significant changes in the structure of the rubber as it ages that are apparently related to both physical and chemical processes. The rate of residual deformation accumulation and decrease in stress relaxation is greater when one side

of the seal is exposed to a vacuum since the vacuum causes a constant loss of low-molecular-mass destruction products as the rubber ages. Figures 3, references 8: Russian.

UDC 678.4.06:621.867:339.4

Predicting Durability of Rubber-Fabric General-Purpose Conveyer Belts
18410056c Moscow KAUCHUK I REZINA in Russian No 9 Sep 88 pp 30-32

[Article by A. A. Pozin, deceased, G. Z. Veksler, G. F. Golikov and L. B. Tomchin]

[Abstract] A method is developed for predicting the durability of conveyer belts that considers the major factor in conveyer belt failures, wear of the belt covering. Equations are suggested for determining the belt covering wear rate, which is independent of belt covering thickness. The coefficients used in the equations were taken from experimental results. The method achieves an accuracy within 20 percent with a probability of 90 percent, quite acceptable for engineering calculations. Figure 1, references 12: Russian.

UDC 678.065:629.111.4:539.4

Influence of Truck Radial Tire Tread Characteristics On Mechanical Strength
18410056d Moscow KAUCHUK I REZINA in Russian No 9 Sep 88 pp 32-34

[Article by M. I. Rekitar, L. A. Protsenko, L. A. Fedorova, and V. N. Prashchikin]

[Abstract] A study is made of the influence of various tire tread design characteristics including tread depth, thickness of the layer beneath the tread slots, tread element size, and certain other characteristics on the tire tread puncture strength, which has been shown to correlate well with tire life. Three equations are generated from the experimental results to illustrate the influence of the major design characteristics on the resistance of tire treads to concentrated loads. Of greatest influence on tread strength was the thickness of the rubber layer beneath the slots in the tread. A shielding layer of capron cord is also recommended, as is an increase in the stiffness of the tread rubber. Figures 2, references 5: Russian.

UDC 678.744:006.065

Standardizing Conductive Elastomer Materials And Products
18410056g Moscow KAUCHUK I REZINA in Russian No 9 Sep 88 pp 45-47

[Article by I. S. Yurovskaya, G. D. Timonin, A. F. Korostelev, and A. F. Galiyeva]

[Abstract] An analysis is made of Soviet versus Western standards and technical documentation for electrically conductive elastomer materials and products. Soviet

products could be brought up to the level of world standards if certain shortcomings in domestic scientific and technical documentation would be eliminated including the unjustified manufacture of many types of rubber mixtures based on general-purpose raw rubber with identical resistance and similar properties; the unavailability of elastomer materials with low resistance; and a lack of standardization in methods of determining resistivity. Tasks for the future include standardization of product types, systematization of products produced by various companies, organization of specialized production of standardized products, development of a single standard for methods for determining electrical characteristics, and development and standardization of methods for determining resistance. References 31: 30 Russian, 1 Western.

UDC 678.5-278.004.14:63

Use of Polymeric Membranes in Sectors of Agroindustrial Complex

18410061a Moscow PLASTICHESKIYE MASSY
in Russian No 10, Oct 88 pp 5-6

[Article by L. V. Gorbunova, S. I. Romanova, and N. G. Kirichenko]

[Abstract] Polymeric membranes have numerous applications in the agricultural industry. In milk processing they are used as pretreatment before concentration, to produce dry protein concentrates, and in the manufacture of low-calorie dairy products. Using membranes increases the efficiency and yield while lowering energy expenditure. The most widespread application of membranes in the food industry is for water purification by reverse osmosis. Microfiltration is effective in the clarification and stabilization of juices and wines, the extraction and concentration of protein from potatoes, the purification of fat-containing waste water, and the preparation of fish broths. Polymeric membranes may be used to increase food stability to storage by regulating their gaseous environment to remove oxygen and increase carbon dioxide levels. In order to encourage more extensive use of polymeric membranes, variety, stability, productivity and selectivity must be increased. The creation of complex membranes will play a major part in accomplishing this goal.

UDC 678.5:547.391.1:66.663.726:621.384

Negative Electron Resists Based on Copolymers of Glycidyl and Methacrylate With Butyl Methacrylate

18410061a Moscow PLASTICHESKIYE MASSY
in Russian No 10, Oct 88 pp 9-10

[Article by D. N. Bayramov, A. F. Amrullayev, R. V. Dzhafarov, and R. V. Binnatov]

[Abstract] In order to effectively use polyglycidyl methacrylate as a negative electron resist in microcircuit production, it must be copolymerized with polymers to produce the appropriate softening temperature, solubility, and adhesion. As part of a search for the appropriate copolymer, 10 copolymers of glycidyl methacrylate (GMA) and butyl methacrylate (BMA) were prepared with a t-butylperbenzoate initiator in methyl ethyl ketone and benzene mixtures under nitrogen. The mole percent of GMA was varied from 40 to 60 percent; over this range, polymer epoxide numbers from 15.2 to 19.6 percent were found. No carbon-carbon double bond bands were seen in the IR spectra of the polymers, while epoxide bands were present. The highest yield, 45 percent, was obtained after 6 hours of reaction; after 8 hours an insoluble gel was formed. The copolymers had adequate electron sensitivity, solubility, ability to form thin layers, and stability in 2-methoxyethylacetate solution. References 7: 4 Russian, 3 Western.

UDC 678.5-19.049:536

Mechanism of Reversible Growth of Radiation Electrical Conductivity in Polytetrafluoroethylene as a Function of Absorbed Radiation Dose

18410061c Moscow PLASTICHESKIYE MASSY
in Russian No 10, Oct 88 pp 30-32

[Article by V. P. Sichkar, O. S. Aleksanina, and V. F. Stepanov]

[Abstract] A study was conducted on the dependence of electrical conductivity in polytetrafluoroethylene (PTFE) suspensions and emulsions on the strength of a dose of ^{60}Co gamma radiation, using intervals of 0.5-0.5 Hz/sec at 293 K. The samples were subjected to preliminary irradiation of not more than 10 kHz at 1.5 Hz/sec. The observed increase in conductivity after preliminary irradiation depended on the method of sample polymerization and preparation. Preliminary weak chemical sorption treatment magnified the increase, while strong treatment diminished it. Preliminary thermal processing magnified the conductivity increase at 2 kHz and 4 kHz doses, but not at 1 kHz or 8 kHz. Type F-4 PTFE films exhibited radiation-induced elongation, which was diminished by preliminary chemical sorption treatment. Type F-4D films did not exhibit this elongation. The results suggest that ionizing radiation elicits increased kinetic mobility in PTFE, due to cleavage of C-C bonds, which accelerates relaxation of residual stress and submolecular rearrangement. This relaxation increases the concentration and mobility of free charge carriers. Similar effects may be observed in other oriented or amorphous polymers. Figures 1; references 7: 6 Russian, 1 Western.

UDC 541(64+15):542.952

Radiation-Induced Polymerization of Heptylmethacrylate-Based Materials. Effect of Plasticizers.

18410075a Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 30 No 10, Oct 88 (manuscript received 28 Apr 87) pp 2052-2056

[Article by A. I. Bolshakov, D. P. Kiryukhin, and I. M. Barkalov, Departmental Institute of Chemical Physics, USSR Academy of Sciences]

[Abstract] The influence of chlorinated paraffin (CP) plasticizer on the kinetics of the radiation-induced polymerization of heptylmethacrylate (HMA) and its mixtures with chlorinated polyethylene (CPE) was studied. A comparison of viscosity as a function of time and calorimetric data indicated that autoacceleration is accompanied by sharp increases in viscosity. This sharp viscosity increase was retarded when CP was present; at CP levels of 60 percent or more, it was not observed. Increasing CP concentrations were accompanied by increasing initial polymerization rates due to accelerated initiation. In HMA containing 40 percent CPE and 40 percent CP, rapid acceleration of polymerization was not seen. Thus, higher doses of radiation were needed for curing. Similar effects were observed with other methacrylates. When CP was added to a mixture of HMA and the monomethacrylate ester of ethylene glycol (MEG), 20 percent MEG (rather than 10 percent) was needed to produce a cross-linked product. The polymerization rate as a function of radiation dose indicated a mixed mechanism for chain termination—both monomolecular and bimolecular. It was also found that increasing CP concentrations in GMA raised the devitrification temperature. EPR indicated that chain elongation is independent of CP concentration; the propagation constant was essentially independent of viscosity and molecular mass. Figures 3; references 5 (Russian).

UDC 541.64:542.9

Behavior of Fire-Resistant Polyester Fiber Composites During Pyrolysis and Burning

18410075f Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 30 No 10, Oct 88 (manuscript received 22 May 87) pp 2170-2174

[Article by L. G. Panova, S. Ye. Artemenko, V. I. Beshshaposhnikova, V. V. Andreyeva, N. A. Khalturinskiy, V. P. Krapotkin, and T. L. Baranova, Saratovskiy Polytechnical Institute]

[Abstract] The use of tricresyl phosphate (TCP) or decabromodiphenyl oxide (DBDO) in polyester terphthalate (PETP) fibers to retard the flammability of epoxide composites was studied. Composites containing TCP-PETP fibers had lower rates of flame propagation, decreased (from 90 percent to 54 percent) mass loss on burning, and an oxygen index of 26.5 percent. Introducing an equivalent amount of TCP into the epoxide resin was less effective. After burning, the coke from the TCP-PETP resin retained its textile fiber structure, while unmodified or TCP-in-resin did not. Using DBDO in the fibers gave greater lowering of flame propagation rates, less mass loss on burning (14 percent), and no independent burning. TCP increased the coke yield at the maximum decomposition temperatures by a factor of four, decreased the decomposition rate, lowered heat production, and increased the initial thermodestruction temperature. Scanning electron microscopy and x-ray analysis revealed phosphorus in the coke. DBDO had no effect on coke formation. DBDO-containing composites were less stress-resistant. Using mixtures of TCP and DBDO (1:4, 1:1, 4:1) gave mass losses on burning of 2.9 percent, 10.5 percent, and 3.8 percent, respectively. This is much less than the losses calculated from additivity. The mixtures also gave composites with improved mechanical stability. Figures 5; references 4 (Russian).

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