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Compensation Effect in Hydrogenation of Aromatic Nitro Compounds on Palladium-Containing Polymers

917M0138A Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHOLOGIYA in Russian Vol 34 No 1, Jan 91 (manuscript received 28 Mar 90) pp 76-78

[Article by M. V. Klyuyev and E. F. Vaynshteyn, Chair of Organic and Biological Chemistry, Ivanovo State University]

UDC 541.128

[Abstract] The compensation effect is described by the following equation $E = \alpha + \beta \delta S_{ca}$, where E is the energy of activation, α and β are constants applicable to the reaction, and δS_{ca} is the entropy of activation. This effect has been observed in a number of enzymatic reactions and in reactions involving coordination compounds such as porphyrins. The present article reports on the application of this effect to hydrogenation of nitrobenzene, m-nitrochlorobenzene, p-nitrochlorobenzene and o-nitrochlorobenzene over 2% Pd in a polyethylene-poly(4-vinylpyridine) matrix and on 1% Pd in anionite catalysts AN-511, AN-541 and AN-251. In the latter case δS_{ca} vs. E and Arrhenius plots yield an isokinetic point corresponding to 301 K (constant β). Evidently, the linear relationship of free energies and equations of the Hammett-Taft type appears to be a result of the linear correlation between E and δS_{ca} . Figures 3; references 4 (Russian).

Catalytic Properties of Zeolites Modified by Fe³⁺ Ions in the Isomerization of m-Xylol

917M0140A Minsk IZVESTIYA AKADEMII NAUK BSSR: SERIYA KHIMICHESKIKH NAUK in Russian No 2, Mar-Apr 91 (manuscript received 19 Sep 90) pp 27-30

[Article by L.N. Malashevich, V.S. Komarov, and A.V. Pismennaya, Institute of General and Inorganic Chemistry, BSSR Academy of Sciences]

UDC 542.952.1:661.183.6

[Abstract] The authors of the study reported herein examined the effect of modification of the zeolites TsVM, TsVK, ferrierite, and mordenite by a trivalent iron ion and investigated their activity and selectivity in the isomerization of m-xylol. The Fe³⁺ cation was introduced into the zeolites by treating their ammonium forms with an aqueous 0.1 N solution of ferric chloride four times, rinsing off the ions, and roasting at 500°C for 3 hours. According to chemical analysis data, the zeolites contained the following amounts of iron (percentage by weight): TsVK, 0.82; TsVM, 0.68; mordenite, 0.95; and ferrierite, 0.27 (which amount to 33.9, 28.1, 28.2, and 18.9% of their ion exchange capacity). The remaining

portion of the cationic sites in the resultant specimens were decationated inasmuch as the degree of replacement of Na⁺ by NH₄⁺ in the starting zeolites amounted to 95-96%. Isomerization of m-xylol in the resultant specimens was conducted in accordance with a method published elsewhere at 250-500°C. At temperatures of 400 and 450°C, the isomerization of m-xylol in the zeolites TsVM and TsVK was accompanied by disproportionation and the formation of trimethylbenzenes and toluene in measurable quantities. The same phenomenon occurred in the case of mordenite at 400°C. The disproportionation reaction was less significant in the Fe- and decationated ferrierite specimens. The Fe- and decationated forms of the zeolites TsVM and TsVK were the most active catalysts of the isomerization of m-xylol. The ferrierite specimens were the least active. The iron-containing forms of the aforesaid catalysts were less active than the decationated forms. The reverse was true of mordenite, however. The activity of its Fe forms was higher than that of its decationated forms. Despite the fact that the activity of Fe-containing zeolites is reduced in comparison with that of the decationated forms, the yield of n-xylol remained the same or was even higher. The authors concluded that modifying zeolites with iron ions has a positive effect on their productivity with respect to n- and o-xylols and reduces the amount of starting material (m-xylol) required to form by-products. Modifying ferrierite with iron ions also results in a significant increase in its para-selectivity, thus permitting the more purposive isomerization of m-xylol and n-xylol. Figure 1, table 1; references 4 (Russian).

The Effect of Reduction on the Catalytic Activity and State of Metals in Applied Copper-Cobalt Oxidation Catalysts

917M0140B Minsk IZVESTIYA AKADEMII NAUK BSSR: SERIYA KHIMICHESKIKH NAUK in Russian No 2, Mar-Apr 91 (manuscript received 15 Oct 90) pp 48-52

[Article by L.Ya. Mostovaya, T.S. Petkevich, N.A. Kovalenko, and S.Ye. Bogushevich, Institute of Physical and Organic Chemistry, BSSR Academy of Sciences]

UDC 665.335.9.095.1

[Abstract] In a continuation of their work presented in earlier publications, the authors of the study reported herein examined the effect that pretreatment of copper-cobalt catalysts in a reducing medium has on the activity of these catalysts in the oxidation of CO and on the status of the active phase. The catalysts were prepared by impregnation of type ShN-2 aluminum oxide carrier with copper and cobalt nitrate solutions and then drying them at 390 K and roasting them at temperatures between 520 and 920 K. The copper amounted to between 0.35 and 4.70% (by weight), and the cobalt amounted to 0.15 to 1.80% (by weight) with a Cu:Co ratio of 2. In some cases, before impregnation by the

copper and cobalt nitrate solutions, the carrier was modified with 0.5 to 0.8% (by weight) Cu and subjected to staged roasting in air for 3 hours at 570 K and then at 820 K for 3 hours. Diffuse reflection spectra were recorded on an SF-26 spectrophotometer with a PDO-1 attachment, and the EPR spectra were recorded on an ERS-230 spectrometer ($\lambda = 3$) at 293 K. The fact that high activity required not just a copper-cobalt spinel but also the presence of copper associates led the authors to conclude that the latter also participate in the catalytic process. For catalysts of the composition $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ there appeared to be a direct dependence between the intensity of the oxygen peak in the photoelectronic spectra identified as O^- and the concentration of copper. Hydrogen pretreatment was shown to enhance catalytic activity. Figures 2; references 10: 6 Russian, 4 Western.

An Investigation of the Process of the Decomposition of Sulfuric Acid on a Chromic Phosphate Catalyst

917M0186A Leningrad ZHURNAL PRIKLADNOY KHMII in Russian Vol 64 No 1, Feb 91 (manuscript received 5 Dec 89) pp 257-261

[Article by Ye.V. Ivanova, V.N. Kovalev, A.F. Petropavlovskiy, V.Ye. Soroko, and A.V. Forsov, Leningrad Technological Institute imeni Lensovet and Leningrad Mining Institute imeni G.V. Plekhnov]

UDC 660.257.609

[Abstract] One of the main drawbacks of known catalysts of the decomposition of sulfuric acid is that they result in sulfatization of the active component and/or carrier. The transition of oxides to sulfates sharply reduces catalysts' activity. One way around this problem is to use catalysts whose sulfatization temperature is below the temperature of the sulfuric acid decomposition process. In light of this fact, the authors of the study reported herein examined the process of the decomposition of sulfuric acid on a chromic phosphate catalyst. Specifically, they examined the effect of preparation method on the catalyst's properties. They studied catalysts produced by two methods: 1) precipitation by urea from a chromic (III) nitrate and phosphoric acid solution and 2) redox precipitation by formalin from a chromic (VI) oxide and phosphoric acid solution. They studied the effect of hydrothermal processing of hydrogels of chromic phosphate on the physicochemical characteristics and activity of chromic phosphate specimens. Subjecting catalysts to this treatment increased their specific surface significantly. This increase was attributed to a phase transition that resulted in the dispersion of the hydrogel's primary particles. Studies of the effect of adding aluminum, copper, cobalt, and nickel nitrates to the chromic (VI) oxide and phosphoric acid solution indicated that adding a second cation to chromic phosphate does not increase catalysts' activity. Other experiments

performed demonstrated that changing the phosphorus:chromium molar ratio affects both the physicochemical properties of the specimens and their activity during the process of the decomposition of sulfuric acid. A simple specimen with a phosphorus:chromium ratio of 1 was found to be the most stable under the conditions of the said process. The authors also demonstrated that the said process occurs in the kinetic range when catalyst particles less than 0.75 mm in diameter are used at temperatures up to 1,173 K with acid flow rates ranging from 0.83×10^{-2} to $3.33 \times 10^{-2} \text{ cm}^3/\text{s}$. Finally, they derived an equation expressing the degree of sulfuric acid decomposition as a function of contact time, temperature, and acid concentration. They concluded that their equation was suitable for describing the process of the decomposition of sulfuric acid on a chromic phosphate catalyst in the range of temperatures from 1,000 to 1,200 K and pressures from 0.1 to 3.0 MPa. Figures 5, table 1; references 9: 8 Russian, 1 Western.

The Oxidation of Hydrogen Sulfide on a Complex Iron-Containing Catalyst

917M0186B Leningrad ZHURNAL PRIKLADNOY KHMII in Russian Vol 64 No 1, Feb 91 (manuscript received 22 Feb 89) pp 261-266

[Article by T.G. Alkhazov, A.I. Kozharov, and I.M. Mirzoyev, Azerbaijan Oil and Chemistry Institute imeni M. Azizbekov]

UDC 66.097.3:661.217

[Abstract] The authors of the study reported herein advocate returning to the Claus' method of direct oxidation of hydrogen sulfide by the oxygen in air in order to scrub hydrogen sulfide from tail gases. They studied the oxidation of hydrogen sulfide on a complex catalyst containing the following (% by weight): Zn, 21; Fe, 17.5; Cr, 33.5; and O, 28. The catalyst was prepared in accordance with the conventional method. The catalyst had a specific surface of $24 \text{ m}^2/\text{g}$, apparent density of 2.6 g/cm^3 , true density of 4.7 g/cm^3 , total pore volume of 0.17 g/cm^3 , and porosity of 45%. The catalytic reaction resulted in the by-products sulfur dioxide and water (steam). Data are presented on the effect of oxygen concentration reaction time and temperature, as well as the effect of the aforementioned by-products on the process of hydrogen sulfide oxidation. The authors conclude that in the concentration and temperature ranges studied, a significant amount of the SO_2 formed results directly from H_2 , bypassing elemental sulfur. Figures 4, tables 3; references 10: 7 Russian, 3 Western.

An Investigation of the Productivity and Selectivity of Copper-Containing Catalysts of Methanol Synthesis

917M0186C Leningrad ZHURNAL PRIKLADNOY KHMII in Russian Vol 64 No 1, Feb 91 (manuscript received 5 Apr 90) pp 267-271

[Article by I.G. Popov, V.S. Sobolevskiy, L.F. Reshetnyak, G.P. Cherkasov, and A.S. Anokhina]

UDC 55.097.3:(66.091+547.261)

[Abstract] In an effort to improve the quality of catalysts of methanol synthesis, the authors of the study reported herein examined the effect of process temperature on the effectiveness of selected copper-containing catalysts of methanol synthesis. The commercial catalysts SNM-1 and JCJ were tested along with DV-8-2 (which is being produced experimentally) and the laboratory prototype catalyst MTsA-1. DV-8-2 is based on the system copper-zinc-chromium-aluminum and was developed for use in methanol synthesis at pressures up to 35 MPa, whereas the other three catalysts are based on the system copper-zinc-aluminum and were developed for methanol synthesis at pressures up to 10 MPa. The catalyst reduction and synthesis processes were conducted at a space velocity of 30,000 h⁻¹ with the following gas composition (% by weight): CO₂, 5.5; CO, 14.0; H₂, 50.5; N₂, 30.0; and H₂-CO₂/CO + CO₂, 2.3. The charge amounted to 30 cm³. The temperature dependence of the catalysts' productivity was studied in the range of temperatures from 200 to 360°C. Their stability after superheating to 360°C was tested by reducing the temperature to 280°C. The three catalysts, tested at a pressure of 10 MPa, demonstrated maximum productivity at different temperatures: SNM-1 was most productive between 210 and 220°C, a temperature of 240°C was determined to be optimal for JCJ, and MTsA-1 exhibited maximum productivity at 250-260°C. All three resulted in approximately the same amount of methanol at their respective optimal temperatures (the difference only amounted to about 5%). DV-8-2 was observed to have a much lower productivity. Studies of the catalysts' comparative selectivities at 10 MPa indicated that MTsA-1 and JCJ have a virtually identical selectivity (>95%). Both were thus recommended for use in commercial methanol synthesis at pressures of 8-10 MPa. Even though DV-8-2 was less productive, it was still recommended for synthesis processes conducted under pressures of 25 to 35 MPa. Figures 2, tables 2; references 9: 7 Russian, 2 Western.

The Effect of Carrier on the Process of Sintering the Active Component of a Nickel Catalyst of Hydrocarbon Conversion

917M0186D Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 64 No 1, Feb 91 (manuscript received 18 January 90) pp 271-276

[Article by L.Yu. Fedchenko, Ye.N. Denbnovetskaya, V.V. Veselov, and I.G. Donets, Gas Institute, UkSSR Academy of Sciences]

UDC 66.012.46

[Abstract] The sintering of the active component applied to the alumina carrier is one of the main reasons why nickel catalysts of natural gas conversion experience a reduction in their activity at high temperatures. In an effort to overcome this problem, the authors of the study reported herein examined the effect of the carrier on the process of the aforesaid sintering during the catalyst

conversion of hydrocarbons. The examined the effect of a number of metal oxide additives on the properties of the alumina carrier and catalyst used in catalytic conversion of hydrocarbons. They discovered that adding small amounts of metal oxides has various effects (depending on the individual additive) on the carrier's microstructure and is an effective means of controlling the carrier's pore structure. K₂O and MgO additives were found to slow the transition of precorundum forms of Al₂O₃ contained in the starting alumina into the highly dispersed form α -Al₂O₃, to help maintain large particles of precorundum forms of Al₂O₃ in the carrier's structure, and to thus reduce the carrier's effectiveness as a stabilizer of the disperse structure of the applied nickel. They further discovered that adding 3% (by weight) BaO or ZrO₂ to the structure of an alumina carrier results in the formation of α -Al₂O₃, which has a higher dispersion than that of α -Al₂O₃ in a carrier without additives. The authors go on to hypothesize that this is precisely the form that results in applied nickel with the greatest thermal stability. They therefore go on to recommend ZrO₂ (in the amount of 3% by weight) as the optimal additive to alumina used in the process of the catalytic conversion of hydrocarbons. Figures 2, tables 1; references 14: 10 Russian, 4 Western.

An Investigation of the Composition of Tars on Deposited on the Surface of a Cu-Zn-Cr-Al Catalyst for Dehydrogenation of Cyclohexanol

917M0186E Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 64 No 1, Feb 91 (manuscript received 5 Dec 89) pp 370-375

[Article by V.Z. Fridman and F.Kh. Sapozhnikova, Kuzbas Polytechnic Institute]

UDC 541.127:547.514.721:546.33

[Abstract] The process of the dehydrogenation of cyclohexanol on a Cu-Zn-Cr-Al catalyst is only one of many high-temperature processes conducted in an oxygen-free medium that is characterized by the build-up of tars on the catalyst surface. In an effort to gain more information about the tars typically formed during such processes, the authors of the study reported herein examined the build-up of tars that occurs when the copper-zinc-chromium-aluminum catalyst NTK-4 is used in the dehydrogenation of cyclohexanol. Specimens of the spent NTK-4 catalyst were extracted from a commercial cyclohexanol dehydrogenation unit that had been used for 11 months. Accumulated tar compounds accounted for as much as 25% of the specimens' surfaces. The tars in question were extracted from the catalyst surface by boiling in acetone for 12 hours. They were then subjected to elemental analysis and mass spectrometry and IR spectroscopy studies. The chromatogram of the tar compounds extracted from the catalyst surface contained 43 peaks. Mass spectra could only be obtained for 12 compounds, and 8 of those could not be determined with a high degree of probability. The authors present several

diagrams detailing what they propose to be the structures of the compounds deposited on the catalyst surface. These compounds are said to be saturated compounds containing -OH, -C=O, and -C-O-C- functional groups produced by the cracking, dehydration, and etherification of cyclohexanol and its transformation products. Also included is a table detailing data extracted from the mass spectra of the compound having file position 245 on the chromatogram. Figures 2, table 1; references 7 (Russian).

Genesis of Active Component of Oxide Vanadium-Phosphoric Catalysts

927M0003C Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 57 No 8, Aug 91 (manuscript received 04 Oct 90) pp 815-819

[Article by V.A. Zazhigalov, V.M. Belousov, G.A.-Kmarshko, A.I. Pyatnitskaya, and N.P. Boronina, Physical Chemistry Institute, UkSSR Academy of Sciences, Kiev]

UDC 541.128.1+541.183+541.451+535.15

[Abstract] The authors of the study reported herein used the methods of infrared Fourier spectroscopy and scanning electron microscopy to study the formation of the phase $\text{VOHPO}_4 \cdot 0.4\text{H}_2\text{O}$ as it is synthesized from V_2O_5 and H_3RO_4 in an organic solvent. The authors began their investigation of the dynamics of the formation of the phase $\text{VOHPO}_4 \cdot 0.4\text{H}_2\text{O}$ with a study of the granulometric composition of the starting V_2O_5 . Specimens taken at 3, 6, and 15 hours into the synthesis process were subjected to x-ray crystallographic analysis. In the second phase of the research, a V_2O_5 fraction with a grain size of 150 to 250 μm was studied at 15 and 25 hours into the synthesis process. The results, coupled with scanning electron microscopy studies, enabled the authors to establish that the dispersion of the starting V_2O_5 affects both the rate and the completeness of phase formation. In large granules of V_2O_5 , the formation of the phase V-P-O affects the near-surface band, which may migrate to the depths of the grain upon subsequent heating. This authors hypothesized that this phenomenon would greatly affect the catalytic properties of a V-P-O catalyst during the process of partial oxidation of C_4 hydrocarbons. Their hypothesis was confirmed by data demonstrating that only after 50 hours of synthesis in the presence of large grains were suitable process indicators achieved. Because the band of rather rapid (under 15 hours) formation of the compound V-P-O is between 50 and 60 μm , the authors concluded that the grain size of V_2O_5 should not exceed 100 to 120 μm . This recommendation is confirmed by data on the effectiveness of V_2O_5 in the partial oxidation of n-butane. Figure 1, tables 3; references 11: 3 Russian, 8 Western.

The "Anomalous Activity" of Cobalt Catalysts of the Hydrogenation of Carbon Monoxide on a Rutile-Anatase Carrier

927M0003D Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 57 No 8, Aug 91 (manuscript received 6 Jul 90) pp 819-823

[Article by I.T. Chashechnikova, V.M. Vorotyntsev, V.V. Shimanovskaya, A.M. Puziy, and G.I. Golodets, Physical Chemistry Institute, UkSSR Academy of Sciences, Kiev]

UDC 541.128.13

[Abstract] In a continuation of their previous research on catalysts of the hydrogenation of carbon monoxide, the authors of the study reported herein examined cobalt catalysts based on chemical and mechanical mixtures with a rutile:anatase ratio of 7:3. Their primary objective in so doing was to determine why a contact based on a chemical mixture whose carrier includes the virtually inertial component anatase manifests better catalytic properties than does a catalyst based on pure rutile. Through their experiments they demonstrated that a cobalt catalyst based on a mechanical mixture of rutile and anatase has a much lower catalytic activity and is much less selective with respect to liquid hydrocarbons than is a catalyst based on pure rutile. The authors further demonstrated that the inferior catalytic activity and selectivity of a mechanical rutile-anatase mixture is due to the fact that the anatase is located primarily on the surface of the carrier containing two phases of titanium dioxide. Cobalt applied onto a chemical rutile-anatase mixture was found to manifest better catalytic properties than does a cobalt-rutile contact. This was attributed to the fact that thanks to the structure of the two-phase titanium dioxide particles, the rutile (which facilitates the high activity of cobalt-titanium dioxide catalysts for Fischer-Tropsch synthesis) is located on the surface. The authors further conclude that it is the two-phase nature of the particles that is responsible for the carrier's optimal pore structure that is required for Fischer-Tropsch synthesis. Figures 2, tables 2; references 8: 6 Russian, 2 Western.

The Hydrogenation of CO , C_2H_2 , and Their Mixtures on a Rhodium-Titanium Catalyst

927M0003E Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 57 No 8, Aug 91 (manuscript received 7 Aug 90) pp 823-826

[Article by S.N. Orlik, G.G. Girushtin, and Yu.I. Pyatnitskiy, Physical Chemistry Institute, UkSSR Academy of Sciences, Kiev]

UDC 541.128.13

[Abstract] In a previous communication, the authors of the study reported herein demonstrated that unlike iron- and nickel-containing catalysts used at atmospheric pressure, rhodium and palladium catalysts result in the

formation of oxygen-containing compounds when used with $\text{CO-H}_2\text{-C}_2\text{H}_2$ mixtures. In the present communication, they report their study of the activity and selectivity with respect to oxygen-containing compounds of a number of palladium and rhodium catalysts and bimetallic contacts including lead, rhodium, and cobalt. The said catalysts were applied to various carriers in reactions of the hydrogenation of CO, acetylene, and their mixtures at atmospheric pressure. The hydrogenation products were subjected to chromatographic analysis. The authors also studied the effect of varying the flow velocity of the reaction mixture, the effect of temperature on the concentration of alcohols in the reaction mixture leaving the reactor, the dependence of the distribution of hydrocarbons by molecular mass, and the effect of the CO:H_2 ratio on alcohol yield. After summarizing their results, the authors developed a series of recommendations regarding the most favorable conditions for synthesizing oxygen-containing compounds during the hydrogenation of CO in the presence of acetylene on a rhodium-titanium catalyst at atmospheric pressure: 1) the CO:H_2 ratio should be between 1:1 and 6:1 (the yield of oxygen-containing compounds is highest at a CO:H_2 ratio of 5:1); 2) the concentration of acetylene should be between 5 and 10% (by volume); 3) the flow velocity of the reaction mixture should be between 25 and 75 ml/min (thus providing a contact time of 3 to 9 seconds); and 4) the temperature should be between 180 and 240°C. Figures 3; reference 1 (Russian).

The Catalytic Reduction of 2-Chloro-4-Nitroaniline by Hydrogen in the Liquid Phase on Raney's Nickel

927M0004C Ivanovo IZVESTIYA VYSSHIKH
UCHEBNIKH ZAVEDENIY: KHIMIYA I
KHIMICHESKAYA TEKHOLOGIYA in Russian
Vol 34 No 5, May 91 (manuscript received 26 Jun 90)
pp 91-95

[Article by M.P. Nemtseva, V.P. Gostikin, N.I. Plyashchnik, and Ye.P. Redkozubova, Department of Physical and Colloidal Chemistry, Ivanovo Chemical Technology Institute and Polymer Chemistry Scientific Research Institute, Tambov]

UDC 547.791.8.541.128.3

[Abstract] The catalytic reduction of substituted nitrochlorobenzenes by hydrogen is generally accompanied by the splitting off of chlorine. The degree of dehalogenation is highly dependent on the nature of the catalyst, concentration of nitro compound, pressure of the hydrogen, solvent, and temperature and is determined by the nature and position of the substituents in the benzene ring. Consequently, the optimal conditions of conducting the process so as to ensure the minimal splitting off of chlorine must be determined individually for each nitrochloro derivative. In view of this fact, the authors of the study reported herein examined the effect of the makeup of the binary solvent 2-propanol—water,

the concentration of nitro compound, the pressure of hydrogen, and temperature on the rate of hydrogen absorption and degree of dehalogenation during the reduction of 2-chloro-4-nitroaniline on Raney's nickel. To reduce 2-chloro-4-nitroaniline, the authors used Raney's nickel produced by a standard nickel-aluminum alloy by leaching out with a 25% NaOH solution for 5 hours. The experiments were conducted in a reactor with intensive stirring of the liquid phase at a pressure of 0.1 to 1.0 MPa and temperature of 273 to 338 K. One gram of catalyst, 10 μg Raney's nickel, and 100 cm^3 liquid phase were used. An LKhM-8MD chromatograph with a flame ionization detector was used. The effect of hydrogen pressure on the rate and selectivity of the process was studied at an initial 2-chloro-4-nitroaniline concentration of 0.3 mol/l. The effect of the makeup of the binary solvent 2-propanol—water on the rate and selectivity of the process was studied at atmospheric pressure and temperatures of 274 and 338 K. One gram or 6×10^{-3} mole 2-chloro-4-nitroaniline was added to the reactor. The tests performed established that the degree of dehalogenation occurring during the catalytic reduction of 2-chloro-4-nitroaniline does not depend on hydrogen pressure. Rather, it was found to decrease as the process temperature decreases and the initial concentration of nitro compound and content of 2-propanol in the solvent increase. These findings led the authors to conclude that reducing 2-chloro-4-nitroaniline with minimal splitting off of chlorine requires conducting the process at low temperatures in weakly polar or nonpolar solvents and continuously removing any water generated by the reaction from the reaction zone. The authors further recommended that the pressure be increased to 1-2 MPa and that a highly dispersed catalyst be used in order to increase the reaction rate. Figures 4, table 1; references 9: 8 Russian, 1 Western.

The Kinetics and Mechanism of the Reduction of 2-Nitro-2'-Hydroxyazobenzene by Hydrogen on Raney's Nickel in the Liquid Phase

927M0004D Ivanovo IZVESTIYA VYSSHIKH
UCHEBNIKH ZAVEDENIY: KHIMIYA I
KHIMICHESKAYA TEKHOLOGIYA in Russian
Vol 34 No 5, May 91 (manuscript received 27 Jul 90)
pp 95-100

[Article by O.V. Lefedova, V.P. Gostikin, and M.V. Ulitin, Department of Physical and Colloidal Chemistry, Ivanovo Chemical Technology Institute]

UDC 547.791.8:541.128.13

[Abstract] Several other publications have demonstrated that the catalytic reduction of 2-nitro-2'-hydroxy-methylbenzene to substituted benzotriazole occurs in two parallel directions. One culminates with the formation of o-phenylenediamine and o-aminoparacresol, and the other is accompanied by the formation of benzotriazole. Nowhere, however, are the reasons for the formation of these two parallel reaction

directions or the possible mechanism of the transformation of 2-nitro-2'-hydroxy-methylbenzene under catalysis conditions discussed. The objective of the present article is to substantiate a possible mechanism of the transformation of 2-nitro-2'-hydroxy-methylbenzene that occurs during its catalytic reduction by hydrogen on Raney's nickel in the liquid phase. The reduction process was performed on a liquid-phase catalytic reduction unit with intensive stirring of the liquid phase in a static mode as described elsewhere. The catalyst used consisted of Raney's nickel and porous nickel obtained from skeleton nickel by removing the residual aluminum from it. A 1-M solution of sodium alkali and 2-propanol were used as solvents. The course of the reaction was judged by measurements of the volume of absorbed hydrogen and thin-layer chromatography and polarography analysis of samples of the hydrogenation products. The analysis performed established that the reduction of o-nitroazobenzene in the presence of Raney's nickel occurs in accordance with associative and dissociative mechanisms. The former involves weakly bound molecular forms of hydrogen absorbed on the catalyst surface, whereas the latter involves strongly bound atomic forms of hydrogen absorbed on the catalyst surface. The following features of the reduction of 2-nitro-2'-hydroxy-methylbenzene in an alkaline medium were also established: 1) the amount of hydrogen absorbed in the first period of the reaction is less than the amount of reacted 2-nitro-2'-hydroxy-methylbenzene, which means that the latter could be reduced owing to the hydrogen of the catalyst and oxidation of the nickel surface; 2) nitroazobenzene is the main component of the intermediate compounds formed in an alkaline medium; and 3) when 2-nitro-2'-hydroxy-methylbenzene is completely reduced, the amount of n-oxide of benzotriazole in the solution continues to increase, whereas the amount of nitroazo compound decreases, thus indicating an intramolecular regrouping resulting in the transformation of the nitroazo compound to n-oxide of benzotriazole. Finally, the authors conclude that the selectivity of the process of catalytic reduction of 2-nitro-2'-hydroxy-methylbenzene to substituted benzotriazole can, in all likelihood, be regulated by changing the nature of the solvent or by adding various additives to it to change the state of the adsorbed hydrogen. Figures 2, table 1; references 16 (Russian).

Thermal Dissociation Rate Constant for Gaseous C_2F_5I

927M0006A Moscow KINETIKA I KATALIZ
in Russian Vol 32, No 3, May-Jun 91 (manuscript
received 15 May 90) pp 529-534

[Article by I. S. Zaslonko, Yu. K. Mukoseyev, G. A. Skorobogatov, V. N. Smirnov, and V. K. Khripun, Chemical Physics Institute, Moscow]

UDC541.124-13:542.921.4:547.412.262.5:533.6.011.72

[Abstract] Thermal decomposition of perfluoroethyl iodide was initially investigated by quasistationary

pyrolysis at 610-790K temperature range. However, this method is known to provide only partial information. In the present work an experimental study of the thermal decomposition of the above compound was undertaken and the results interpreted within the framework of the RRKM (Rice-Ramsperg-Kassely-Marks) theory. The rate constant was determined by using a shock tube technique and measuring the drop in optical density in the vicinity of the first absorption band of CF_3I . The rate constant for the recombination reaction $C_2F_5 + I = C_2F_5I$ was also derived. Figure 1; references 16: 9 Russian, 7 Western.

Kinetic Features of Carbideization of Niobium in Methane

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in Russian Vol 32, No 3, May-Jun 91 (manuscript
received 8 Aug 89) pp 564-570

[Article by K. V. Asatryan and S. L. Kharatyan, Chemical Physics Institute, Yerevan]

UDC541.127:[547.211+546.882]:546.261:539.219.3

[Abstract] A study was made of some the kinetic features of the high temperature reaction of niobium with methane using an electrothermographic technique under static conditions. Niobium filaments were heated electrically in the methane. Below 25 mm Hg methane pressure, two diffusion layers of carbideization products (Nb_2C and NbC) were observed to form. The growth rates of these products, at these low pressures, are independent of pressure. Above 30 mm pressure, a definite stage exists where a pyrographitic layer begins to form on the surface. This stage also takes place at the start of the process at 150-200 mm. The kinetic parameters for the parabolic growth of the carbide layers and methane pyrolysis on the NbC surface were determined, and the coefficients for solid phase diffusion of carbon in both carbide phases of niobium were computed. Figures 4; references 18: 11 Russian, 7 Western.

Monomolecular Reactions on Surface of Silica. Part III. Fluoridation of $SiOH$ and Hydrolysis of SiF Group

927M0006C Moscow KINETIKA I KATALIZ
in Russian Vol 32, No 3, May-Jun 91 (manuscript
received 13 Apr 90) pp 576-585

[Article by V. M. Gunko, Surface Chemistry Institute, Kiev]

UDC541.124'183:546.284:542.944.1'983:539.19

[Abstract] To resolve a discrepancy between experimental and calculated results, a study was made of the title reactions. Rate constants (with chemical activation) were determined by the RRKM theory. It was demonstrated that a low fluoridation rate of calcined silica at low levels of filling (to facilitate the monomolecular

adsorption HF complexes), provides maximum structural stability of the SiOH - HF complex. Figures 3; references 17: 12 Russian, 5 Western.

Quantum-Chemical Study of Role of Protons in Catalytic Conversion of Ethylene and Allene over Rhodium Complex

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in Russian Vol 32, No 3, May-Jun 91 (manuscript
received 23 Apr 90) pp 586-593

[Article by Ye. A. Kochetkova and A. F. Shestakov,
Structural Macrokinetics Institute; Chemical Physics
Institute, Chernogolovka]

UDC541.128:541.124-
145:542.952.6:547.313.2'315.1:546.97:539.19

[Abstract] Polymerization of unsaturated compounds over complexes of transition metals in protonic media is an unconventional approach to the preparation of oligomers and polymers that has not been thoroughly investigated. In the present work a quantum-chemical study within the framework of the expanded Hueckel method was made of the reactions of aquachloride rhodium complexes with ethylene, allene, and protons. One possible mechanism for the reaction consists of protonation of the complex to form a Rh-H bond where the substrate becomes included in subsequent reactions. Another possible mechanism is direct electrophilic attack by a proton on the coordinated substrate. Calculations support validity of the first mechanism. References 25: 8 Russian, 17 Western.

Activity of Zeolites in Reactions of Methanol with Hydrogen Sulfide

927M0006D Moscow KINETIKA I KATALIZ
in Russian Vol 32, No 3, May-Jun 91 (manuscript
received 30 Mar 89) pp 636- 641

[Article by A. V. Mashkina and V. N. Yakovleva, Catalysis Institute, Novosibirsk]

UDC541.128.13:541.124:541.183:[547.261+546.221.1]:
549.67

[Abstract] Methanol reacts with hydrogen sulfide in the presence of zeolites to form methyl mercaptans and dimethyl sulfide. At 350-400°C, the zeolites NaX, NaY, NaZSM-5, HNaY, and HZSM-5 have various degrees of activity. Evaluation of the latter, however, is difficult since comparisons were made only at constant contact times and deep or total methanol conversion. In the present work a quantitative comparison was made of various zeolites in regard to activity in the above reaction, based on kinetic data. Activity diminishes in the series HNaY and HZSM-5 HNaY NaX NaY. Methyl

mercaptan and dimethyl sulfide are formed in the presence of all zeolites, although via different routes. Decationated zeolites, containing proton sites, promote reactions between surface methoxyl groups and H₂S to form dimethyl sulfide. Zeolites containing "Lewis acid-base site" pairs, favor formation of methyl mercaptan. References 9: 2 Russian, 9 Western.

Molybdenum-Containing Catalysts for Hydrodesulfurization on Ti-Oxide Base

927M0006F Moscow KINETIKA I KATALIZ
in Russian Vol 32, No 3, May-Jun 91 (manuscript
received 22 Jan 90) pp 652-658

[Article by M. A. Lurye, I. Z. Kurets, O. V. Ovchinnikova, and D. F. Kushnarev, Petro- and Coal Chemical Synthesis Institute, Irkutsk]

UDC541.128.3:542.945.27'94:547.732:546.774'824-
31+665.658.2

[Abstract] During recent years, titanium dioxide has attracted much attention as a carrier for hydrofining catalysts. In many cases it facilitates preparation of catalysts having greater activity than the traditional aluminum oxide carrier. Owing to the differences in physical chemical properties, formation of Ti-containing catalysts is markedly different from that of its aluminum oxide analogs. In the present work, the properties of Mo-containing hydrofining catalysts, prepared by impregnation of hydrated titanium dioxide, were examined. A study was made of the effects of pH of the impregnating ammonium para- molybdate solution and the heat treating conditions on specific surface, as well as the catalyst composition and pretreatment thereof on its activity in thiophene hydrogenation. Addition of a promoter demonstrated that while raising thiophene conversion, it has no significant effect on the butane fraction in the C₄ products. Comparison testing of Ti-Mo-Ni and Al-Mo-Ni catalysts in hydrofining heavy crudes demonstrated also that the Ti-containing catalyst gives higher degrees of sulfur and metal (especially vanadium and nickel) purging. References 20: 4 Russian, 16 Western.

Kinetics of Benzene Hydrogenation over Plasma-Supported Planar Nickel Catalyst

927M0006G Moscow KINETIKA I KATALIZ
in Russian Vol 32, No 3, May-Jun 91 (manuscript
received 14 May 90) pp 671-677

[Article by A. A. Fomin, M. S. Granovskiy, S. I. Serdyukov, M. S. Safonov, and O. I. Veselkova, Moscow State University imeni M. V. Lomonosov]

UDC541.128.13:541.127:542.941.7:547.532:546.74:
533.92

[Abstract] Using catalysts having regular spatial packing instead of the traditional grainy layer makes it possible to significantly increase compactness in the reaction zone of a catalytic reactor, while maintaining the same throughput rate and gas dynamic resistance. Ordered spatial configuration of the catalyst and heat exchanger elements enables elimination of the effects of diffusion throttling and making full use of the catalyst mass while facilitating effective heat transfer from the reaction. Catalysts in the form of a porous layer on the surface of a planer or ribbon substrate are most suitable in designing reactors having optimal transport ducts and heat exchange elements. Special methods of fabricating planer catalysts provide the possibility of varying their macrokinetic and technological parameters, e.g. the plasma-vacuum method used to prepare skeletal nickel catalyst, active in benzene hydrogenation. One of the universal methods for preparing catalyst coatings having specific properties is plasma dusting which enables wide scale variation in composition, porosity, and thickness of catalyst coating. In the present work plasma dusting with nickel on a nickel substrate was used to prepare a planer catalyst. The activity of this catalyst was significantly greater than that of the initial nickel in benzene hydrogenation. The kinetics of benzene hydrogenation over this catalyst was studied and a reaction mechanism is proposed. Figures 4; references 13: 8 Russian, 5 Western.

The Structure of Intermediate Cobalt Compounds in Metal Cluster Catalysts

927M0013D Moscow KOORDINATSIONNAYA
KHIMIYA in Russian Vol 17 No 6, Jun 91 (manuscript
received 2 Nov 89) pp 849-854

[Article by V.V. Sarayev, L.O. Nindakova, O.M. Reshetnikova, T.V. Dmitriyeva, and F.K. Shmidt, Petrochemical and Coal-Chemical Synthesis Institute, Irkutsk State University]

UDC 543.422.27:541.49:546.73:547.1.118

[Abstract] In a continuation of their research on metal cluster catalysts, the authors of the study reported herein examined the structure of Co (II) complexes formed in Ziegler-type systems, i.e., $\text{CoX}_2\text{-PBu}_3\text{-R}_n'\text{M}$ (where $\text{X} = \text{Cl}^-$ or Acac^- and $\text{R}_n'\text{M} = \text{PhMgBr}$, PhCH_2MgBr , and NaBH_4). A secondary purpose of their research was to collect data on the transformations of Co (I, II) complexes in their reaction with carbon monoxide. Electron spin resonance and ultraviolet and infrared spectroscopy studies performed on the said compounds enabled the authors to hypothesize the structure of the Co (II) hybrid complex and estimate the degree of covalence of the Co-H and Co-P bonds. The compound synthesized was determined to be a low-spin compound with a trigonal-pyramid structure. The characteristic features of the structure of mono- and dibenzyl Co (II) complexes containing a π -allyl-type bond are also discussed. The authors demonstrate that the reaction of $\text{CoCl}_2(\text{PBu}_3)_2\text{CO}$ with NaBH_4 results in the formation of the ionic complex $[\text{Co}(\text{PBu}_3)_n(\text{CO})_m]^+[\text{Co}(\text{CO})_4]^-$. Figure 1, tables 2; references 11: 5 Russian, 6 Western.

Extracting Iridium From High-Temperature Slime Sulfatization Solutions

917M01861 Leningrad ZHURNAL PRIKLADNOY KHMII in Russian Vol 64 No 1, Feb 91 (manuscript received 23 Jan 90) pp 418-419

[Article by Yu.S. Kanonov, L.I. Korneva, and V.G. Khizhnyak, Institute of Chemistry and Chemical Metallurgy Processes, Siberian Department, USSR Academy of Sciences]

UDC 546.92:541-11

[Abstract] The extraction of iridium from high-temperature slime sulfatization solutions in the nickel industry has been the subject of a number of research studies. In view of the interest in this topic, the authors of this concise report examined the use of nickel powder in the precipitation of iridium from solutions subjected to electrooxidation. Solutions simulating the high-temperature slime sulfatization solutions used at the Severonickel Combine were used in the studies. The first

solution contained green iridium (III, III, IV) sulfate with 20 mg/l iridium, 300 g/l sulfuric acid, and 40 g/l sodium chloride. The second solution contained all of the ingredients in the first solution plus 5 g/l nickel and 10 g/l iron. Solution 3 contained everything contained in solution 1 plus 5 g/l nickel (II), 10 g/l iron (III), and 10 g/l copper (II). Iridium 192 was added to all solutions in the very same form as stable iridium to monitor the distribution of iridium between the solution and sediment. Centrifugation was used to separate the sediment from the solution. Four experiments were conducted with solution 2, five with solution 1, and six with solution 3. No iridium was precipitated from solution 1. The highest iridium yields were obtained when solution 3 was used. The authors concluded that success in precipitating iridium at a temperature of 100°C is dictated by the adsorbability of the sediments. Preliminary electrochemical treatment was not found to result in any significant improvement. This was attributed to the high stability of the iridium compound in the form of green sulfate. Table 1; references 3 (Russian).

A Polarographic Study of the Complexing of Amines and Their Derivatives With Metal Ions

917M0137B Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 57 No 5, May 91 (manuscript received 2 Apr 90) pp 497-500

[Article by A.V. Grodyskiy and V.F. Gromovaya, Institute of General and Inorganic Chemistry, UkSSR Academy of Sciences, Kiev, and Institute of Bioorganic Chemistry and Petrochemistry, UkSSR Academy of Sciences, Kiev]

UDC 541.13

[Abstract] The authors of the study reported herein conducted a polarographic study of the complexing of amines and their derivatives with metal ions. The study is based on the measurement of the dependence of the shift in the potential of the half-wave ($\phi_{1/2}$) on the concentration of free ligand. This shift is proportional to the complexing log. The laws presented and used in the study are based on the principle that the reaction of the formation and dissociation of free metal-free ligand complexes occurs rather quickly in both direction. The complexing of ions is defined as a function of the ligand under conditions of slow dissociation of the complexes formed. A system of 10 complexing equations is presented along with tentative stability constants of four different Me^{n+} -type complex compounds that were determined on the basis of polarographic studies using an LR-60 polarograph. The studies demonstrate that monoethanolamine, cyclohexylamine, and benzoate of monoethanolamine reduce the reduction waves of Zn^{2+} , Cd^{2+} , and Fe^{2+} and form complex compounds with them. Figures 3, tables 2; references 8 (Russian).

The Laws Governing Structure Formation Due to the Marangoni Effect in Electrochemical Systems

917M0137C Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 57 No 5, May 91 (manuscript received 4 May 90) pp 500-506

[Article by V.V. Nechiporuk and I.L. Elgurt, Chernovtsy University]

UDC 541.13

[Abstract] Uneven surface tension is one of the most important factors impairing hydrodynamic stability in systems containing a liquid-liquid interface. In view of this fact, the authors of the study reported herein examined the effect of the laws governing structure formation due to the Marangoni effect in electrochemical (i.e., liquid electrode-liquid electrolyte) systems. The conditions of the occurrence of three-dimensional dissipative structures during the electrodeposition of metals on liquid electrodes are examined. The critical value of the Marangoni number is shown to be a function of the laws governing the kinetics and conditions under which the process is conducted and the ratio of the thicknesses of

the electrode and electrolyte layers. Neutral current-wave number and potential-wave number curves are determined for electroplating and potentiostatic modes. It is demonstrated that the instability of stationary states narrows as the concentration of electrically active ion decreases and the thickness of the electrolyte layer increases. The laws established show that structure formation in systems containing a liquid electrode-electrolyte interface is the result of positive feedback between the mass transfer in processes in the bulk and the electrode reaction at the surface (realized through surface tension). A series of 29 equations and groups of equations is included. Figures 3; references 7: 5 Russian, 2 Western.

Laser Activation of Electrochemical Evolution of Hydrogen on Nickel

917M0179A Moscow ELEKTROKHIMIYA in Russian Vol 27 No 4, Apr 91 (manuscript received 14 Mar 90) pp 442-447

[Article by I.O. Yefimov, A.G. Krivenko, and V.A. Benderskiy, Institute of Chemical Physics Energy Problems, Chernogolovka]

UDC 541.138:620.193

[Abstract] Research has shown that the laser activation effect, i.e., the acceleration of electrochemical reactions during a nondestructive laser effect, occurs within a broad range of laser pulse intensities and durations. The mechanism of laser activation is of both theoretical and practical interest from the standpoint of its possible use in creating new methods of microdimensional electrochemical treatment. For this reason, the authors of the study reported herein conducted an in-depth study of laser activation of the electrochemical evolution of hydrogen on nickel. They discovered that the generation of nanosecond laser pulses with an intensity exceeding 10 MW/cm^2 onto a cathode-polarized nickel electrode results in the formation of current pulses corresponding to the transfer of a charge (Q) to the solution that equals the quantity of hydrogen adsorbed on the irradiated surface. The dependences of Q on energy and pH were shown to have the form of adsorption isothermic lines. The studies conducted enabled the authors to hypothesize that laser activation of two-stage electrode processes involving intermediate adsorbed particles may be associated with a reduction in their surface concentration owing to rapid desorption when subjected to a laser effect. The current pulses observed were due to the subsequent restoration of their initial surface filling as a result of the electrochemical discharge of hydrogen ions (at pH levels of about 3 or less) and water molecules (at pH levels of about 3 or more). Figures 5; references 15: 10 Russian, 5 Western.

The Effect of Lithium Hydroxide on the Properties of Supersaturated Zincate Solutions Obtained in Nickel-Zinc Systems

917M0179B Moscow ELEKTROKHIMIYA in Russian
Vol 27 No 4, Apr 91 (manuscript received 15 Feb 90)
pp 512-518

[Article by M.S. Zubov, R.R. Dzhurayev, V.I. Baulov, and A.V. Kotov]

UDC 541.136.3

[Abstract] Stabilizing the supersaturated zincate solutions formed during the discharge of alkaline current sources is one way of improving the characteristics of both the current sources themselves and storage batteries. In view of the practical importance of this problem, the authors of the study reported herein studied a number of physicochemical properties of supersaturated zincate solutions with and without lithium hydroxide additives. Test supersaturated zincate solutions were prepared by the anodic dissolution of zinc in model nickel-zinc batteries filled with 7N KOH with a zinc oxide additive (55 g/l) at a temperature of -10°C and a current density of 0.5 mA/cm² for 6 days. The lithium hydroxide was added to the supersaturated zincate solutions obtained after the discharge. It was added in the form of a finely dispersed powder. The concentration of zincate in the solution was determined by titration with Trilon B with an indicator. The falling ball method was used to measure the solutions' relative viscosity. The refractivity of the thermostatted solutions was determined on an IRF-22 refractometer, and the sediments precipitated from the supersaturated zincate solutions were analyzed by IR spectroscopy, x-ray phase analysis, and emission spectroscopy. The presence of lithium hydroxide was found to result in a sharp increase in solution stability. Solutions not containing lithium hydroxide, on the other hand, ended up with less than half the initial amount of zincate. It was established that the process of the "aging" of a system containing lithium hydroxide not only entails the formation of zinc oxide sediment but also the formation of orthorhombic zinc hydroxide crystals. The IR spectra of the crystals in question were found to contain absorption bands characteristic of bridge and terminal OH groups. Valence fluctuations were observed at 3,250 cm⁻¹, and very weak crystallization water bands were observed in the vicinity of 1,630 and 925 cm⁻¹. The presence of orthorhombic crystals in the system with lithium hydroxide led the authors to hypothesize that the latter facilitates the formation of Zn(OH)₂ or protects it from reacting with KOH. They further emphasized the importance of the role of the entropy factor in stabilizing supersaturated zincate solutions. Figures 4; references 22: 15 Russian, 7 Western.

Electrochemically Initiated Polymerization of Vinyl Monomers. Vinyl Acetate in Sulfuric Acid Solutions

917M0179A Moscow ELEKTROKHIMIYA in Russian
Vol 27 No 4, Apr 91 (manuscript received 24 Aug 89)
pp 527-529

[Article by Ye.I. Aksimentyeva, K.G. Bogoslovskiy, Ye.I. Kovalchuk, and L.A. Mirkind, Spekttr Scientific Production Association, Moscow]

UDC 541.183:547

[Abstract] The technique of electrochemically initiated polymerization has attracted a great deal of attention because of its advantages over conventional methods of applying polymer coatings. The technique has proved especially interesting with respect to vinyl monomers. In an effort to develop a better understanding of the effect of monomers' structure on the specifics of their anode behavior, the authors of this concise report have studied the surface phenomena occurring on a platinum anode in the presence of vinyl acetate. The procedures they followed when synthesizing the test vinyl acetate and taking all adsorption and kinetic measurements were in complete conformity with procedures published in detail elsewhere. The IR spectra of vinyl acetate films produced by electrochemically initiated polymerization and those of films produced by the conventional method were found to be identical. This was interpreted as indirect proof of the associative (i.e., without destruction of molecules) behavior nature of the adsorption of vinyl acetate, which is something that vinyl acetate shares with other unsaturated compounds researched on this plane. The adsorption and kinetic measurements made indicated that vinyl acetate synthesized by the technique of electrochemically initiated polymerization obeys the same adsorption laws that acrylonitrile has been shown to obey in other publications. The high monomer adsorbability observed under conditions of the generation of labile sulfoxyl radicals was attributed to localization of the stage of the initiation of polymerization on the surface. The absence of polymer in the bulk of the solution was seen to confirm that in the case in question (as opposed to the case of acrylonitrile), chain growth also occurs in a thin reaction layer near the electrode. Figures 3; references 12 (Russian).

The Effect of Passivating Adsorption on the Formation of a Laser-Deposited Ni Surface

917M0179D Moscow ELEKTROKHIMIYA in Russian
Vol 27 No 4, Apr 91 (manuscript received 2 Dec 88;
after revision 25 Oct 90) pp 535-585

[Article by Yu.V. Seryanov, Yu.I. Surov, and L.V. Aravina, Saratov]

UDC 541.183

[Abstract] The process of local laser-stimulated electrochemical precipitation of nickel is extremely promising

for use in producing images on foil-coated dielectrics in view of the possibility of automated manufacture of printed circuit boards and microcircuits with micron-range resolution. In view of the importance of this area of investigation, the authors of the study reported herein used an experimental unit based on an LTN-102 laser (wavelength, 1.06 μm ; power, 120 W) to examine the effect of passivating adsorption on the formation of a laser-deposited nickel surface. They produced nickel coatings on copper foil by electrolysis of a buffered sulfuric acid electrolyte with the following composition (mol/m^3): $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, 180; Na_2SO_4 , 500; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 244; H_3BO_3 , 352; and NaCl , 85. A pH level of 5 was used along with a nickel anode. Standard electroplating (current density, 60 A/m^2) and potentiostatic laser electrolysis (laser irradiation intensity, 21 MW/m^2 ; potential, 0.88 V relative to a normal hydrogen electrode) techniques were used. Specimens were subjected to x-ray, electron microscopy, and Auger electron spectroscopic studies. The authors concluded that the low effective interaction time and thermal activation of passivating adsorption processes occurring during the electrodeposition of nickel under the effect of a scanning laser beam dictate the preferential acceleration of nucleation center formation vs. linear crystal growth. This in turn facilitates the accelerated formation of extremely fine crystalline coatings that are entirely suitable for the laser-electrochemical "sketching" of elements of the topology of printed circuit boards and microcircuits. Figures 2; references 10: 9 Russian, 1 Western.

Electroprecipitation of Tellurium From Citrate Electrolytes

917M0179E Moscow ELEKTROKHIMIYA in Russian
Vol 27 No 4, Apr 91 (manuscript received 13 Apr 90)
pp 538-540

[Article by K.R. Rasulov, Tashkent State Pedagogical Institute imeni Nizami]

UDC 541.138:621.35:669.777

[Abstract] The demand for tellurium in semiconductor technology and microelectronics has increased significantly in recent years. In view of this increasing need, the authors of the study reported herein examined the effect of citric acid and ultrasound on the process of electrochemical precipitation as a technique of producing tellurium raffinate from nitric acid solutions. The cathodic behavior of tellurium was studied in solutions of 0.1-0.3 M Te + 0.3 M $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$ + 2.5 M HNO_3 . The technique used to prepare the electrolyte for tellurium raffinate from T-2 commercial-grade powder tellurium (96% Te) has been described in detail elsewhere. The solutions for the polarization studies were prepared from type TA-1 commercial-grade tellurium. It was discovered that adding citric acid to nitric acid tellurium solutions results in a sharp increase in tellurium solubility. This increase was found to be similar to that observed when TeO_2 is dissolved in sulfuric acid in the presence of

citrate ions. Increasing the tellurium's solubility was found to make it possible to extend the range of usable cathode currents by a factor of 10 to 12 and to result in raffinate of relatively high purity. The authors succeeded in obtaining tellurium raffinate with a purity of 99.98% from T-2 commercial-grade tellurium at commercially significant cathode current densities. Figure 1, tables 2; references 7 (Russian).

Suppressing Contact Exchange During the Copper Plating of Steel in Sulfuric Acid Electrolytes

917M0179F Moscow ELEKTROKHIMIYA in Russian
Vol 27 No 4, Apr 91 (manuscript received 2 Jan 89)
pp 540-542

[Article by G.A. Bubnova, G.F. Kostrova, and L.D. Pekarskiy, Simferopol affiliate, Central Planning, Design, and Technology Office]

UDC 541.138.3

[Abstract] The electrodeposition of copper on carbon steels in electrolytes without complexing agents is complicated by the contact exchange process. Substances that increase cathode polarization on account of adsorption processes are generally used to suppress contact exchange. This is accomplished by adding surfactants either to the electrolyte or else to pretreatment solutions. In a continuation of this line of research, the authors of the study reported herein studied the effect that preliminary electrochemical treatment of steel in an activation solution (between 200 and 300 kg/cm^3 H_2SO_4) with the addition of a combination of surfactants (thiourea, dye, metal salt) has on the quality of copper precipitated from a standard sulfuric acid copper plating electrode with the brightener B-7211. The tests conducted established that treatment in a cathode mode in an activation solution containing optimal concentrations of the test surfactants facilitates the formation of copper coatings with high adhesion to iron-containing bases. A significant potential shift to the negative value range was observed during the process of electrodeposition of the copper. This phenomenon was explained by proceeding from the mechanisms of cathode reactions on iron in sulfuric acid copper plating electrolytes. The studies also demonstrated that cathode polarization in a sulfuric acid copper plating electrolyte depends on the magnitude of the current in the surfactant complex-containing activation solution. The authors cited the reduction in polarization observed at high cathode current values both in the activation solution and in the copper plating electrolyte itself and the respective reduction in the bond strength of the cathode precipitate as confirmation of their hypothesis that the inhibiting effect of the surfactants studied is based on an adsorption mechanism. Figures 2; references 3 (Russian).

Investigation of the Thermokinetic Characteristics of the Corrosion of Lithium in Aqueous Lithium Hydroxide Solutions

917M0179G Moscow *ELEKTROKHIMIYA* in Russian Vol 27 No 4, Apr 91 (manuscript received 5 Jun 90) pp 542-544

[Article by N.D. Koshel and A.S. Plashenko, Dnepropetrovsk Chemical Technology Institute imeni F.E. Dzerzhinskiy]

UDC 541.138

[Abstract] The electrochemical behavior of lithium in aqueous solutions of alkalis has been studied extensively in connection with the possibility of creating aqueous lithium current sources with a high specific power and high specific energy. In a continuation of this line of research, the authors of this concise report have studied the thermokinetic characteristics of the corrosion of lithium in aqueous lithium hydroxide solutions. Specifically, they used the gravimetric method to study the temperature dependence of the rate of lithium corrosion within a broad range of alkali concentrations and temperatures. For their experiments, they used lithium disks 13 mm in diameter and 1.75 mm thick. They found that the corrosion of lithium is not subordinate to a Arrhenius equation. An examination of the entire range of states studied by the authors revealed three regions in which the slope of the temperature dependence of corrosion speed differed. After discussing these three regions in detail, the authors proceed to describe the corrosion rate of lithium in terms of the following exponential Arrhenius function with a temperature-dependent effective process activation energy:

$$i_{\text{corr}}^0 = A \exp(-bc) \exp[-E(T, c)/(RT)]; E = 9 \times 10^4 - d(373 - T) - rc,$$

where $\ln A = 35$, $b = 0.408$, $d = 146$, and $r = 1,455$ are constants determined by the least squares method. They state that these expressions have a logical physical substantiation and describe the corrosion of lithium with adequate precision over a broad range of conditions. Figure 1; references 10: 5 Russian, 5 Western.

Formation of an Ion Exchange Surface on Electrodes by the Electrochemical Copolymerization Method

917M0186H Leningrad *ZHURNAL PRIKLADNOY KHIMII* in Russian Vol 64 No 1, Feb 91 (manuscript received 29 Jan 90) pp 322-326

[Article by V.A. Smirnov, L.N. Maksimova, N.P. Kotenko, and O.I. Nesterova]

UDC 621.3.035.2:541.183.12

[Abstract] The creation of electrolyzers in which one or both of the electrodes is in direct contact with the surface of the ion exchange membrane is one way of improving

processes of electrolysis of chlorides and sulfates of alkaline metals. The authors of the study reported herein examined the possibility of creating an ion exchange surface on various cathode materials by the method of electrochemical polymerization of acrylamide and fluorinated monomer used in the production of ion exchange membranes. For their electrochemical copolymerization, the authors used a 0.2-L acrylic plastic vat and an emulsion consisting of the following: 7 mol/L acrylamide, 0.2 mol/L zinc chloride, and 7 mol/L formalin. They tested several materials with a low supersaturation of hydrogen as prospective cathodes: steel, porous nickel, type VVP and Ural graphite fibers, and VVP electrochemically nickel-plated fabric. The electrodes' surface was preliminarily neutralized by cathode polarization in a 12% sodium hydroxide solution. The surface was then rinsed by the stream method and dried. A one-sided coating was obtained by insulating one of the electrode's sides with an adhesive strip. After precipitation of the polymer coating, the specimens were dried at 40 to 50° for 1 hour. Potentiostatic measurements were taken to derive polarization dependences. The experiments conducted confirmed the fundamental possibility of forming an ion exchange surface on electrodes by the method of electrochemical copolymerization. The following were determined to be optimal conditions for forming an ion exchange surface on porous electrodes of nickel and graphite: current density, 20 mA/cm²; precipitation time, 40 to 60 s; monomer concentration, 0.16 mol/l; and surfactant concentration, 0.05 g/L. The coatings thus produced were demonstrated to have good adhesion, good corrosion and chemical resistance in acids and alkalis, and an exchange capacity of 0.73 to 1.28 mmol/g dry polymer. Figures 3, tables 3; references 5: 4 Russian, 1 Western.

The Kinetics and Mechanism of Electrode Reactions Involving Mercury in Bromide Solutions

927M0001A Kiev *UKRAINSKIY KHIMICHESKIY ZHURNAL* in Russian Vol 57 No 7, Jul 91 (manuscript received 15 Mar 90) pp 733-739

[Article by L.F. Kozin, Institute of General and Inorganic Chemistry, UkSSR Academy of Sciences, Kiev]

UDC 541.13

[Abstract] Mercury (II) bromides are widely used in refining mercury to a high purity by electrolysis. Despite this fact, the kinetics and mechanism of the discharge and ionization of mercury in bromide solutions have remained unstudied. This is largely because mercury bromides are sparingly soluble in water and the resultant solutions are complex from a composition standpoint. In view of these facts, the authors of the study reported herein examined the kinetics of the discharge and ionization of mercury in aqueous-saline bromide solutions. The studies were conducted in ammonium bromide solutions consisting of 1×10^{-5} to 0.5 M Hg²⁺, 4.5 M NH₄Br, and 3.5 M HBr. The polarization curve, double-pulse

galvanostatic, and coulometry methods were used to determine the kinetic parameters of the reactions and to study the cathodic and anodic current efficiencies of mercury under various experimental conditions. The authors then used the experiment results to derive kinetic equations for the electrode processes occurring in accordance with mechanisms involving concomitant (anodic) and antecedent (cathodic) chemical reactions of the intermediates involved. The authors concluded that in the case of the anodic dissolution of mercury in a concentrated ammonium bromide solution, the end products of the electrode process, i.e., HgBr_4^{2-} ions, are formed in accordance with a disproportionation reaction. The current efficiency of cathodic processes was found to be less than 100%. This was because, even under conditions of laminar flow of the mercury electrode, ions of univalent mercury are entrained into the volume of the solution, accumulate in it until threshold concentrations are reached, and then dissociate. This in turn leads to the formation of colloidal particles of metallic mercury that turn the electrolyte black. These colloidal particles eventually coagulate into finely dispersed mercury drops that cover the walls of the electrolyzer and its components. These finely dispersed particles generally diminish the electrolyzer's separative power when high-purity mercury is being produced. Figures 5; references 15: Russian, Western.

The Activating Role of Chloride Ion During the Contact Exchange of Metals on Stainless Steels

927M0001B Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 57 No 7, Jul 91 (manuscript received 30 Jul 90) pp 739-743

[Article by E.S. Morozenko, A.S. Molotkov, A.V. Gorodyskiy, and V.M. Beletskiy, Institute of General and Inorganic Chemistry, UkSSR Academy of Sciences, Kiev]

UDC 541.13:621.793.3

[Abstract] The processes of contact (phase) exchange of metals have been well studied in simple systems of the type Fe/CuSO_4 and H_2SO_4 , where pure iron or low-carbon steel is used as the displacing metal. For various reasons, however, these same processes have been much less well studied in alloyed and stainless steels. In view of this fact, the authors of the study reported herein studied the effect of chloride ions on the occurrence of contact exchange of metals on high-alloy and stainless steels as a function of their dopant content. They studied chromium and chromium-nickel steels with various amounts of dopants (chromium and nickel) and main component (iron). Specifically, they studied the 20Cr13 alloyed chromium steel, 12Cr18Ni10Ti stainless chromium-nickel steel, and 36NiCrTiAl ferrochromium-nickel steel. For comparison, they also studied St45 carbon steel, chromium, nickel, and copper. Studies incorporating polarization measurements and potentiometry

reveal that with respect to the steels studied, the activating effect of chloride ions is greatest in St45 steel and becomes successively smaller in 20Cr13, 12Cr18Ni10Ti, and 36NiCrTiAl steels. The rate of contact exchange of metals in the four steels studied decreases in the very same order and is actually completely absent in 36NiCrTiAl. The authors thus demonstrate that the activating effect of chloride ions in contact exchange processes depends on the degree of surface passivation, which is in turn connected to chemical composition. The authors also succeed in illustrating that the potentiometric used in their research may be used to determine the conditions for implementing contact exchange on stainless steels. Figures 3, table 1; references 7 (Russian).

Voltammetry of Deposition of Nickel Onto Pressed Graphite Materials

927M0001C Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 57 No 7, Jul 91 (manuscript received 13 Jul 90) pp 743-747

[Article by D.B. Chernyy, I.I. Karpov, G.P. Prikhodko, and I.G. Chernysh, Institute of Surface Chemistry, UkSSR Academy of Sciences, Kiev]

UDC 546.7+661.66+667

[Abstract] The authors of this article present the results of their polarization studies of the electrodeposition of nickel onto type GAK-2 and GSM-2 graphite materials and heat-expanded graphite pressed under a force of 15 MPa. They used a PI-50-1 potentiostat in a potentiostatic mode to extract polarization curves in still and stirred electrolytes. They used an electrolyte with the following composition (g/l): $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, 240; $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 30; and H_3BO_3 , 30. The measurements were taken at a pH of 6 and at temperatures of 293, 298, 323, and 348 K. A comparison of the polarization curves of the deposition of nickel at various temperatures on electrodes made of GSM-2 and heat-expanded graphite revealed that the coating formation process begins at potentials ranging from -0.5 to -0.8 V on heat-expanded graphites and at potentials between -0.6 and -0.75 V on GSM-2. The authors managed to determine that electrodes made of heat-expanded graphite are characterized by lower critical electrodeposition currents and higher metal deposition rates than are electrodes made of artificial graphites. The authors developed and presented a three-dimensional diagram of the link between the electrical and temperature parameters of the process of the electrodeposition of nickel on an electrode made of heat-expanded graphite. The studies conducted enabled the authors to establish qualitative dependences of the said process parameters on the crystalline chemical ordering of the graphite material and the presence of surface functional groups whose composition and number are linked to the surface preparation of the graphite electrodes and the conditions of their preliminary electrochemical treatment. Figures 5, tables 2; references 9: 5 Russian, 4 Western.

The Electroprecipitation of Refined Aluminum From an Ether Hydride Electrolyte

927M0001D Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 57 No 7, Jul 91 (manuscript received 10 Sep 90) pp 751-754

[Article by A.L. Levinskas and R.P. Zhilinskene, Vilnius University]

UDC 541.135.2

[Abstract] The electroprecipitation of aluminum from ether electrolytes is conducted under conditions of an etherate medium of extreme effective basicity, i.e., with a delayed electroorganic transformation reaction generally involving diethyl ether. In electroplating technologies aluminum coatings and layers are generally obtained from an ether hydride electrolyte. Such electrolytes are generally characterized by high productivity and performance stability and yield a highly pure refined metal (99.99% pure by mass). The use of ether hydride electrolytes sometimes results in traces of atmospheric corrosion on the mirror surface of aluminum galvanic copies. This occurs when the concentration of lithium ions in the bath becomes elevated after a number of corrections in the bath's composition have been made. In an effort to eliminate this problem, the authors of the study reported herein examined the conditions of the cocrystallization of lithium and aluminum and attempted to optimize the composition of ether hydride electrolytes for contemporary aluminum electroplating technologies. For their experiments, they used three reaction mixtures (AlCl_3 [1.9 to 2.1 M], LiAlH_4 [0.2 to 0.4 M], and LiH [0.4 to 2.0 M]) and various dopants (titanium, indium, arsenic, antimony, and silver) in amounts ranging from 0.001 to 0.01 mol/l. They discovered that the implantation of lithium in refined aluminum is stimulated by an increase in the volume concentration of lithium cations. They further discovered that the process of lithium implantation is analogous to the coprecipitation of the aforementioned alloy-forming metals and aluminum. The order of the lithium inclusions does not, however, exceed 10^{-4} to $10^{-3}\%$ by mass. The results obtained led the authors to recommend that processes of the electroprecipitation of refined aluminum from ether hydride electrolytes include electrolysis bath elements and correction methods that make it possible to stabilize the lower bound of the lithium concentration in the ether hydride electrolyte at a level between 0.2 and 0.4 mol/l. Figures 3; references 11: 10 Russian, 1 Western.

Contact Exchange of Metals on a Ferrochromonickel Alloy

927M0003F Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 57 No 8, Aug 91 (manuscript received 20 Sep 90) pp 830-834

[Article by A.V. Gorodyskiy, E.S. Morozenko, A.S. Molotkov, and V.M. Beletskiy, Institute of General and Inorganic Chemistry, UkSSR Academy of Sciences, Kiev]

UDC 541.13:621.793.3

[Abstract] In an effort to determine the conditions required for contact exchange of metals on the surface of the alloy 36NiCrTiAl, the authors of the study reported herein conducted a series of polarization and potentiometric studies of the behavior of the said alloy in mixed electrolytes based on HCl and H_2SO_4 . The studies were performed in accordance with a method published elsewhere. The following were among the specific problems investigated: the dependence of the anode current and losses of metal on the concentration of hydrochloric and sulfuric acids in a 1:1 ratio, the change in the compromise potential of the study metal as a function of the HCl concentration in 0.48- and 0.6-M solutions of copper sulfate in the presence and absence of H_2SO_4 , and the corrosion behavior of the alloy 36NiCrTiAl in 0.6-M solutions of copper sulfate containing 0 to 4.5 mol/l hydrochloric acid. A significant increase in the rate of metal ionization in a mixture of HCl and H_2SO_4 in an anodic process was established. By using the potentiometric method, the authors were able to demonstrate that contact exchange of metals on high-alloy ferrochromonickel alloys of the type 36NiCrTiAl is possible in the presence of mixed sulfate-chloride activators capable of acting on both the active and passive sections of the metal's surface simultaneously. They determined that when an HCl concentration of 2.5 mol/l is reached, pitting corrosion ceases and the change in the compromise potential slows significantly, subsequently reaching a stationary value. Figures 4; references 9: 8 Russian, 1 Western.

Current Efficiencies of Zinc on Gallam Electrodes in Acid Chloride Electrolytes

927M0003G Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 57 No 8, Aug 91 (manuscript received 6 Jul 90) pp 834-839

[Article by L.F. Kozin and Ye.O. Berezhnoy, Institute of General and Inorganic Chemistry, UkSSR Academy of Sciences, Kiev]

UDC 620.193.7:546.47

[Abstract] Electrolysis of aqueous solutions of salts with liquid electrodes is a promising method of producing highly pure metals. In a continuation of the research that has been done on gallam electrodes, the authors of the study reported herein investigated the current efficiencies of zinc on gallam electrodes in acid chloride electrolytes. For their liquid electrodes, the authors used an alloy containing 7 atomic percent zinc. They studied its current efficiencies for electrolytes containing 0.05 to 2 M ZnCl_2 , 0.005 to 1 M HCl , and 0.1 to 2 M NH_4Cl . By making a series of corrosion measurements, they managed to demonstrate that the corrosion potential of zinc gallam is subordinate to the equation of the kinetic theory of corrosion. They found that the relationship between the anodic and cathodic current efficiencies of zinc follows a complex course. The cathodic current

efficiency of zinc during the electroreduction of Zn^{2+} ions is strongly dependent on the concentration of HCl in the electrolyte. The cathodic current efficiency of zinc decreases as the concentration of HCl increases. When the acid content in the electrolyte amounts to 1 M, the rate of hydrogen evolution close to the gallam anode initially increases and then decreases, thus confirming the additional dissolution of zinc as compared with the quantity corresponding to Faraday's law. The authors explain the "difference-effect" established during the anodic dissolution of zinc from a gallam electrode from the standpoint of the theory of the homo- and heterostage dissolution of metals. The studies performed led the authors to conclude that the optimal acid chloride electrolyte for producing zinc (i.e., an electrolyte providing a close-to-100% current efficiency) is one consisting of 2 M ZnCl_2 , 4 M HN_4Cl , and 0.01 M HCl. The corrosion rate of zinc gallam in the said electrolyte is at the sensitivity threshold of a gas coulometer and is on the order of $0.1 \mu\text{g Zn}/(\text{cm}^2\text{min})$ in the absence of a current. Figures 4; references 7: 5 Russian, 2 Western.

The Electrochemical Properties of Diffusion and Electrolytic Chromium-Containing Coatings in Saline Solutions

927M0003H Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 57 No 8, Aug 91 (manuscript received 20 Sep 90) pp 839-842

[Article by G.A. Tkach and V.B. Bayrachnyy, Kharkov Polytechnic Institute]

UDC 620.193.41

[Abstract] The authors of the study reported herein examined the electrochemical properties of pure chromium and its coatings produced by the method of diffusion carbide surface alloying. Wear-resistant chromium coatings were applied in thicknesses ranging from 10 to $15 \mu\text{m}$ to 10-mm-diameter disks made of St45 steel. Their electrochemical properties in solutions of Na_2SO_4 and MgSO_4 and their mixtures with NaCl were studied by means of a series of polarization measurements taken with a Pi-50-1.1 potentiostat in a thermostatted cell in a galvanodynamic cyclic mode in the range of potential from 1.5 to 3 V and the range of current densities from 0 to $100 \text{ mA}/\text{cm}^2$. The nature of electrolytes consisting of mineralized salt systems based on sodium and magnesium sulfates and chlorides was found to affect the rate of the corrosion process. Magnesium ions were found to retard the corrosion process; the rate of the anodic reactions occurring was found to be faster in mixtures of sulfates with sodium chloride. Coatings produced by diffusion carbide surface alloying were determined to have a greater corrosion resistance than electrolytic chromium coatings do. The authors established the passive-state and activation potentials and currents of passive-state corrosion of the different solutions and coatings studied. The said values are presented in table form. Figures 2, table 1; references 4 (Russian).

Electrocatalytic Activity of Platinum Catalysts on Carbon Carriers

927M0019A Moscow ELEKTROKHIMIYA in Russian Vol 27 No 5, May 91 (manuscript received 02 Apr 90) pp 563-570

[Article by V. S. Bagotskiy, G. V. Shteynberg and N. A. Urison, Institute of Electrochemistry imeni A. N. Frumkin, USSR Academy of Sciences, Moscow]

UDC 541.138.3

[Abstract] An electrochemical analysis was conducted on the impact of structural characteristics of carbon supports on the catalytic activity of Pt/C catalysts when external limitations on mass exchange are minimized. Analysis of several Pt/C systems (5% Pt) in ionization and hydrogen release from 10 N H_2SO_4 demonstrated that the specific activities were predicated on the nature of the carbon carrier. Studies with AG-3 and KM-2 activated carbon and acetylene carbon black showed that specific activities were greater for nonporous carriers in oxidation of hydrogen than on porous supports, despite the fact that the surface area of Pt on the latter carrier was 3- to 4-fold greater than on the former. In addition, activity of Pt/C catalysts was also influenced by pore size and increased with hydrophobicity, the latter property determining the nature and extent of binding of sulfate ions within and on the surface of the carrier. The data were interpreted to indicate that one of the key factors underlying electrocatalytic efficiency of Pt/C electrodes is the manner of distribution of Pt crystallites in and on the carbon grains. Figures 6; tables 2; references 10: 9 Russian, 1 Western.

Adsorption and Electropolymerization of C-14 Labeled Aniline on Platinum Electrodes

927M0019B Moscow ELEKTROKHIMIYA in Russian Vol 27 No 5, May 91 (manuscript received 17 Jan 90) pp 576-581

[Article by M. A. Spitsyn, A. V. Shlepakov V. N. Andreyev, Institute of Electrochemistry imeni A. N. Frumkin, USSR Academy of Sciences, Moscow]

UDC 541.183

[Abstract] C-14 labeled aniline was employed in analysis of the nature of aniline adsorption and electropolymerization on Pt/Pt in relation to time and electrode potential in 0.5 M H_2SO_4 . Analysis of aniline adsorption and polyaniline accumulation plots on the electrodes provided confirmation for previous observations that at $E_r > 0.8 \text{ V}$ in $> 10\text{E-}3 \text{ M}$ aniline solution two parallel processes occur: synthesis of a polymeric film and its oxidative decomposition. As a first approximation, under galvanostatic conditions polyaniline synthesis and accumulation is directly related to the coulombs transferred, with the Q/I ratio being proportional to doping of

the polymeric film with aniline monomers. Figures 3; tables 1; references 10: 4 Russian, 6 Western.

Assessment of Pulsed Current Parameters in Electroplating

927M0019C Moscow ELEKTROKHIMIYA in Russian
Vol 27 No 5, May 91 (manuscript received 10 Apr 90)
pp 605-612

[Article by N. A. Kostin, Dnepropetrovsk Institute of Railroad Engineers imeni M. I. Kalinin]

UDC 541.138.3:621.357.7

[Abstract] Previously reported studies on electroplating using pulsed polarizing currents were expanded to provide information on addition parameters ensuring the formation of smooth, dense, fine crystalline metal coatings. Accordingly, an equation was derived which relates $I_{\max}$, pulse duration and interpulse interval for optimum system performance. Adjusting pulsed electroplating experiments with zinc, nickel and rhodium to the ideal conditions described by the equation yielded surfaces with reflectance coefficients of 85-95%, 17.5-50 nm metal crystallites, and microhardness levels of 1550-8600 mN/m². The corresponding values for these metal films obtained by conventional electroplating were, respectively, 8-11%, 55-500 nm, and 720-6100 mN/m². Figures 3; tables 2; references 9: 6 Russian, 9 Western.

Electrochemical Determination of Steady-State Hydrogen Diffusion Rates Across Iron Membranes

927M0019D Moscow ELEKTROKHIMIYA in Russian
Vol 27 No 5, May 91 (manuscript received 30 May 90)
pp 633-639

[Article by Ye. A. Maleva and K. S. Pedan, Institute of Physical Chemistry, USSR Academy of Sciences, Moscow]

UDC 541.13+541.49

[Abstract] An experimental analysis was performed on the impact of the palladium electrolyte used for coating iron membranes (3.14 cm² cross-sectional area; 70 μ m thickness; < 0.005 % C, < 0.002 % S, < 0.002 P) on steady-state hydrogen diffusion rates across the membranes. The studies were carried at 20degC with the anodal and cathodal half-cells filled with 0.1 N NaOH. Trials with freshly prepared membranes in the case of palladium coatings prepared from nitryl triacetate electrolyte (20 g/L PdCl₂, 40 g/L nitryl triacetate, 20 g/L sodium gluconate) showed that steady-state hydrogen diffusion was ca. 20% greater (20.9 μ A) than the rate (17.3 μ A) obtained with palladium film prepared from an alkaline electrolyte (0.36 g/L PdCl₂, 60 g/L NaOH). In the former case the hydrogen content of the palladium coating was significantly greater (6.70 atom%) than in the latter (1.60 atom%). Heating the membranes at

200degC for 2 h reduced both the diffusion rate (to ca. 13.1-13.6 μ A) and the hydrogen content (to 0.10-0.39 atom%) in both cases. These observations confirm diffusion control of hydrogen transit across the membranes and suggest an essentially equivalent subsurface hydrogen concentration in all cases. Figures 1; tables 1; references 17: 3 Russian, 14 Western.

Electrochemical Behavior of Niobium in CsCl-KCl-NaCl-NbCl₅ Melt

927M0019E Moscow ELEKTROKHIMIYA in Russian
Vol 27 No 5, May 91 (manuscript received 11 Jun 90)
pp 640-647

[Article by I. R. Yelizarova, Ye. G. Polyakov and L. P. Polyakova, Institute of Chemistry and Technology of Rare Element and Mineral Raw Materials, Kola Scientific Center, USSR Academy of Sciences, Apatity]

UDC 541.138.3:669.293

[Abstract] Polarography, linear voltamperometry and constant voltage electrolysis were employed in an assessment of cathodal reduction of Nb at 790-983 K in a KCl-NaCl-CsCl (16.25-15.6-68.15%) eutectic melt containing niobium pentachloride. The resultant findings demonstrated that Nb reduction followed ECE-type mechanisms. The melt contained monomeric and dimeric forms represented by Nv(V) - Nb(IV) transitions, with the Nb ions reduced to the metallic form at various E values. Figures 5; tables 2; references 24: 6 Russian, 18 Western.

Thermodynamics of Two-Stage Adsorption of Cyanide Ions to Gold

927M0019F Moscow ELEKTROKHIMIYA in Russian
Vol 27 No 5, May 91 (manuscript received 03 Jul 90)
pp 683-686

[Article by N. A. Rogozhnikov, Institute of Solid Body Chemistry and Processing of Minerals, Siberian Department, USSR Academy of Sciences, Novosibirsk]

UDC 541.153.52

[Abstract] Impedance studies on the adsorption of CN⁻ to gold have results in the identification of a two-stage adsorption process, corresponding to 2 stages of the adsorbed ions. Thermodynamic analysis of the adsorption phenomenon has shown that the free energy of adsorption for the first stage increases from -11.7 to -29.2 kJ/mole as E is adjusted from -1.2 to -0.6 V. In the case of the second stage the corresponding change in the free energy of adsorption is from 9.7 to -1.6 kJ/mole, indicating that the latter stage is favored on energetic grounds. Presumably, the initial stage of adsorption involves electrochemical mechanisms with retention CN⁻ identity. In the second stage CN⁻ identity as a chemical factor is diminished with formation of AuCN complexes. Figures 3; references 4 (Russian).

Co-adsorption of Tetramethyl- and Tetrabutylammonium Cations at Mercury-Water Interface

927M0020A Moscow ELEKTROKIMIYA in Russian
Vol 27, No 6, Jun 91 (manuscript received
21 Sep 90) pp 691- 698

[Article by B. B. Damaskin, V. Yu. Tyurin, and S. L. Dyatkina, Moscow State University imeni M. V. Lomonosov]

UDC541.183.547

[Abstract] In a previous work adsorption behavior was studied in the system $0.05\text{mM}[(\text{CH}_3)_4\text{N}]\text{BF}_4 + 0.05(1-\text{m})\text{M}[(\text{C}_4\text{H}_9)_4\text{BF}_4$ at the mercury/dimethylsulfoxide interface. Applying the Hurwitz- Parsons method in analyzing this system revealed significant adsorption of tetramethylammonium cations resulting in overcharge on the mercury electrode surface. Since the reason for this result remained unresolved, the present work was undertaken to study adsorption behavior in the same system at the mercury/water interface by measuring differential capacity (C) and threshold potential (d) as a function of electrode potential (E). The shape of the C,E- and d,E-curves attest to the discreet nature of adsorption of tetrabutylammonium cations at the mercury/water interface. Calculations based on experimental data demonstrate that behavior of this system is governed chiefly by specific adsorption of tetrabutylammonium cations and their electrostatic displacement of less active tetramethylammonium cations. Figures 7; references 15: 7 Russian, 8 Western.

Electrochemical Properties of Polymer Films Obtained by Electrochemically Initiated Polymerization of N,N-Dimethyl- and N,N-Diethylaniline

927M0020B Moscow ELEKTROKIMIYA in Russian
Vol 27, No 6, Jun 91 (manuscript received
11May 90) pp 699-705

[Article by Yu. M. Maksimov, M. Kzhaldun, and B. I. Podlovchenko, Moscow State University imeni M. V. Lomonosov]

UDC541.135

[Abstract] Over the past decade, intensive research has been conducted on the development of surface modified electrodes, especially polymers. One promising method for surface modification is electrochemically initiated polymerization. By using aromatic amines as monomers

it is possible to obtain nitrogen-containing polymer coatings, frequently having intrinsic electrochemical activity and ion exchange properties. These features open up the possibility of employing them in electrochemical determination of trace quantities of many metals. In the present work cyclic volt-amperometry was used to study the behavior of polymer films obtained by electrochemically initiated polymerization of N,N-dimethyl- and N,N-diethylaniline on the surface of a glass-carbon electrode in 0.05 M sulfuric acid. These films are shown to be capable of concentrating and retaining multi-charged anions. Values for the coefficient of charge diffusion in the films were calculated. A markedly noticeable intrinsic electrical activity was observed to be present in both polymer films. Figures 7; references 11: 4 Russian, 7 Western.

Electroprecipitation of Tin-Nickel Alloys Having Special Properties. Kinetics of Joint and Individual Precipitation of Metals

927M0020C Moscow ELEKTROKIMIYA in Russian
Vol 27, No 6, Jun 91 (manuscript received
20 Jul 89) pp 706- 713

[Article by V. V. Orekhova and I. D. Roy, Kharkov Polytechnical Institute imeni V. I. Lenin]

UDC541.138.3:621.357

[Abstract] In producing printer plates, much attention is currently being devoted to tin-nickel protective coatings. These coatings must be corrosion resistant in etching solutions, capable of soft soldering at low temperatures (260°C) without using acid flux, and the soldering must be able to withstand "aging", i.e. long term storage and use. Widespread use of electrolytes recommended for preparing tin-lead alloy is restricted in some cases due to the presence of corrosive and toxic fluorides, and in others due to the low dispersion and non- uniformity of precipitated coatings. These shortcomings are missing in electrolytes developed on the basis of a polyligand system of $\text{Sn(II)-Ni(II)-P}_2\text{O}_7^{4-}$ -glycine. However, alloy deposits obtained from these electrolytes, have poor solderability and deteriorate with "aging". This is evidently due to rapid surface oxidation and the presence of surface active organic matter in the electrolyte. In the present work regressive analysis of partial polarization curves and a rotating disk electrode were used to study the kinetics of both joint and individual separation of tin and nickel from the above polyligand system. An electrolyte was developed which has adequate low temperature solderability with non-acid flux, and does not change with "aging". Figures 3; references 11: 9 Russian, 2 Western.

Electroprecipitation of Tin-Nickel Alloy Having Special Properties. Ionic Equilibria and Nature of Discharging Particles

927M0020D Moscow ELEKTROKHIMIYA in Russian
Vol 27, No 6, Jun 91 (manuscript received
9 Feb 90) pp 714-719

[Article by V. V. Orekhova and I. D. Roy, Kharkov Polytechnical Institute imeni V. I. Lenin]

UDC621.537

[Abstract] In a previous report it was demonstrated that during joint separation of tin and nickel from an electrolyte based on the polyligand system $\text{Sn(II)-Ni(II)-P}_2\text{O}_7^{4-}$ -glycine, the intermetallic NiSn coating contains an α -Ni phase. Precipitation of a single-phase alloy not having an α -Ni phase may be achieved by introducing lithium and cobalt salts into the electrolyte. In the present work spectrophotometry and potentiometry were used to study complex formation in the above polyligand system. The nature of reducing particles was discerned on the basis of calculated orders of cathode reactions. A mechanism for the effect of lithium and cobalt salts preventing formation of an α -Ni phase in alloy deposits and facilitating preparation of a single-phase alloy, is presented. The action of the additives is related to changes in concentration of discharging particles in the cathode layer and the flow of redox reactions in the systems Sn(II)-Sn(IV) and Co(II)-Co(III) . Figures 6; references 13: 11 Russian, 2 Western.

Electrochemical Extraction of Absorbed Hydrogen from Metals Under Controlled Potential

927M0020E Moscow ELEKTROKHIMIYA in Russian
Vol 27, No 6, Jun 91 (manuscript received
25 Jun 90) pp 732-736

[Article by V. I. Sobornitskiy and N. G. Krapivnyy, Dnepropetrovsk Chemico-Technological Institute imeni F. E. Dzerzhinskiy]

UDC541.138:620.194

[Abstract] In the classic variant of electrochemical extraction, it is assumed that the hydrogen concentration on the electrode surface during the moment at which ionizing potential is induced jumps from a maximum to zero value. The current arising during such a jump-wise polarization and under such a brief time interval of observation reaches large values, and approaches infinity at $t = 0$. In the present work an improved method is proposed for the electrochemical extraction of hydrogen from metals employing exponential and linear laws of change in hydrogen concentration at the exiting surface of the metal. The problem of diffusion was formulated and solved, expressions were derived for extraction currents, and methods for handling them are presented. The electrochemical extraction variant employing linear resolution of potential was used in a series of experiments on steel 65GKh. Figures 6; references 4 (Russian).

Water Dechlorination Over Granular Charcoals - Analysis of Process Mechanism

917M0187A Kiev *KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 13, No 7, Jul 91 (manuscript received 13 Feb 91 pp 602-607)*

[Article by V. N. Smagin, Ye. A. Lukashev, and L. A. Kvitka, Hydromeliorative Institute, Moscow]

UDC628.1/628.3/541.1

[Abstract] Although chlorination is one of the most widespread methods of water treatment, it has certain drawbacks, such as the probability of forming stable mutagenic and cancerogenic organic chlorine compounds if the water is further treated biochemically. Dumping chlorinated effluents into low volume reservoirs suppresses the life processes of hydrobionites, thereby inhibiting the self-cleaning processes of these reservoirs. To further increase the effectiveness of disinfection by chlorination, various methods are being developed to eliminate the organic chlorine products, eg. adsorption on charcoal. The most promising method for converting active residual chlorine into harmless chloride ion appears to be filtration through granular activated charcoal or sulfocoal. Increasing the effectiveness of this process and predicting its applicability for waters of various compositions requires study of the physical chemistry, adsorption kinetics, topochemical redox reactions, electrochemical corrosion of the charcoal material, diffusion processes, and filtration hydrodynamics. In the present work an attempt was made to examine those elementary processes which determine the mechanism of heterogeneous catalytic dechlorination of water over charcoals, and construct possible kinetic diagrams for these processes which could then be used as kinetic models. Three variants of a detailed mechanism of local aggregates of redox reactions accompanying charcoal corrosion reactions are presented. The model mechanism of reaction aggregates was designed for the purpose of analyzing dynamic behavior on kinetic models. References 34: 18 Russian, 16 Western.

Selection of Pore Structure in Electroadsorbents

917M0187B Kiev *KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 13, No 7, Jul 91 (manuscript received 1 Jan 91) pp 610-614*

[Article by A. P. Artemyanov, V. V. Khabalov, and V. Yu. Glushchenko, Far Eastern State University]

UDC541.183:546.26:541.185

[Abstract] Fulfilling some of the concepts of the electrochemistry of adsorption systems first requires solution of a basic problem, viz. clarification of the principles used in selecting an optimal electroadsorbent from the dual standpoint of having both adequate adsorption capacity, and the capability of effective electrochemical regeneration. In the present work criteria were determined for

selecting optimal pore structure of carbon adsorbents for conducting electroadsorption processes. The effects of pore structure on the electroadsorption properties in aqueous aliphatic alcohol solutions were studied, and a formula is presented which describes electroadsorption properties as a function of polarity variances. A method is proposed for predicting the effectiveness of adsorbents. Figures 3; references 9: 7 Russian, 2 Western.

Spectrophotometric Determination of Germanium in Industrial Effluents

917M0187C Kiev *KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 13, No 7, Jul 91 (manuscript received 27 Feb 91) pp 630-631*

[Article by L. A. Yegorova and L. I. Avramenko, Scientific Production Association "Monokristallreaktiv"]

UDC543.42.062:546.289

[Abstract] A need arose for a highly sensitive method for determining germanium in the effluents of enterprises producing bismuth germanate single crystals, used in the sensory components of ionizing radiation detection equipment. A spectrophotometric method was developed that is based on the formation of a multi-ligand complex of germanium with phenyl fluorone and cetylpyridinium chloride. To prevent interference from other elements, the germanium is first separated by extraction with carbon tetrachloride from 9 molar HCl. The relative standard deviation of a single determination ranging from 2×10^{-3} to 5×10^{-2} does not exceed 0.17. References 5 (Russian).

Use of Natural Dispersed Minerals in Pre-Membrane Water Treatment Processes

917M0187D Kiev *KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 13, No 7, Jul 91 (manuscript received 30 Nov 90) pp 632-642*

[Article by Yu. I. Tarasevich, Colloidal Chemistry and Hydrochemistry Institute, Kiev]

UDC543.42.062:546.289

[Abstract] According to published data, water directed to membrane treatment should have a silt density index (SDI) between 4 and 5, and an iron content of not more than 1 mg/dm³. However, cases have been reported where the SDI was below 5, the iron content below 0.1 mg/dm³, and a ferrous hydroxide film still tended to form on the membrane surface. Therefore, some authors feel that the SDI should be equal to or less than 3. The content of suspended matter in pre-treated water is also limited by the type of membrane equipment being used. In the present work requirements are formulated for water subjected to membrane treatment. To meet these requirements, the water must be pre-treated by filtration through grainy or alluvial gravel. It is further expedient to employ both natural and chemically modified zeolites,

diatomites, perlites, and other minerals to remove dispersed impurities, organic matter, and iron and manganese compounds. Various schemes for pre-treating artesian, sea, river, and sewage waters with natural minerals are discussed. References 74: 53 Russian, 21 Western.

Demineralization of Water in Presence of Sodium Dodecyl Sulfate and Sulfonol

917M0187E Kiev *KHIMIYA I TEKHOLOGIYA VODY* in Russian Vol 13, No 7, Jul 91 (manuscript received 19 Feb 91) pp 648-651

[Article by V. D. Grebenyuk, L. K. Berkeliyeva, R. D. Cheborareva, and Kh. N. Yevzhanov, Colloidal Chemistry and Hydrochemistry Institute, Kiev]

UDC541.183.12

[Abstract] The growing quantities of detergents present in industrial sewage has a harmful effect on the physical chemical properties of both ionogenic and non-ionogenic membranes. Attempts have been made to lower membrane poisoning by including oppositely charged ionogenic groups in the membrane composition during fabrication, although these methods proved to be inadequate. Tests showed that of the domestically produced anionite membranes, MA-100 is the most resistant to poisoning. In the present work a study was made of the electrochemical properties of this membrane during electrodialysis of solutions of sulfonol and dodecyl sulfate. Apparently, this membrane alters its transport properties on contact with anionic detergents and acquires a selectivity to chlorine ions. Reversing the current decreases the negative effects of detergent action on the membrane. Figures 4; references 15: 14 Russian, 1 Western.

Leaching Nickel (II) by Adsorption from Electroplating Effluents

917M0187F Kiev *KHIMIYA I TEKHOLOGIYA VODY* in Russian Vol 13, No 7, Jul 91 (manuscript received 28 Nov 90) pp 651-655

[Article by R. R. Velinova, B. K. Kumanova, and A. A. Asenov, Sofia Technological University]

UDC628.347

[Abstract] Industrial effluents containing heavy metal ions are most frequently treated by such methods as ion exchange, chemical precipitation, membrane filtration, and adsorption, the latter being the most promising owing to the availability of low cost sorbents. Nickel (II) may be leached from electroplating effluents by using peat, wollastonite, clinoptilolite, and other such materials. One of the main difficulties in treating effluents containing nickel (II) ions is their toxicity to the micro-organisms present in active sludge at concentrations of 25 mg per liter. In the present work a study was made of the adsorption characteristics of a synthetic sorbent

prepared from silica-containing industrial waste products. Tests demonstrate that the material is promising as a means of leaching nickel (II) ions from water. It has satisfactory kinetic properties and the process may be controlled to large degree by internal diffusion. Equilibrium studies indicate that the sorption characteristics are comparable with those of other sorbents. Figures 8; references 10: 4 Russian, 6 Western.

Design for Desalination Chamber and Limiting Current During Electrodialysis

917M0187G Kiev *KHIMIYA I TEKHOLOGIYA VODY* in Russian Vol 13, No 7, Jul 91 (manuscript received 8 Jan 91) pp 656-659

[Article by A. G. Belobaba and M. V. Pevnitskaya, Solid Body Chemistry and Minerals Handling Institute, Novosibirsk]

UDC541.135

[Abstract] To intensify the electrodialysis process, the hydrodynamic conditions of flow in the desalination chamber must be perfected and the specific surface of the membrane increased. The latter may be achieved by increasing the number of paired chambers in the unit while still retaining its overall dimensions. An unavoidable consequence, however, is a decrease in intermembrane distance. Decreasing the latter to a fraction of a millimeter could markedly raise the role of friction forces, thereby altering the relationship between the mass transfer rate and the flow velocity of the solution. In the present work a study was made of the effect of intermembrane distance on the relationship between limiting current density, as a characteristic of mass transfer in the electromembrane system, and the linear flow velocity. The study involved chamber designs having hollow channels, channels with promoters, and profiled membrane channels and the effects of design type and intermembrane distance (2 and 0.5 mm) on limiting current density (i_{lim}) as a function of linear flow velocity of the dialysate (v) at 0.5-37 Reynolds numbers. The results demonstrated that for both values of intermembrane distance, $i_{lim} = A \times v^n$, where A is a constant and n is an angular coefficient. In a hollow channel, regardless of intermembrane distance, liquid flow is laminar. At 0.5mm intermembrane distance, using a profiled membrane channel is hydrodynamically similar to that of a channel having a promoter. Figures 2; references 10: 6 Russian, 4 Western.

Treating Suspensions in Magnetized Packings of Contact Rods

917M0187H Kiev *KHIMIYA I TEKHOLOGIYA VODY* in Russian Vol 13, No 7, Jul 91 (manuscript received 28 Jan 91) pp 659-661

[Article by A. V. Sandulyak, N. V. Yatskov, and V. V. Sandulyak, Tool Making Institute, Moscow; Ukrainian Marine Engineering Institute, Rovno]

UDC621.187.152

[Abstract] In a previous work a question arose concerning the use of so-called rod packing, i.e. packing consisting of contacting rods oriented longitudinally to the flow of a cleansing medium, and transverse to the magnetic direction in magnetic filtration-settling units. With packing having relatively short rods (length to diameter ratio about equal to 7), dispersed phase precipitation was entirely comparable to that of using conventional spherical packing. This result appeared to be equally justified with an agreed increase in the working lengths of both types of packing. Whether or not this result remains justified when the working length of the rod packing is increased directly as a result of increasing the relative length (L to d) of the same packing, remains unresolved. In the present work new data are presented on treating suspended magnetite in magnetized packing as described above. Corresponding data are compared with control data for spherical packing and that obtained previously over a relatively short cyclic working rod packing. Ineffective areas in the central portion of the rod packing channels were revealed experimentally using relatively extended rods. Figures 3; references 3 (Russian).

Study of Uranium Sorption from Sea Water over Sorbents Having Amidoxime Groups

917M0187I Kiev *KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 13, No 7, Jul 91 (manuscript received 29 Oct 90) pp 661-664*

[Article by R. S. Prishchepo, G. V. Zarechneva, M. L. Veber, T.Yu. Butenko, N. G. Zhukova, and B. N. Laskorin, Far Eastern Branch Chemistry Institute, Vladivostok]

UDC541.183.5:546.791

[Abstract] Recently, much attention has been devoted to the sorption of elements over sorbents containing amidoxime groups in conjunction with treating industrial wastes as well as recovering metals from natural waters. In the present work results are presented on a study of equilibrium sorption and desorption of uranium on amidoxime sorbents under static and dynamic conditions from sea water enriched with uranium, and natural sea water. Static exchange capacities were determined and it was demonstrated that the sorbents studied (AMO-Kk and AMO-KH-g) possess optimal sorption characteristics over a broad range of pH (1.5 - 8.0). It is therefore recommended to use hydrochloric acid as a desorbing agent. These sorbents are not selective to uranium alone, but also adsorb iron, copper, nickel, zinc, manganese, as well as alkali and alkaline earth elements. Figures 3; references 9: 2 Russian, 7 Western.

Dynamic Membranes from Hydroxopolymers of Aluminum

917M0187J Kiev *KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 13, No 7, Jul 91 (manuscript received 8 Feb 91) pp 664-668*

[Article by D. D. Kucheruk, Colloidal Chemistry and Hydrochemistry Institute, Kiev]

UDC682.165.532.71

[Abstract] Aluminum salts hydrolyze in water according to a mechanism similar to that of water, concluding in the transfer of a proton from a coordinated water molecule to a free molecule. Aluminum salts hydrolyze in a step-wise manner to form hydrolytic products sequentially. Monomeric hydroxo complexes, polymeric hydroxo compounds, and a hydroxide residue have been identified as the three forms in which aluminum ions exist in solution. If a solution contains aluminum chloride in a concentration greater than 10^{-3} kmole per cu meter, and the ratio of hydroxyl ions to aluminum is approximately 1, then dimers are formed as the first stage of hydroxo complex polymerization. As the above ratio increases, the hydroxo complexes continue to polymerize into a definite assortment of hydroxopolymers, and not through any continuous series of possible forms. As the hydroxyl to aluminum ion ratio approaches 2.2, a polycation is observed to form, and in aluminum chloride solutions of 0.2 kmole per cu meter and the same ratio, almost all of the aluminum exists as $[Al_3]_4(OH)_{24}(H_2O)_{12}]^{7+}$. It thus becomes apparent that during formation of dynamic membranes in solutions of aluminum salts, it becomes necessary to consider the state of the aluminum ions associated with hydrolysis. From this standpoint, a study was made of the formation of dynamic membranes from aluminum hydroxo compounds in aluminum chloride solutions. The reverse osmotic properties of these membranes has been demonstrated to depend on the state of the aluminum ions in solution. The highest retention coefficient for Mg^{2+} (0.95), in minimum flow volume occurred with a membrane formed from hydroxopolymers of the above ion at pH 4.6 - 4.9. This membrane was found to be useful in desalination of solutions containing alkaline-earth metals at concentrations approaching 0.06 kmole per cu meter at pH 4.6 - 4.9, 2-3 MPa pressure, and temperature to 325K. Figures 8; references 9: 6 Russian, 3 Western.

Layout Variations of Industrial Sewage Demineralization Stations at Selenginsk Pulp and Cardboard Combine and Technical- Economic Comparison

917M0187K Kiev *KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 13, No 7, Jul 91 (manuscript received 21 Jan 91) pp 669-673*

[Article by V. V. Zimenkov, Scientific-Production Association Pulp-Paper Industry (A-U), Leningrad]

UDC628.165

[Abstract] Work is presently underway at the Selinginsk Pulp and Cardboard Combine in developing a closed-cycle water treatment system. In order to maintain design level, the salt concentration of the effluent must be lowered to from 4,800 to below 500 grams per cu meter. On the basis of data obtained from laboratory and pilot scale tests, methods based on ion exchange, reverse osmosis, and thermal desalination were considered. In the present work the technical and economic indices of the three variation are examined. Thermal desalination appears to be the most expedient. Figures 2; references 5 (Russian).

Effect of the Surface Chemistry and Pore Structure of Modified Silica Gels on the Adsorption of Dyes From Water

927M0002A Kiev *KHIMIYA I TEKHNLOGIYA VODY* in Russian Vol 13 No 8, Aug 91 (manuscript received 5 Mar 91) pp 681-684

[Article by T.D. Khokhlova and Yu.S. Nikitin, Moscow State University imeni M.V. Lomonosov]

UDC 541.183

[Abstract] Adsorbents with a high capacity and high absorption rate are needed to clean dyes from water as well as to concentrate them during analysis of micro-quantities. In view of this fact, the authors of the study reported herein studied factors related to the adsorption of dyes on silica gel surfaces. Two factors were examined in particular. First, the authors examined the effect of chemical modification of the silica gels' surface. They examined the effects of hydroxylation, dehydroxylation, hydrophobization by trimethylchlorosilane, and introduction of covalently bound amino groups. Next, they considered the effect of specific surface and pore diameter on adsorption. During their studies, the authors examined 13 acidic and basic dyes. They studied the dyes' adsorption on modified (as mentioned above) silica gels with specific surfaces ranging from 74 to 660 m²/g. The experiments performed indicated that two of the treatment methods, i.e., hydrophobization of silica gel with trimethylchlorosilane and dehydroxylation by calcination at 750°C have a remarkably similar effect. Both significantly increase the adsorption of basic dyes. The authors attribute this effect to the fact that the two said treatment methods increase the hydrophobicity of the silica gel surface and that adsorption from water is primarily due to hydrophobic interactions. Aminopropylated silica gels were found to possess a high anion-exchange capacity with respect to acid dyes. These data, coupled with the data obtained in the studies of pore size and specific surface, enabled the authors to recommend trimethylsilanated and dehydroxylated KSK-2 silica gel with a specific surface of 300 to 400 m²/g and an average pore diameter of about 10 nm as having the highest adsorption capacity with respect to acidic dyes. The highest absorption capacity with respect to acidic dyes

was found to be achieved by using KSK-1 and KSK-2 amino silica gels with a specific surface ranging from 100 to 400 m²/g and average pore diameters between 30 and 10 nm. The dependence of adsorption capacity on the modified silica gels' structural characteristics was found to be stronger in the case of basic dyes than in the case of acidic dyes. Figures 3, tables 2; references 2 (Russian).

Photometric and Fluorimetric Determination of Thallium in Surface and Drinking Waters

927M0002B Kiev *KHIMIYA I TEKHNLOGIYA VODY* in Russian Vol 13 No 8, Aug 91 (manuscript received 12 Mar 91) pp 689-692, 765

[Article by A.T. Pilipenko, A.V. Terletskaia, Ye.Ya. Matveyeva, and T.L. Shevchenko, Institute of Colloidal Chemistry and Water Chemistry imeni A.V. Duman-skiy, UkSSR Academy of Sciences]

UDC 543.3:546.683

[Abstract] Because of its high toxicity, the maximum allowable concentration of thallium in surface and drinking waters has been set at 0.1 µg/l. The methods currently used to determine thallium concentration levels in water have a detection threshold of 1-10, 0.5-10, and 50 µg/l. In view of the inadequacy of these methods, the authors of the study reported herein developed a method of determining thallium (I) and thallium (III) in surface and drinking waters. The new method entails preliminary extraction concentration in the form of complexes with sodium diethyldithiocarbamate and analysis of the concentrates by the extraction-photometry or extraction-fluorometry methods based on the formation of Tl (I)-Br-rhodamine 6Zh associates. The proposed method results in a concentration coefficient of 200 with liter samples and in a thallium extraction of 80-90% at thallium contents of 0.25 to 5 µg/l. The interval of thallium levels that could be determined by the photometric method ranged from 0.15 to 5 µg thallium per liter. The interval that could be determined by the fluorimetric method ranged from 0.03 to 1 µg thallium per liter. The relative standard deviation was between 0.07 and 0.1. The new method has been used to analyze drinking water in the cities of Chernovtsy and Kiev, waters from the Dnepr and Dnestr Rivers, and runoff and sewage from a number of enterprises in the area. When used to determine thallium concentrations in natural and drinking waters, the new method resulted in a detection rate of 80-90%. When used to analyze sewage of unknown composition, the level at which additives were detected was much lower (10 to 40%). This was taken to indicate the presence of impurities in the samples that interfere with the determination process. Figure 1, table 1; references 14: 9 Russian, 5 Western.

Development of Water Desalination Methods

927M0002C Kiev *KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 13 No 8, Aug 91 (manuscript received 22 Mar 91) pp 693-727*

[Article by A.T. Pilipenko, I.G. Vakhnin, and V.I. Maksin, Institute of Colloidal Chemistry and Water Chemistry imeni A.V. Dumanskiy, UkSSR Academy of Sciences]

UDC 628.105

[Abstract] This review summarizes world literature on desalination of mineralized waters that was written in the period encompassing 1984 and 1990. The authors begin their review with an overview of the increasing importance of desalination technologies and the highlights of desalination research in various countries throughout the world during the 16-year period covered. Separate sections of the review are devoted to each of the following topics: distillation, use of renewable energy sources in the desalination of water, freezing, membrane desalination methods, and reverse osmosis. The final section focuses on the special problems of preparing potable water from desalinated waters. The authors conclude that the best desalination methods discussed in the literature of the period under consideration are combined methods in which membrane (preferably reverse-osmosis) techniques are used initially and are then followed by thermal (evaporation) methods coupled with complete processing of the brines. Methods based on this general scheme are recommended as being the most feasible from an economic standpoint and inflicting the least (virtually no) damage on the environment. The review and 720-item bibliography include works from countries throughout the world, including the United States, Japan, Eastern and Western Europe, and various Arab countries. References 720: 195 Russian, 525 Western.

Calculating Treatment To Clean Nickel From Rinse Waters on a Carboxyl Cation Exchanger

927M0002D Kiev *KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 13 No 8, Aug 91 (manuscript received 17 Jan 91) pp 728-730*

[Article by G.M. Kolosova and N.G. Skrovtsov, Geochemistry and Analytical Chemistry Institute imeni V.I. Vernadskiy, USSR Academy of Sciences, Moscow]

UDC 541.183

[Abstract] The process of metal electroplating entails the use of large amounts of rinse waters. In view of the increasing shortage of water and the urgency of developing low-waste and no-waste technologies to recycle rinse waters used in such processes as electroplating, the authors of the study reported herein have selected and substantiated a method of making the calculations required to design a process for ion-exchange cleaning of

wastewaters from electroplating shops that would enable the waters to be recycled. They considered the problem of cleaning nickel from two types of rinse waters, i.e., deionized water and tap water. Specifically, they concerned themselves with estimating the duration of the filtration cycle of a column of known size given specified process conditions and estimated the required length of the sorbent layer for the specified filtration cycle time. The data they obtained by using their selected computation method were in close agreement with actual experiment results in the case of deionized water. The calculated and actual experiment results obtained for the case of tap water were found to be in satisfactory agreement (the discrepancy did not exceed 15%). Figures 2; references 10 (Russian).

Final Adsorption Treatment of Biologically Treated Municipal Sewage by Activated Carbons With Different Porous Structures

927M0002E Kiev *KHIMIYA I TEKHOLOGIYA VODY in Russian Vol 13 No 8, Aug 91 (manuscript received 20 Feb 91) pp 730-733*

[Article by T.M. Levchenko, N.A. Klimenko, L.N. Gora, R.P. Kanavets, and L.A. Savchina, Institute of Colloidal Chemistry and Water Chemistry imeni A.V. Dumanskiy, UkSSR Academy of Sciences, Kiev]

UDC 541.183

[Abstract] Biologically treated municipal sewage is considered to be the main reserve for commercial water supply in the future. The pore structure of the activated carbon adsorbents used in biological treatment processes is extremely important to the effectiveness of the said processes. In view of this fact, the authors of the study reported herein studied the dynamics of the adsorption of organic matter from biologically treated municipal sewage in dense layers of activated carbons with different pore structures. A filtration rate of $3 \text{ m}^3/(\text{m}^2 \cdot \text{h})$ was used with a layer height of 34 cm, which provided a constant contact time of 20 minutes. KAD and AG-3 factory-produced activated carbons on microporous active anthracite were tested along with modified specimens of KAD carbon and active anthracite obtained by impregnation with surfactant solutions followed by final activation. The experiments established that the dynamic capacity of modified activated anthracites (acanthi) relative to the organic matter in the biologically treated municipal sewage is three- to fourfold the capacity of active anthracites before modification and six- to ninefold the capacity of factory-produced activated carbons. The authors thus succeeded in demonstrating the rationality of using acanthi for final treatment of biologically treated municipal sewage. Figure 1, table 1; references 12 (Russian).

The Role of Preliminary Ozone Treatment in Cleaning the Water of Lake Yulemister

927M0002F Kiev *KHIMIYA I TEKHOLOGIYA VODY in Russian* Vol 13 No 8, Aug 91 (manuscript received 05 Mar 91) pp 736-739

[Article by S.V. Preys, E.K. Syyrde, and L.I. Pyldoya, Tallinn Polytechnic Institute]

UDC 628.16

[Abstract] The authors of the study reported herein examined the effect of preliminary ozone treatment on the quality of subsequent treatment of natural waters. They also compared the efficiency of preliminary chlorination and ozone treatment from the standpoint of consumption of oxidizing agents and from the standpoint of quality of water treatment. They conducted their studies on water samples taken from Lake Yulemister, which is the water source of the city of Tallinn (Estonia). Samples of lake water were drawn after the water had first passed through microfilters with pore sizes up to 120 μm . The water samples used in the tests were brought into contact with an ozone-and-air mixture in a 1.4-l-capacity sparger with a water layer 0.3 m high. An Ozon-2M generator was used to produce the ozone. The ozone concentration in the ozone-and-air mixture ranged from 2.4 to 4.0 mg/l. Comparative tests in which control samples were subjected to chlorination without preliminary ozone treatment were also conducted. Preliminary ozone treatment was found to result both in a reduction in the total number of cells present in the treated samples and in the rupture of the filaments of blue-green algae present. Using ozone in a dose of about 7 to 8 mg/l followed by coagulation reduces the biomass present in waters undergoing treatment to virtually 0. Although the effect of preliminary ozone treatment on chromaticity and turbidity was not as dramatic, it was nevertheless significant. Preliminary ozone treatment made it possible to achieve an 80 to 90% reduction in turbidity and the number of cells present, whereas chlorination with the same dose of oxidizing agent resulted in a 65-70% reduction. Figures 3, table 1; references 7: 1 Russian, 6 Western.

A Membrane in Form of a Hollow Fiber for Nanofiltration

927M0002G Kiev *KHIMIYA I TEKHOLOGIYA VODY in Russian* Vol 13 No 8, Aug 91 (manuscript received 30 Jan 91) pp 739-740

[Article by L.P. Perepechkin, L.N. Nechayeva, V.G. Sobakin, G.L. Bychkova, L.L. Bolyuk, and V.S. Khrabrova, Khimvolokno Scientific Production Association and All-Union Scientific Research and Design Institute of Artificial Fibers, Serpukhov, Moscow Oblast]

UDC 628.183

[Abstract] Nanofiltration is a membrane separation process that occupies an intermediate position between

reverse osmosis and ultrafiltration. It is characterized by low selectivity in relation to salts with univalent cations and organic compounds with a molecular mass of <150 and by higher selectivity in relation to di- and polyvalent cations and organic compounds with a molecular mass of >300 . The authors of the study reported herein examined the possibility of using a hollow acetate fiber for nanofiltration processes. Specifically, they studied the temperature and pressure dependence of the selectivity and permeability of hollow acetate fiber during hydrothermal treatment at temperatures ranging from 70 to 94°C and at pressures ranging from 0.5 to 2.5 MPa. They proceeded to develop a process to produce the said hollow acetate fiber. The fiber produced was in turn used in manufacturing separation devices with a working surface of 100 m^2 . The separators made it possible to partially demineralize water with a hardness of 7.6 mgEq/l. At 1.0 MPa, the separator demonstrated a selectivity of 80% with respect to hardness salts and was able to function successfully at a capacity of 8.6 m^3/d . The separator was found to manifest a linearly dependence of capacity on working pressure. The authors determined that using hollow fiber for nanofiltration makes it possible to correct the ionic composition of water while significantly reducing the water's hardness and salt content. The new hollow fiber and process of producing it may be used in manufacturing separation devices for partial demineralization of natural waters. Figure 1, tables 3; reference 1 (Russian).

The Effect of the Accumulation of Hydrogen Peroxide During Reverse-Osmosis Desalination of Sea Water

927M0002H Kiev *KHIMIYA I TEKHOLOGIYA VODY in Russian* Vol 13 No 8, Aug 91 (manuscript received 23 Jan 91) pp 741-745

[Article by Yu.S. Veselov, Central Scientific Research Institute of Ship Machinery Building and Proletarskiy zavod Association, Leningrad]

UDC 628.165.08

[Abstract] In an effort to assess the possibility of setting up a desalination process in which filters and membranes could be rendered self-cleaning, the author of the study reported herein conducted a set of experiments to determine the content, accumulation, and effect of the accumulation of hydrogen peroxide in actual sea and desalinated waters. He conducted his research on an experimental reverse-osmosis desalination unit consisting of coarse and fine filters, a high-pressure plunger pump, a desalination module containing a bundle of semipermeable membranes assembled in the form of a role, pipelines, and fittings. Sea water was passed through the unit at a hydrostatic pressure of 0.5 MPa. First, it was passed first through the coarse and fine filters. Next, the high-pressure plunger pump pumped it through the desalination unit at a pressure of 4 to 6 MPa. The permeate was collected in a tank, and the brine was

discharged under gauge pressure. The experimental reverse-osmosis desalination unit, which was mounted on a scientific research vessel, was used to treat and collect more than 70 water samples throughout the World Ocean. Tests performed on the water samples indicated that the content of hydrogen peroxide in the samples increased by a factor of 3.4 to 27.5 after passing through the coarse and fine filters. The content of hydrogen peroxide in samples of permeate was also higher (by a factor of 1.23 to 2.7) than in samples drawn before the membranes. Data collected by the author indicated that the salinity of the sea water did not have any significant effect on the accumulation of hydrogen peroxide. Instead, he attributed the effect observed to the processes of the vital activity of the marine microorganisms trapped by the filters and to corrosion and cavitation processes occurring in reverse-osmosis desalination units. The author further concludes that the effect of the accumulation of hydrogen peroxide may be used in reverse-osmosis desalination units to provoke a self-cleaning (inhibiting) situation. Figures 4, table 1; references 9: 8 Russian, 1 Western.

Estimating the Operating Efficiency of Batch and Continuous Electrocoagulators

927M0002I Kiev *KHIMIYA I TEKHOLOGIYA VODY* in Russian Vol 13 No 8, Aug 91 (manuscript received 19 Feb 91) pp 745-748

[Article by A.I. Gladkiy, Ye.Ya. Sokol, and M.Yu. Gapunina, Kharkov Department, All-Union Scientific Research Institute of Water Supply, Sewage Systems, Water Development Works, and Hydrogeology]

UDC 628:543.227:661.78.0654

[Abstract] Electrocoagulation is an effective method of treating the highly toxic spent cutting fluids discharged by metal working enterprises. Two basic types of electrocoagulators, i.e., batch and continuous types, are currently used in the electrocoagulation processes. In an effort to compare the efficiency of batch and continuous electrocoagulators, the authors of the study reported herein compared their efficiency in cleaning concentrated oil-emulsion sewage in an electrocoagulator that was developed at the Kharkov department of the All-Union Scientific Research Institute of Water Supply, Sewage Systems, Water Development Works, and Hydrogeology and installed at the Gomselmash Production Association. The new electrocoagulator was

designed to operate in both batch and periodic modes and to clean spent type NGL-205 cutting fluid at a rate of about 25 m³/d. Tests comparing the electrocoagulator's operation in continuous and batch modes showed that when the new electrocoagulator is used to reduce the level of petroleum products in spent cutting fluid to the levels stipulated in sanitary standards, the continuous mode is only 60% as efficient as the batch mode. The continuous mode is even less efficient when the amounts of petroleum products in the spent cutting fluids are higher than the levels normally encountered. Figures 2, tables 2; references 6 (Russian).

The Use of a Mixed-Action Filter To Clean Sewage From the Process of Nickel Plating

927M0002J Kiev *KHIMIYA I TEKHOLOGIYA VODY* in Russian Vol 13 No 8, Aug 91 (manuscript received 25 Feb 91) pp 760-762

[Article by G.M. Kolosova and N.G. Skvortsov, Institute of Geochemistry and Analytical Chemistry imeni V.I. Vernadskiy, USSR Academy of Sciences, Moscow]

UDC 661.183:628.33

[Abstract] In an effort to develop a better method for treating the sewage generated by nickel plating processes, the authors of the study reported herein have proposed a new method of treating the said sewage by using a mixed-action filter. In essence, the new method calls for using a mixture of weakly acidic cation exchanger in H-form and a highly basic anion exchanger in OH-form. This combination of cation and anion exchangers makes it possible to return the treated water to the wash tank. Tests conducted by the authors demonstrated that the volume of water treated increases as the relative volume of anion exchanger in the mixed layer is increased from 0.5 to 2.0 volume parts per volume part cation exchanger. They conclude, however, that a 1:1 cation exchanger-to-anion exchanger ratio is ultimately best because it forestalls any jump of nickel ions into the filtrate, which would prevent the capacity of weakly acidic cation exchanger from being used to its full extent. The proposed method makes it possible to eliminate changing a weakly acidic cation exchanger to its Na-form after acid regeneration and to eliminate the use of an additional highly acidic cation exchanger to extract sodium. This in turn makes the sewage treatment process much less expensive and much faster and also reduces the number of individual operations entailed in the treatment process. Figure 1, tables 2; references 4 (Russian).

UDC 536.63:541.11

Calculation of Formation Enthalpy for New Oxide Superconductors

917M0160a Moscow ZHURNAL FIZICHESKOY
KHIMII in Russian Vol 65, No 4, April 1991
(manuscript received 29 Jun 90) pp 1119- 1120

[Article by L. A. Reznitskiy, Moscow State University
imeni M. V. Lomonosov, Chemistry Department]

[Abstract] An approximation method was used to calculate $\delta_f H_{298}$ of the newly-synthesized high-temperature superconductors $YBa_2Cu_{3.5}O_{7.5}$ (I) and $YBa_2Cu_4O_8$ (II), which have critical temperatures of 40 K and 80 K respectively. The enthalpy of formation from oxides of I was calculated as 142 kJ/mole from YO_8 , BaO_{10} , $Cu^{n+}O_4^-$ and 127 kJ/mole from YO_8 , BaO_{10} , $Cu^{2+}O_2$, $Cu^{3+}O_4$, with a square-pyramidal environment for Cu^{2+} and square $Cu^{3+}O_4$. Compound II gave 142 kJ/mole using the first method and 124 kJ/mole using the second. The enthalpy of formation of compound I from its elements was found to be 2773 kJ/mole by the first procedure and 2758 kJ/mole by the second, while that of compound II was 2854 kJ/mole and 2836 kJ/mole. References 5: 4 Russian, 1 Western.

UDC 539.217.5

Calculation of Permeability of Heterogeneous Membranes

917M0160b Moscow ZHURNAL FIZICHESKOY
KHIMII in Russian Vol 65, No 4, April 1991
(manuscript received 31 Aug 90) pp 1120- 1123

[Article by Yu. K. Tovbin and Ye. V. Votyakov, Scientific Research Physical Chemistry Institute imeni L. Ya. Karpov, Moscow]

[Abstract] The permeability of heterogeneous membranes reflecting the molecular characteristics of the diffusant-matrix system was calculated using a lattice model including different types of sorption sites. An expression for the coefficient of permeability was derived in terms of site sorption constants, diffusant transition constants, distances between sites, number of transition channels, and site distribution functions. The concentration dependence of the diffusion coefficient was plotted for various structures and compositions of the matrix. Increasing the binding energy of the strong binding sites and their content decreased the diffusion coefficient. The permeability coefficient was found to be strongly dependent on membrane features and to differ significantly from the widely used parallel diffusion case. The equations derived permit simpler calculation of membrane permeability, at any level of membrane charging, and for any number of sorption site types. Figures 2; references 7: 6 Russian, 1 Western.

UDC 541.183.7

Adsorption of Phenols from Aqueous Solutions onto Polarized Carbon Fibers

917M0160c Moscow ZHURNAL FIZICHESKOY
KHIMII in Russian Vol 65, No 4, April 1991
(manuscript received 7 Aug 90) pp 1127- 1131

[Article by I. V. Sheveleva, N. V. Zryanina, and A. V. Voyt, USSR Academy of Sciences, Dalnevostochnoye Otdel, Institute of Chemistry, Vladivostok]

[Abstract] The adsorption of phenol, p-nitrophenol, salicylic acid, and p-aminophenol onto polarized carbonaceous fibers based on cellulose hydrate fabric (UT), cellulose hydrate felt (UV), and polyacrylonitrile twists (PAN) was studied. While phenol exhibited an uninterrupted decrease in adsorption with increasing negative charge, the three other sorbates exhibited maxima at varying voltages, depending on both sorbate and sorbent. For the UV fibers the maxima were similar for all three substituted sorbates, which was not the case for UT fibers, due to more intense Faraday processes. Desorption was more complete from the PAN fibers. The adsorption isotherms of phenol and salicylic acid on PAN fibers demonstrated that surface charge has more influence than solution pH. Adsorption on uncharged surfaces was best described by the Dubinin-Astakhov equation, while adsorption on polarized PAN fibers was best described by the Freundlich equation. The data obtained demonstrate that the PAN fibers undergo the strongest decrease in adsorption when their potential is shifted in the cathodic direction. Structural features and surface properties influence adsorption. Electrochemical polarization is useful for sorbent regeneration. Figures 3; references 8: 6 Russian, 2 Western.

UDC 577.387:541.183.123.3

Sorption of Adenosine Triphosphate by Anionite AV-17-2P

917M0160d Moscow ZHURNAL FIZICHESKOY
KHIMII in Russian Vol 65, No 4, April 1991
(manuscript received 3 Sep 90) pp 1131- 1136

[Article by V. F. Selemenev, V. N. Chikanov, T. A. Lovchinovskaya, Yu. I. Kiselev, and T. A. Kovaleva, Voronezhskiy State University imeni Lenin Komsomol]

[Abstract] The features of the interaction of the various ionic forms of ATP with AV-17-2P anion exchange resin were studied. Using IR, the pH regions for the existence of each ATP ionic form were found to be ATP^{2+} below pH 1.0, ATP^{1+} at pH 1.0-2.0, zwitterion at pH 2.0-3.0, ATP^0 at pH 3.0-4.2, ATP^{2-} at pH 4.2-6.5, ATP^{3-} at pH 6.5-9.0, and ATP^{4-} above pH 9.0. Increasing the negative charge on the nucleotide by increasing solvent pH was found to increase sorbent selectivity. Concentration exchange constants were determined at pH 3.4 and 5.8. Values obtained ranged from 2.3 for ATP^0 at pH 3.4 to

29 for ATP^{2-} at pH 5.8. These rather large values are due to the presence of nonexchange, sorbate-sorbate interactions. IR spectral data suggests that hydrogen bonds and interionic associations are involved. Comparison of the exchange constants obtained for ATP^- and ATP^{2-} indicates that maximum adsorption occurs in the neutral pH region. After 24 hours of contact between ATP and the resin about 3% transformation to AMP was observed; after 50 hours at 8 this value was 20%. Figures 3; references 11: 10 Russian, 1 Western.

UDC 541.183;541.14

UV-Laser Chemistry of Dimethylcadmium Adsorbed on Silicon

917M0160e Moscow *ZHURNAL FIZICHESKOY KHIMII* in Russian Vol 65, No 4, April 1991 (manuscript received 17 Dec 90) pp 1137- 1142

[Article by V. N. Varakin, and A. P. Simonov, Scientific Research Physical Chemistry Institute imeni L. Ya. Karpov, Moscow]

[Abstract] Mass spectroscopic analysis of neutral particles and ions desorbed with pulses from a 222 nm KrCl laser was used to study the kinetics of adsorption and decomposition of $\text{Cd}(\text{CH}_3)_2$ on n-Si(100). Plotting normalized signals for Cd, CH_3 , CdCH_3^+ , and CH_3^+ demonstrated the existence of at least four adsorption states. Nonlinear dependence of signal on energy density was found for all fragments except CH_3^+ . Comparison to previously published work of the authors using a XeCl laser demonstrated that the trimethylcadmium was the source of the CH_3^+ and the CdCH_3^+ ions. Formation of Cd^+ was not seen with the XeCl laser. The data indicate that this ion is formed from the efficient photodecomposition of $\text{Cd}(\text{CH}_3)_2$. The selectivity of the KrCl laser for CH_3 desorption renders it a promising tool for the deposition of cadmium films on silicon. Figures 3; references 14: 2 Russian, 12 Western.

UDC 541.128

Interaction of Hydrocarbons with Surface of Zeolite-Containing Cracking Catalysts

917M0160f Moscow *ZHURNAL FIZICHESKOY KHIMII* in Russian Vol 65, No 4, Apr 1991 (manuscript received 28 Jun 90) pp 1142- 1145

[Article by T. V. Kichapina, Ye. M. Knyazeva, L. N. Kurina, L. P. Shilyayeva, and S. V. Dolinskaya, Tomsk State University imeni V. V. Kuybyshev]

[Abstract] Temperature programming desorption was used to study the adsorption of n-octane, iso-octane and cumene on a 25% zeolite type Y containing cracking catalyst. The three hydrocarbons were found to exhibit desorption curves with two temperature maxima, at 593-633 K and at 823 K, reflecting the existence of two stable bound forms. The quantitative predominance of

the lower temperature form may be due to coke formation at higher temperatures. Desorption kinetics of the lower temperature form followed a second order Polyan-Winger equation, with activation energies of 130-150 kJ/mole. Above 723K only methane and propylene are desorbed, while below this temperature C_1 - C_3 hydrocarbons were seen, as well as isobutane from n-octane and benzene from cumene. This is evidence for dissociative adsorption. Cumene was the most stably adsorbed of the three hydrocarbons. Increasing the temperature of catalyst vacuum treatment lowered desorption temperature maxima to 563-603 K, with the amount of high temperature form decreased to trace levels and activation energies of 110-130 kJ/mole. This may be caused by selective removal of strong adsorption sites from the catalyst. Steam treatment of the catalyst for 12 hours eliminated the high temperature forms, lowered activation energies to 115-130 kJ/mole, decreased desorption of C_1 - C_3 gases, and increased desorption of isobutane and benzene. IR spectra of the catalyst confirmed the selective removal of strong sites. When the catalyst was steam treated for 24 hours one broad desorption peak, representing methane and propylene for the octanes and just propylene for cumene, was noted. Figures 3; references 2: Russian.

Production and Properties of Ternary Oxides in the System $\text{BaO-InO}_{1.5}\text{-CuO}$

917M0180A Moscow *ZHURNAL NEORGANICHESKOY KHIMII* in Russian Vol 36 No 4, Apr 91 (manuscript received 18 Sep 90) pp 819-822

[Article by A.A. Yevdokimov, O.A. Skordina, S.A. Smirnov, and V.V. Fomichev, Moscow Institute of Fine Chemical Technology imeni M.V. Lomonosov]

UDC 546.431.562.682

[Abstract] As part of a systematic search for new copper-, indium-, and alkaline metal-containing high-temperature superconductors, the authors of the study reported herein studied the phase relationships existing in the subsolidus region of the ternary system $\text{BaO-InO}_{1.5}\text{-CuO}$. They synthesized and studied about 50 specimens and determined their phase ratios in the subsolidus range of the system at 900°C. They also demonstrated the existence of the new ternary oxides $\text{Ba}_3\text{In}_4\text{Cu}_3\text{O}_{12}$ and $\text{Ba}_2\text{InCuO}_{4.5}$. These compounds were discovered to crystallize in a tetragonal singony, and their subnucleus parameters were found to equal $a = 4.283$, $c = 4.253$ angstroms and $a = 4.185$, $c = 4.064$ angstroms, respectively. $\text{Ba}_3\text{In}_4\text{Cu}_3\text{O}_{12}$ was shown to melt incongruently at 1,020°C, and $\text{Ba}_2\text{InCuO}_{4.5}$ was shown to do so at 1,000°C. The latter was further found to undergo a reversible polymorphous transformation at 880°C. The ternary oxide $\text{Ba}_3\text{In}_4\text{Cu}_3\text{O}_{12}$ was found to possess metallic conduction at ambient temperature (unlike $\text{Ba}_2\text{InCuO}_{4.5}$) and a highly pronounced "perovskite" subnucleus structure. The authors proceeded to

study selected electrophysical and spectral properties of these two compounds. The compounds $\text{Ba}_3\text{In}_2\text{Sc}_2\text{Cu}_3\text{O}_{12}$, $\text{Ba}_3\text{In}_2\text{Lu}_2\text{Cu}_3\text{O}_{12}$, and $\text{Ba}_3\text{In}_2\text{Pb}_2\text{Cu}_3\text{O}_{12-8}$, which are structurally related to the two aforesaid compounds, were also studied from the standpoint of their electrophysical and spectral properties. Figures 2, tables 2; references 13: 5 Russian, 8 Western.

Fluorozirconate Glasses

917M0180B Moscow ZHURNAL
NEORGANICHESKOY KHIMII in Russian Vol 36
No 4, Apr 91 (manuscript received 28 Jun 90)
pp 828-838

[Article by E.G. Rakov, Moscow Chemical Technology Institute imeni D.I. Mendeleyev]

UDC 546.161.833

[Abstract] This review examines the chemical problems entailed in producing fluorozirconate glasses. The requirements regarding the purity of such glasses are discussed with particular emphasis on the following types of impurities: transition metals; rare earth metals; oxygen-containing compounds; chloride, sulfate, phosphate, and other ions; hydrogen-containing compounds; inert gases; and lower fluorides of glass-forming metals. The following hydrometallurgical purification methods are covered: ion-exchange sorption, liquid extraction, and oxidizing methods. Discussed in a section devoted to the main anhydrous methods of producing fluorides are fluorination by using NH_4HF_2 , HF, F_2 , fluorine halides, xenon compounds, and NF_3 and other substances. The following methods of vapor-phase purification of fluorides are reviewed: distillation from the solid phase and from a melt, chemical precipitation from the gaseous phase, and chemical transport reactions. The use of a vacuum and inert atmosphere, an active atmosphere, and chemical and electrochemical reduction are discussed in the section on purifying melts. The author concludes that while the main method of synthesizing fluorozirconate glasses is that of synthesis of individual components (simple metal fluorides) and their mixtures followed by melting in a protective or active atmosphere, an alternative route is possible. That route is to mix solutions of precursor fluoride salts and precipitate a charge for melting fluorozirconate glass from a mixed solution. He cites two principal advantages of the latter approach: 1) complex fluorides have less of a tendency to form crystal hydrates, and 2) they have a lower hygroscopicity. He further states that the alternative method makes it simpler to purify the components of fluorozirconate glasses thanks to its standardization. References 137: 24 Russian, 113 Western.

The Crystalline Structures of BaMgP_2O_7 and PbZnP_2O_7

917M0180C Moscow ZHURNAL
NEORGANICHESKOY KHIMII in Russian Vol 36
No 4, Apr 91 (manuscript received) pp 851-854

[Article by Ye.V. Murashova, Yu.A. Velikodnyy, and V.K. Trunov, All-Union Scientific Research Institute of Chemically Pure Reagents and Especially Pure Chemicals (IRYeA) Scientific Production Association, Moscow]

UDC 546:548.736

[Abstract] In an attempt to systematize existing data about the crystalline structure of the pyrophosphates with the common formula $\text{MM}'\text{P}_2\text{O}_7$, the authors of the study reported herein conducted an x-ray crystallographic analysis of two representatives of the group, i.e., BaMgP_2O_7 and PbZnP_2O_7 . The studies conducted led the authors to conclude that while the two compounds studied (and hence other pyrophosphates) are not isostructural but rather belong to two different structural types, they may nevertheless be grouped into one structural family based on the principle of the similarity of the arrangement of their atoms regardless of their local symmetry. The structures of all pyrophosphates may be characterized by one type of skeleton, i.e., $[\text{M}'\text{P}_2\text{O}_7]_3\infty^{2-}$. The authors further concluded that the difference between the two structural types within the family is related above all to the differing nature of the bivalent cations included in the compounds. Figure 1, tables 4; references 6: 1 Russian, 5 Western.

A Study of Reaction in $\text{KF-CuF}_2\text{-LnF}_3$ ($\text{Ln} = \text{Yb, Lu}$) Systems

917M0180D Moscow ZHURNAL
NEORGANICHESKOY KHIMII in Russian Vol 36
No 4, Apr 91 (manuscript received 27 Jul 90)
pp 1041-1043

[Article by Ye.Ye. Fadeyeva, Ye.I. Ardashnikova, and M.P. Borzenkova, Moscow State University imeni M.V. Lomonosov]

UDC 546.[32.562.668.669].161

[Abstract] In view of the interest in the superconductive properties of perovskite-like layered oxide high-temperature superconductors in which some of the oxygen atoms are replaced by fluorine atoms, the authors of the study reported herein examined the reactions occurring in the system $\text{KF-CuF}_2\text{-LnF}_3$ ($\text{Ln} = \text{Yb, Lu}$). As starting substances, the authors used potassium, copper, ytterbium, and lutetium fluorides and binary fluorides formed in the systems KF-CuF_2 and KF-LnF_3 . The isothermal (250°C) sections of the state diagrams of compounds of the aforesaid system were studied and subjected to triangulation under the assumption of the

existence of K_2LnF_5 compounds. The authors demonstrated that under the conditions selected, a solid solution forms that is based on the compound K_2CuF_4 and that has a narrow homogeneity range (more than 98 mol.% K_2CuF_4). No other ternary fluoride phases were detected. The state diagrams of $KF-LnF_3$ systems were refined and discussed in relation to other publications on the compounds in question. Specifically, the authors explain why they believe that K_2LnF_5 is a distinct compound rather than a δ -modification of K_3LnF_6 phases. Figure 1, table 1; references 8: 6 Russian, 2 Western.

Melt-Solid Phase Equilibria in the System Pb-GaAs-GaSb

917M0180E Moscow ZHURNAL
NEORGANICHESKOY KHIMII in Russian Vol 36
No 4, Apr 91 (manuscript received 25 Jul 90)
pp 1067-1071

[Article by A.M. Grebenyuk, A.M. Litvak, A.A. Popov, N.A. Charykov, V.V. Sherstnev, and Yu.P. Yakovlev, Leningrad Physical Technical Institute imeni A.F. Ioffe, USSR Academy of Sciences]

UDC 621.315.592

[Abstract] The extreme importance of studying the fusibility curves of systems of the type $Pb-A^3B^5$ stems from the significant reduction in the concentration of free charge carriers in epitaxial A^3B^5 layers produced by precipitation from lead melts. This reduction makes it possible to significantly improve the electrophysical characteristics of instruments based on A^3B^5 compounds. Specifically, the reduction in question makes it possible to reduce dark currents and increase the breakdown voltage of semiconductor heterostructures. In view of these facts, the authors of the study reported herein conducted an experimental study and thermodynamic computation of the fusibility curve of the previously unstudied system $Pb-GaAs-GaSb$ and the three-component reciprocal system $InAs-InSb-GaAs-GaSb$. Included in this article are the fusibility curves of the system $Pb-GaAs-GaSb$ and the reciprocal system $InAs-InSb-GaAs-GaSb$. The authors note that their computation results presented in the curves are in good agreement with experimentally obtained values. They further note that because of the comparatively high purity of the semiconductor binary compounds under consideration, heterostructures based on the system $InAs-InSb-GaAs-GaSb$ have lower free charge carrier concentration values than do compounds obtained from the system $In-Ga-As-Sb$. Figures 2; references 4: 3 Russian, 1 Western.

Phase Equilibria in the System CuBr-HgBr₂

917M0180F Moscow ZHURNAL
NEORGANICHESKOY KHIMII in Russian Vol 36
No 4, Apr 91 (manuscript received 22 Oct 90)
pp 1072-1073

[Article by A.M. Podorozhnyy and V.V. Safonov, Moscow Institute of Fine Chemical Technology imeni M.V. Lomonosov]

UDC 541.123.2

[Abstract] In view of the scarcity of published data on CuBr and HgBr₂, the authors of this concise communication used the methods of differential thermal analysis and x-ray phase analysis to study phase equilibria in the system CuBr-HgBr₂. They studied the system in concentrations ranging from 10 to 90 mol.% CuBr-HgBr₂ and used their results to plot a phase diagram of the said system. They conclude that the eutectic composition corresponds to 83 mol% HgBr₂ and melts at 230°C. Observable in the diagram are regions of solid solutions based on polymorphous modifications of copper (I) bromide. The solid solution based on β -CuBr decomposes in accordance with a eutectoid scheme at 250°C. The eutectoid point corresponds to a content of 35 mol% HgBr₂. A solid solution based on γ -CuBr was observed to form at 230°C. The range of the existence of the α -CuBr solid-solution phase was determined to not exceed 1 to 3 mol%. The phase diagrams of $CuX-HgX_2$ ($X = Cl, Br, I$) were thus characterized by the presence of solutions based on copper halides. In the bromide system, unlike the chloride system, the components were found to be completely mutually soluble in a melt, and unlike the iodide system, no intermediate compounds were present. Figure 1; references 5: 3 Russian, 2 Western.

Phase Equilibria in the System MgO-As₂O₅

917M0180G Moscow ZHURNAL
NEORGANICHESKOY KHIMII in Russian Vol 36
No 4, Apr 91 (manuscript received 17 Jul 90)
pp 1074-1077

[Article by I.V. Ashlyayeva, B.K. Kasenov, and A.Z. Beylina, Chemical Metallurgy Institute, Kazakhstan Academy of Sciences, Karaganda]

UDC

620.181+536.76+541.121/123+541.45+546.19+546.46

[Abstract] The authors of the study reported herein used a series of physicochemical analysis methods (including x-ray phase analysis) to study phase equilibria in the system $MgO-As_2O_5$. They established the formation of the two following incongruently melting compounds in the system: $Mg(AsO_3)_2$ (melting point, 680°C); $Mg_2As_2O_7$ (melting point, 980°C). They also established the formation of a congruently melting compound, i.e., $Mg_3(AsO_4)_2$ (melting point, 1,350°C). Finally, they established the formation of the compound $Mg_4As_2O_9$, which is unstable at ambient temperature, formed on the basis of a solid-phase reaction at 735°C, and decomposes peritectoidally at 1,190°C. The system was discovered to have the following eutectic points: $As_2O_5-Mg(AsO_3)_2$ (20.0 mol% MgO ; 700°C) and $Mg_3(AsO_4)_2-MgO$ (80.0 mol% MgO ; 1,330°C). Figures 4, table 1; references 9: 5 Russian, 4 Western.

MCl-NdCl₃-H₂O (M = K, NH₄) Systems at 50-100°C

917M0180H Moscow ZHURNAL
NEORGANICHESKOY KHIMII in Russian Vol 36
No 4, Apr 91 (manuscript received 23 Aug 90)
pp 1078-1081

[Article by N.V. Bunyakina, D.A. Storozhenko, Yu.V. Syusko, and V.G. Shevchuk, Poltava Construction Engineering Institute]

UDC 541.123.3+546.131'32'39'657

[Abstract] The authors of this concise report claim to be the first to use the isothermal method to study the systems KCl-NdCl₃-H₂O and NH₄Cl-NdCl₃-H₂O in the temperature range from 50 to 100°C. For their starting substances, they used recrystallization-purified chemically pure potassium and ammonium chlorides and NdCl₃·6H₂O. The authors demarcated regions of crystallization of the starting salts and binary compounds of the composition MCl-NdCl₃·5H₂O in the systems' polythermal lines at 75 and 100°C. The individuality of binary chlorides was confirmed by chemical, microphotographic, crystalline optics, and x-ray phase techniques. Also included are tables summarizing the authors' data on solubility in the systems KCl-NdCl₃-H₂O and NH₄Cl-NdCl₃-H₂O solubility lines of both systems at 75 and 100°C and on the roentgenographic characteristic of binary potassium, ammonium, and neodymium chlorides. Figures 3, tables 3; references 8: 6 Russian, 2 Western.

The Composition and Electron Structure of Vacuum Condensates Obtained by Vaporization of LnTaO₄ (Ln = Sc and Y and Lanthanides)

927M0001E Kiev UKRAINSKIY KHIMICHESKIY
ZHURNAL in Russian Vol 57 No 7, Jul 91 (manuscript received 6 Jul 90) pp 697-700

[Article by G.A. Teterin, M.Ya. Khodos, L.P. Yermolina, Yu.F. Zhuravlev, and T.M. Shkolnikova, Physicochemical Institute, UkSSR Academy of Sciences, Odessa, and Chemistry Institute, Ural Department, USSR Academy of Sciences, Sverdlovsk]

UDC 546.883.5:539.216.2

[Abstract] The authors of the study reported herein examined the composition and electron structure of vacuum condensates produced by the method of direct electron beam vaporization of orthotantalates of scandium, yttrium, and lanthanides. The starting materials were synthesized by the method of coprecipitation from chloride solutions. The residue was filtered by washing off the NH₄⁺ and Cl⁻ ions and drying at 120°C followed by 4 hours of roasting in air at 1,200°C. The resultant vacuum-vaporized materials were formed into tablets and roasted for 4 hours at 1,500°C. The tablets' composition was determined by chemical and x-ray analysis.

Thin-layer condensates were then produced by the method of direct electron beam vaporization on a VU-1-A. Coatings were condensed onto copper and molybdenum substrates at a condensation temperature of about 150°C and a rate of about 5 to 10 A/s. The resultant layers were about 0.40 to 0.75 μm thick. X-ray photoelectron spectroscopy was used to analyze the films' elemental composition and valence state. The results obtained led the authors to conclude that under the effect of high-energy radiation it is primarily the more volatile tantalum-containing components that transform into a vapor-gas phase after the tantalates melt from the melt's surface. This explains the observed titanium enrichment of the layers. As the surface of the metal is depleted of tantalum-containing components, the vapor-gas phase and consequently the condensate are enriched with rare earth metal oxides. Then, as new portions of the vacuum-vaporized material melt as the tantalum ions are diffused from the bulk of the melt to its surface, the film's composition is observed to be relatively depleted of rare earth elements. It was further determined that, all else being equal, the composition and optical and performance properties of the condensate produced depend on the nature of the rare earth ion. The phase composition of the target was found to play a significant role in the vaporization of complex vacuum-vaporized material. The deviation of the film's composition from that of the starting material was found to diminish when stable complex oxides melting at relatively high temperatures were vaporized. Figure 1, tables 2; references 3 (Russian).

Gas-Liquid Equilibrium in the System Methane-Hydrogen Sulfide at Temperatures Below 273 K

927M0001F Kiev UKRAINSKIY KHIMICHESKIY
ZHURNAL in Russian Vol 57 No 7, Jul 91 (manuscript received 15 Jun 90) pp 701-704

[Article by N.L. Yarym-Agayev, L.D. Afanasenko, V.G. Matviyenko, Yu.Ya. Ryabkin, and G.B. Tolmacheva, Donetsk Polytechnic Institute]

UDC 541.123.2

[Abstract] Designing a process flow for refining high-sulfur natural gas requires data regarding the parameters of phase equilibria in the system methane-hydrogen sulfide at temperatures below 273 K. Because the literature does not contain any such data, the authors of the study reported herein used that static analytic method to study gas-liquid equilibrium in methane-hydrogen sulfide systems at temperatures of 273.2, 252, 239.9, and 222.2 K. They determined the critical and maximum pressures of the said system at the four temperatures studied. These are presented in three tables and three graphs. Also presented are coefficients of fourth-order correlation equations for computing the parameters of the system methane-hydrogen sulfide in its critical range

in the temperature interval from 192 to 378 K. Figures 3, tables 3; references 2 (Western).

Controlling Physicochemical Properties of Modified Silica by Thermooxidation of the Modifying Layer

927M0001G Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 57 No 7, Jul 91 (manuscript received 13 Jul 90) pp 723-727

[Article by Yu.I. Tarasevich, A.V. Nazarenko, S.V. Bondarenko, and I.Ya. Pishchay, Institute of Colloidal Chemistry and Water Chemistry, UkSSR Academy of Sciences, Kiev]

UDC 541.183

[Abstract] Materials obtained by chemical modification of a silica surface are widely used as sorbents, carriers, catalysts, fillers, and thickening agents for plastic lubricants. Thermooxidation of the modifying layer is one effective method of changing its structure and physicochemical properties. In view of the importance of such modification, the authors of the study reported herein examined the effect on the temperature of heat-treating polydimethylsiloxane-modified silicas on the chemical nature of the surface, adsorption properties, and thermal stability of the resultant materials. The studies were conducted on the diatomite carrier Khromaton N (produced in the Czech and Slovak Federated Republic) and the macroporous silica Silokhrom-2. As a modifier, the authors used type PMS-100 commercial polydimethylsiloxane containing linear oligomers $(CH_3)_3Si[OSi(CH_3)_2]_nCH_3$ with a mean molecular mass of 5,000. The tests performed established that increasing the temperature at which polydimethylsiloxane-modified silica is heat-treated from 200 to 400°C thus results in the formation of a modifying layer with a reticular structure and in the appearance of "surface" micropores. These distinctions of the modifying layer's structure increase the hydrophobicity and thermal stability of the modified material. Figures 2; references 12 (Russian).

Properties of Type 123 High-Temperature Superconducting Ceramic Containing Transition Metal Ions

927M0003A Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 57 No 8, Aug 91 (manuscript received 2 Oct 90) pp 798-800

[Article by S.A. Nedilko, G.V. Panchenko, N.V. Anshukova, and A.I. Golovashkin, Kiev University]

UDC 546.65'562.87+537.312.62

[Abstract] The authors of the study reported herein used x-ray diffraction and infrared spectroscopy to study the possibility of isomorphic replacement of copper by two

transition metal ions in the high-temperature superconducting [HTSC] ceramic $YBa_2Cu_{3-2x}M_x'M_x''O_{7-8}$ (where M' and M'' stand for Zn, Ni, and Mn). They examined the systems $YBa_2Cu_{3-2x}Mn_xNi_xO_{7-8}$, $YBa_2Cu_{3-2x}Ni_xZn_xO_{7-8}$, and $YBa_2Cu_{3-2x}Mn_xZn_xO_{7-8}$, where $0.05 \leq x \leq 1.00$. The said compounds were obtained by chemical homogenization, i.e., by coprecipitation of the components in the form of carbonates or oxalates followed by heat treatment in two stages. The x-ray diffraction and infrared spectroscopy studies revealed that replacing copper ions by ions of manganese and nickel results in a reduction in the temperature of the transition to a state of superconductivity and, eventually, in a total loss of HTSC properties when $x \geq 0.5$. In the systems $YBa_2Cu_{3-2x}Ni_xZn_xO_{7-8}$ and $YBa_2Cu_{3-2x}Mn_xZn_xO_{7-8}$, even a slight replacement of copper when $x \leq 0.05$ was found to result in a total loss of superconducting properties. Figure 1, table 1; references 14: 3 Russian, 11 Western.

Phase Formation in $BaCO_3(Nb, Ta)_2O_5-ZnO$ Systems

927M0003B Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 57 No 8, Aug 91 (manuscript received 2 Apr 90) pp 801-803

[Article by G.N. Novitskaya, O.Z. Yanchevskiy, A.G. Belous, and S.V. Polyanetskaya, Institute of General and Inorganic Chemistry, UkSSR Academy of Sciences, Kiev]

UDC 546(02+548.3+431+882+883+47)

[Abstract] Others have demonstrated that improving the properties of the ceramics $Ba(Nb_{2/3}Zn_{1/3})O_3$ and $Ba(Ta_{2/3}Zn_{1/3})O_3$ hinges on the ordering in the B sublattice of the Nb(Ta) and Zn atoms. For this reason, the authors of the study reported herein studied the process of phase formation during synthesis of the specified compounds. To synthesize the said compounds, the authors used analytic-grade $BaCO_3$ and ultrapure Nb_2O_5 , Ta_2O_5 , and ZnO . Two synthesis methods were used. In the first case, the required amounts of $BaCO_3$, $Nb_2O_5(Ta_2O_5)$, and ZnO were mixed, and the mixture was annealed in the temperature range from 600 to 1,400°C for 3 to 8 hours. In the second case, $ZnNb_2O_6$ and $ZnTa_2O_6$ were synthesized first, mixed with $BaCO_3$ in the required ratio, and then subjected to annealing. The findings of x-ray crystallographic analysis performed on the $ZnNb_2O_6$ synthesized were in agreement with data published elsewhere in the literature. According to the authors' research, $ZnTa_2O_6$ crystallizes in a tetragonal system with cell parameters of $a = 14.260$ and $c = 7.255$ angstroms and is the structural analogue of $ZnNb_2O_6$, for which $a = 14.27$ and $c = 7.34$ angstroms. Phase formation of $ZnNb_2O_6$ was found to begin at 600°C and culminate at 800°C. Phase formation of $ZnTa_2O_6$ required higher temperatures. Only traces of $ZnTa_2O_6$ were apparent at 600°C, and a single-phase product was not formed until 950°C. As a result of their

research, the authors succeeded in establishing that using presynthesized ZnNb_2O_6 and ZnTa_2O_6 when producing $\text{Ba}(\text{Nb}_{2/3}\text{Zn}_{1/3})\text{O}_3$ and $\text{Ba}(\text{Ta}_{2/3}\text{Zn}_{1/3})\text{O}_3$ facilitates ordering in the B sublattice. Figure 1, tables 2; references 7: 3 Russian, 4 Western.

The Thermal Decomposition of Tungsten Carbonyl on Iron and Cobalt

927M0004A Ivanovo IZVESTIYA VYSSHIKH UCHEBNIKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHOLOGIYA in Russian Vol 34 No 5, May 91 (manuscript received 20 Jul 90) pp 79-82

[Article by V.I. Podoprigora and A.K. Bayev, Analytic Chemistry Department, Belorussia Technological Institute imeni S.M. Kirov]

UDC 531.3.546.785

[Abstract] A number of research papers have dealt with the thermal decomposition of tungsten carbonyl. None, however, has presented data regarding selecting the kinetic range of the propagation of the reaction or the range in which the conditions of stationarity in the system are met. In addition, the kinetic characteristics presented in the aforesaid research papers are extremely contradictory. In view of these facts, the authors of the study reported herein conducted their own research on the kinetic characteristics of the thermal decomposition of $\text{W}(\text{CO})_6$ on iron and cobalt. They conducted their experiment in a differential-flowthrough unit with recording of gas-phase heat conduction. The reactor was precoated with iron and cobalt by pyrolysis of the respective carbonyl compound. The kinetic parameters of the thermal decomposition of $\text{W}(\text{CO})_6$ at temperatures of 503, 513, 520, 531, 538, 545, 553, 560, and 568 K were recorded, plotted on a graph, and summarized in table form. The thermal decomposition was found to begin slowly, increase in speed, pass through a maximum, and then slow down. The activation energies of the thermal decomposition of $\text{W}(\text{CO})_6$ on Fe and Co were determined to equal 86.6 ± 3.6 and 86.5 ± 3.2 kJ/mol, respectively. The reproducibility of the values obtained for degree of transformation did not exceed 1%, and that of the values of the maximum rates and times required to reach these values did not exceed 3%. The relative error in determining the specific reaction rates amounted to 4.6%. The specific reaction rates as determined by different equations did not differ by more than

20%, and the spread of analogous values in parallel experiments did not exceed 3%. Figures 3, table 1; references 6 (Russian).

The Effect of Pulverizing SiC Powder on the Strength of Materials Supporting a Reaction

927M0004B Ivanovo IZVESTIYA VYSSHIKH UCHEBNIKH ZAVEDENIY: KHIMIYA I KHIMICHESKAYA TEKHOLOGIYA in Russian Vol 34 No 5, May 91 (manuscript received 17 Jul 90) pp 83-86

[Article by V.Yu. Zelinskiy, V.A. Gumennyy, and V.M. Mirollyuz, Department of Construction Materials and Construction Processes, Ust-Kamenorgorsk Road Construction Institute]

UDC 621.762

[Abstract] Silicon carbide reaction-supporting materials may be considered promising new-generation materials in several respects. The theoretical and technological principles of producing reaction-supporting materials from fractionated powders have been developed in a cycle of research projects conducted by the associates of the Materials Science Problems Institute of the U.S.S.R. Academy of Sciences. In a continuation of this line of research, the authors of the study reported herein examined the possibility of using prepulverized skeleton particles in the composition of reaction-supporting silicon carbide materials in order to increase their strength. M100 fractionated powder (conforming to All-Union State Standard [GOST] 26327-84) was pulverized in a vibratory mill at a vibration amplitude of 1.5 mm and a vibration frequency of 25 s^{-1} . At the same time, control materials were prepared from the powders M5 and M50 and a 35:65 mixture of the two. The powders and ceramics were analyzed in accordance with the standard methods. The specimens were analyzed to determine their specific surface, hydrostatic density, open porosity, flexural strength for a three-point loading scheme, and spalling microstructure. Scanning electron microscopy and fluctuation of diffracted x-radiation were among the test methods used. The tests conducted established that the possibilities of increasing the strength of reaction-supporting silicon carbide material made of fractionated particles are quite limited. The effectiveness of using pulverized powder was found to depend on the structural state. The wide range of polydispersion of skeleton particles and the formation of aggregates was found to reduce strength sharply. The material was observed to become stronger when the powder's grain profile and density were stabilized. Figures 2, tables 2; references 7 (Russian).

Solid Solutions Based on CuCr_2Se_4

927M0005A Moscow IZVESTIYA AKADEMII NAUK
SSSR: SERIYA NEORGANICHESKIYE MATERIALY
in Russian Vol 27, No 6, Jun 91 (manuscript received
7 Jul 90) pp 1109-1115

[Article by T. I. Koneshova, General and Inorganic
Chemistry Institute imeni N. S. Kurnakov, Moscow]

UDC54-165

[Abstract] Spinel CuCr_2Se_4 has attracted much attention owing to the fact that it is a ferromagnetic having a Curie temperature of 164°C , and that by substitution of any of its elements it is possible to synthesize phases having different signs and degrees of conductivity, type of magnetism, Curie temperature, magnetic moment, etc. Until recently, all studied solid solutions of the above were prepared either by direct synthesis from very pure elements or binary compounds in evacuated quartz ampules, or by growing single crystals with the aid of transport reactions or from molten solutions. Alloyed CuCr_2Se_4 also has a spinel structure, and in the present work it was demonstrated that solid solutions may be prepared by partial substitution of practically all the spinel components. Data are presented from which it was concluded that there are no correlations between CuCr_2Se_4 solid solutions and the magnetic or electrical properties of the resulting spinels. References 29: 5 Russian, 22 Western.

Internal Elastic Deformations in Silicon

927M0005B Moscow IZVESTIYA AKADEMII NAUK
SSSR: SERIYA NEORGANICHESKIYE MATERIALY
in Russian Vol 27, No 6, Jun 91 (manuscript received
12 Oct 89) pp 1116-1118

[Article by V. Ye. Kustov, T. V. Kritskaya, N. A. Tripachko, L. I. Khirunenko, V. I. Shakhovtsov, and V. I. Yashnik, Physics Institute]

UDC546.28

[Abstract] Oxygen and carbon are two of the basic uncontrolled impurities in grown silicon crystals which have significant effects on the thermal and radiation stability of the latter. Thus, during thermal and secondary radiation defect formation, elastic deformation, caused by the presence of these impurities, plays an important role. Internal elastic fields in silicon are detected X-ray measurements of lattice parameters and by measuring non-uniform elastic expansion of EPR lines of a strain-sensitive site. In the present work a technique employing paramagnetic strain probing was used to determine density of deformation charges in industrial grade silicon. The basic sources of internal elastic deformation in silicon having relatively low levels of doping are oxygen and carbon which have deformation charges quantitatively similar, but opposite in sign. Elastic deformations, related to these contaminants, are

partially compensated if the concentrations of the two are comparable. Figure 1; references 9: 4 Russian, 5 Western.

Effect of Concentration Dissimilarities on Internal Stresses in Gallium Arsenide Single Crystals

927M0005C Moscow IZVESTIYA AKADEMII NAUK
SSSR: SERIYA NEORGANICHESKIYE MATERIALY
in Russian Vol 27, No 6, Jun 91 (manuscript received
21 Sep 89) pp 1127-1130

[Article by N. S. Zadorozhnyy, V. F. Kovalenko, M. G. Milvidskiy, and A. V. Prokhorovich, Semiconductor Institute, Kiev]

UDC546.681.3'191

[Abstract] During the growth of $\text{A}^{\text{III}}\text{B}^{\text{IV}}$ single crystals at high temperature gradients, a basic residual stress is the so-called thermoplastic stress, caused by the dislocation stress field stemming from the plastic deformation process. One source of this deformation is thermoelastic stresses, whose level is determined by the thermal conditions under which the crystal is grown, especially the temperature gradient between the casting zone and the crystallization front. Under this concept, thermal stresses are equal (with opposite sign) to the thermoelastic stresses relaxed at high temperatures. However, research on the distribution of residual (internal) stresses present in single crystals at 300 K, and dislocation densities in gallium arsenide cross sections, indicated that in real crystals such stresses are caused by other, more significant factors. One such factor is the gradient of compound composition within the limits of homogeneity. Recent work has shown that non-uniform spread in concentration of doping agents throughout the bulk can also cause internal stresses. In the present work the effect of concentration non-uniformity on internal stresses in gallium arsenide single crystals was studied. It was demonstrated that the basic source of stress is the overall concentrational non-uniformity of the gallium arsenide caused by non-uniformity of the doping agent, as well as non-uniformity in composition of the compound within the limits of homogeneity. Figures 2; references 7: 6 Russian, 1 Western.

 $\text{In}_x\text{Ga}_{1-x}\text{As}$ Epitaxy from Molecular Bundles Supported on InP

927M0005D Moscow IZVESTIYA AKADEMII NAUK
SSSR: SERIYA NEORGANICHESKIYE MATERIALY
in Russian Vol 27, No 6, Jun 91 (manuscript received
4 Jan 89) pp 1136-1141

[Article by G. G. Dvoryankina, V. F. Dvoryankin, A. G. Petrov, A. A. Kudryashov, and L. B. Khusid, Radio Engineering and Electronics Institute, Moscow]

UDC546-165:537.311.33

[Abstract] A study was made of the growth process of $\text{In}_x\text{Ga}_{1-x}\text{As}$ layers supported on InP by the epitaxial method from molecular bundles.

The structure, surface morphology, and electrical properties of these layers were also studied over a broad range of compositions ($x = 0.2-0.8$). The quality of the $\text{In}_x\text{Ga}_{1-x}\text{As}$ layer deposited on the InP is shown to be more sensitive to tensile than to compression deformation. Various mechanisms for electron dispersal throughout the $\text{In}_x\text{Ga}_{1-x}\text{As}$ layers are considered. Figures 4; references 11: 5 Russian, 6 Western.

Electrical Conductivity of Cadmium Sulfide at Pressures over 25 GPa

927M0005E Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA NEORGANICHESKIYE MATERIALY in Russian Vol 27, No 6, Jun 91 (manuscript received 25 Oct 89) pp 1147-1150

[Article by A. N. Babushkin, G. V. Babushkina, Z. I. Uritskiy, and L. Ya. Kobelev, Ural State University imeni A. M. Gorkiy]

UDC536.42

[Abstract] Cadmium sulfide has applications in acoustics and optical electronics. Its physical properties are well known at pressures to approximately 5 GPa and studies have been made at various higher pressures for the behavior of thermal emf, electrical conductivity, and resistance. Other studies showed the existence of a maximum in electrical resistance at 32-34 GPa, while X-ray studies showed that a structural phase transition from rock salt to ortho-rhombic takes place at 56 GPa. In the present work it was demonstrated that a reconfiguration in electron structure takes place in CdS at 29-31 GPa and that this is the cause of the maximum in resistance. Figures 3; references 12: 9 Russian, 3 Western.

Structure and Optical Properties of Polycrystalline Zinc Selenide

927M0005F Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA NEORGANICHESKIYE MATERIALY in Russian Vol 27, No 6, Jun 91 (manuscript received 16 Oct 89) pp 1176-1179

[Article by A. Ya. Aksenovskikh, A. N. Bryzgalov, V. V. Musatov, B. M. Slepchenko, and L. M. Khalilov, Chelyabinsk Pedagogical Institute]

UDC535.361:539.24

[Abstract] Polycrystalline materials of group $A^{II}B^{VI}$ are being used widely in infra-red optics owing to the many advantages over that of single crystals, e.g. low cost availability, less inter-grain defects such as dislocations in the elastic stress region, and the fact that polycrystalline components can have significant dimensions. However, they are also subject to radiation loss at the grain boundaries. In the present work a series of zinc selenide polycrystals, prepared by ceramics technology under

various conditions was studied. Transmission coefficients in the infra-red region and statistical analysis of grain structures indicate that the basic mechanism for loss of radiation is due to reflection from inter-grain boundaries. Comparison of experimental and theoretical data makes it possible to determine the parameter of optical non-uniformity of inter-grain boundaries. Figures 2; references 4 (Russian).

Effect of Copper on Structure Formation in Boron Selenide Coatings on Molybdenum and Tungsten

927M0005G Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA NEORGANICHESKIYE MATERIALY in Russian Vol 27, No 6, Jun 91 (manuscript received 13 Sep 89) pp 1226-1230

[Article by Yu. V. Dzyadykevich and N. I. Zablotskaya, Ternopol State Pedagogical Institute imeni Ya. A. Galan]

UDC546.56'27

[Abstract] Saturation of high melting metals in powder mixtures by diffusion is a simple and convenient process, although the great length of time required to form a coating, which often exceeds that of the other operations in component production, hinders broad scale use of this method in production. The saturation process may be accelerated by addition of an activator such as copper. Noting the advantages of sequential saturation of high melting metals with boron and silicon, and keeping in mind the fact that in the siliciding process, the growth of MSi_2 layers by diffusion takes place at a slower rate than that without boron, study of the action of copper on the process of structure formation and the quality of boron silicide coatings becomes pertinent. In the present work it was demonstrated that participation of copper in sequential boron silicide coating of molybdenum and tungsten results in thicker coatings in the boride and silicide phases. The presence of 3 percent copper (by weight) in the saturation mix shifts the barrier properties of the MV phase toward greater thicknesses and facilitates formation of silicide layers on high melting metals having equi-axial structures with good shielding properties. Figures 2; references 18: 17 Russian, 1 Western.

New Compound NiSi_3P_4 and Its Properties

927M0005H Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA NEORGANICHESKIYE MATERIALY in Russian Vol 27, No 6, Jun 91 (manuscript received 11 Oct 89) pp 1311-1313

[Article by O. N. Ilnitskaya, V. A. Bruskov, P. Yu. Zavaliy, and Yu. B. Kuzma, Lvov State University imeni I. Franko]

UDC548.736.3+546.74.28.181.1

[Abstract] While studying component interaction in the system Ni-Si-P, a new compound having an approximate

composition of the title compound was detected. Single crystals were prepared by calcining pre-pressed powder charges in evacuated quartz ampules at 100 k daily temperature increments until reaching 1170 K, where the samples were maintained for 100 hours. After cooling to 1070 K and calcining for an additional 400-500 hours, the ampules were quenched in cold water. Physical properties and possible structures are presented. Figures 2; references 4: 1 Russian, 3 Western.

Structural Features of Pyrolytic Carbon Fibers

927M00051 Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA NEORGANICHESKIYE MATERIALY in Russian Vol 27, No 6, Jun 91 (manuscript received 21 Sep 89) pp 1318-1319

[Article by V. A. Ksenofontov, V. M. Shulayev, V. M. Kulinich, and Yu. F. Guzychko, Physical Technical Institute, Kharkov]

UDC661.666:537.534.3:548.522

[Abstract] Carbon fibers prepared by pyrolysis of hydrocarbons in the gaseous phase are successfully competing with PAN carbon fibers in many physical properties such as strength, high Young's modulus, high auto-emission characteristics with long term stability, etc. The unique properties of pyrolytic carbon are due to their structure, while gas phase technology makes it possible to realize a wide variety of structural and morphological forms. One morphological variety obtained by gas phase technology with catalytic activation is "tubular" fiber. Electron microscopic images show what appears to be a hollow tube. In the present work this material was subjected to mass spectrometric and ion-microscopic analysis. The "hollow" tubes were demonstrated to contain carbon in various phases. Figures 3; references 5: 3 Russian, 2 Western.

Seeding Defect Legacy in Growth of $Y_3Fe_5O_{12}$ Single Crystals from Barium-Borate Solution-Melts

927M0005J Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA NEORGANICHESKIYE MATERIALY in Russian Vol 27, No 6, Jun 91 (manuscript received 20 Oct 89) pp 1325-1326

[Article by N. A. Sokolova and V. L. Temerov, Physics Institute imeni L. V. Kirenskiy]

UDC548.52

[Abstract] When growing single crystals by seeding, it is possible for the seed itself to be a source of defects in the growing crystal. Ferro-garnet crystals are normally grown by seeding with a defect-free, slow-growing crystal grain obtained by spontaneous crystallization and having the same nucleus parameter as the growth material. However, preparation of such seeds requires considerable resources and precludes economical use of the seeding

material. Attempts have thus been made to investigate tolerable deviations from the ideal in the characteristics of seeds. In the present work the effects of seed surface quality on the formation of growth defects in $Y_3Fe_5O_{12}$ single crystals was studied. Crystals were prepared from solution in BaO melt with B_2O_3 employing a ring-shaped crystal carrier which enabled stable growth of 6-8 crystals simultaneously. The latter also made it possible to compare defects and quality in crystals grown from different seeds under identical thermophysical and hydrodynamic conditions. The results demonstrate that the legacy of defects originating from the crystal bulk leads to a worsening in the quality of grown crystals. The best quality crystals were grown from natural grain seeds. Figure 1; references 4: 2 Russian, 2 Western.

Effect of Surface Composition of Semiconductor Ceramic $Ba(Ti, Sn)O_3$ on Temperature of Region of Positive Temperature Coefficient of Resistivity

927M0005K Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA NEORGANICHESKIYE MATERIALY in Russian Vol 27, No 6, Jun 91 (manuscript received 20 Oct 89) pp 1327-1328

[Article by B. B. Leykina and Yu. P. Kostikov, Resistor and Capacitor SRI (State), Leningrad]

UDC546.824 431-31

[Abstract] Semiconductor materials based on barium titanate and having positive temperature coefficients of resistivity over a given temperature range are normally prepared from solid solutions having isovalent substituents in either the barium or titanium sub-lattice. Shifting the positive temperature coefficient of resistivity is combined with shifting the phase transition temperature in ferroelectric-paraelectrics. In the system $(Ba, Sr)TiO_3$ the shift in Curie temperature and initiation of the region of positive temperature coefficient of resistivity take place at the same time, the break in temperatures not exceeding 3° C. In $Ba(Ti, Sn)O_3$ the shift in initiation of positive temperature coefficient of resistivity zone takes place much slower than the shift in Curie temperature. In the present work the difference in behavior of these two systems is explained as being due to the reduction of tin dioxide and its elimination from the surface layer, thereby resulting in non-uniform distribution along the radius of the grain, and causing a shift in transition temperature in the surface layers of the grain as compared to the bulk of the material. References 4 (Russian).

A Mass Spectrometry Study of the Reaction Products of Gallium Chloride and Chloride With Hydrazides of Carbonic Acids by the Method of Fast-Atom Bombardment

927M0013B Moscow KOORDINATSIONNAYA KHIMIYA in Russian Vol 17 No 6, Jun 91 (manuscript received 15 May 90) pp 781-785

[Article by M.G. Ivanov, I.I. Kaninichenko, V.G. Baklykov, N.A. Klyuyev, and A.N. Popov, Ural Polytechnic Institute imeni S.M. Kirov]

UDC 541.49+543.51

[Abstract] In a previous communication, the authors of the study reported herein showed that the reaction of indium chloride with hydrazides entails the formation of complex compounds whose composition and ligand coordination method depend on the reaction conditions and nature of the organic radical. In the present article, they report the results of their continuing studies in this direction. Specifically, they report on their study of the reaction of gallium chloride and bromide with hydrazides of acetic, benzoic, and p-aminobenzoic acids. By using the method of fast-atom bombardment, they conducted a mass spectrometry study of the structure of the resultant compounds. The studies revealed that ions with a deprotonated imidol form of coordinated hydrazide have an elevated gaseous-phase stability. The peaks of the fission product ions found for complexes with hydrazide of p-aminobenzoic acid confirmed that hydrazide molecules bound to the gallium participate in the coordination through the nitrogen atom of the amino group of the benzene ring. The mass spectra of the negative ions and Raman spectra confirmed the presence of a $[\text{GaBr}_4]^-$ ion in the structure of the gallium bromide-benzoic acid hydrazide complex. On the basis of the totality of the data obtained from the various spectrometry and spectroscopy studies performed, the authors hypothesized the structure $[\text{GaBr}_4]\text{HBr} \cdot 2\text{L} \cdot 6\text{H}_2\text{O}$. Tables 3; references 12: 10 Russian, 2 Western.

The Complexing of Copper (II) With Oxamide

927M0013C Moscow KOORDINATSIONNAYA
KHIMIYA in Russian Vol 17 No 6, Jun 91 (manuscript
received 2 Jan 90) pp 833-835

[Article by S.I. Neykovskiy, V.K. Steba, Ye.S. Smirnova,
V.D. Parkhomenko, and F.M. Tulyupa, Dnepropetrovsk
Construction Engineering Institute and Dnepropetrovsk
Chemical Technology Institute]

UDC 541.49

[Abstract] The authors of the study reported herein synthesized and studied the composition and structure of the new complex compound $\text{CuL} \cdot \text{H}_2\text{O}$ (III) formed in the system $\text{CuAcet}_2\text{-H}_2\text{L-H}_2\text{O}$. The reaction mixture, which contained 0.30 g oxamide and 0.62 g CuAcet_2 (with a Cu:L molar ratio of 1:1), was placed in 50 ml distilled water and boiled until a green-colored copious precipitate appeared and the solution became colorless. The new compound turned out to be a crystalline substance that is sparingly soluble in water and alcohol. It was found to contain the following (%): C, 14.32; H, 1.60; and N, 16.53. The following were calculated (%) for $\text{CuC}_2\text{N}_2\text{H}_4\text{O}_2$: C, 14.33; H, 2.40; and N, 16.71. Infrared spectroscopy studies performed on the new compound led the authors to hypothesize that the ligand molecule in the study complex is covalently bound with copper (II) cations through the oxygen and nitrogen atoms; this resulted in the formation of four-membered chelate cycles with a polymer structure. Studies of the behavior of H_2L and $\text{CuL} \cdot \text{H}_2\text{O}$ upon heating in the temperature range from 20 to 500° revealed that the thermolysis of noncoordinated oxamide occurs in a single stage, whereas that of $\text{CuL} \cdot \text{H}_2\text{O}$ occurs in two. Figure 1, table 1; references 9: 7 Russian, 2 Western.

The Oxidation of Titanium-Aluminum Alloys in an Air Atmosphere at High Temperatures

917M0186F Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 64 No 1, Feb 91 (manuscript received 29 May 90) pp 249-257

[Article by V.I. Dyachkov, Leningrad State University]

UDC 620.193.5:669.295.5

[Abstract] In a continuation of their previously published research on the kinetics and composition of the products of the oxidation of titanium-aluminum alloys, the authors of the study reported herein examined the oxidation of Ti-Al alloys in an air atmosphere at temperatures between 1,173 K and 1,473 K. For their experiments, the authors used Ti-Al alloys with the following percentages (by weight) of alloy-forming element (C_{Al}): 0.28, 0.60, 1.50, 2.20, 3.40, 4.70, and 5.90. The also studied a Ti-Al alloy based on titanium iodide. They discovered that at temperatures up to 1,373, alloys with $C_{Al} \leq 0.6\%$ (by weight) are generally less heat resistant than titanium. Alloys with $C_{Al} > 0.6\%$ (by weight), on the other hand, have an elevated oxidation resistance. Above 1,373 K, all of the alloys studied (with the exception of $C_{Al} = 3.4\%$ by weight) turned out to be more heat resistant than titanium in the initial period of oxidation. As the oxidation process continues, however, the alloys were found to become less heat resistant than titanium. The kinetics of the overall process of the oxidation of Ti-Al alloys at temperatures between 1,173 and 1,423 K and the kinetics of scale formation (which occurs at 1,273 K) were determined to be essentially subject to an Evens equation. The growth of a diffusion layer of oxygen was found to follow a close-to-parabolic law. The authors further concluded that alloying titanium with aluminum increases the duration and expands the temperature bounds of the effect of Evens' law. Finally, the authors observed that as the surface zone of the metal of oxidized alloy specimens became depleted of aluminum (after 3 hours), the layer of scale close to the outer surface became enriched with aluminum. Figures 5, tables 4; references 20: 16 Russian, 4 Western.

The Effect of Direct Electric Current on the Process of the Hydration Aging of $YBa_2Cu_3O_y$ Ceramic

917M0186G Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 64 No 1, Feb 91 (manuscript received 6 Apr 90) pp 331-334

[Article by P.A. Tikhonov, M.V. Kalinina, A.V. Komarov, V.P. Popov, and V.B. Glushkova]

UDC 537.311.312:546.641'56'431

[Abstract] The superconductivity of high-temperature superconductors is known to deteriorate to some degree when they undergo a chemical reaction with the environment. The literature contains information to the effect that a direct electric current with a density of $> 1 \text{ A/cm}^2$ slows the aging process of $YBa_2Cu_3O_y$ ceramic, whereas currents with a density half that amount or less have no such effect. In view of the fact that the literature does not contain any systematic data on this subject, the authors of the study reported herein examined the characteristic course of the process of hydration aging of $YBa_2Cu_3O_y$ ceramic. They then proceeded to focus their attention on the effect of direct currents (especially high-density currents, i.e., $I > 1 \text{ A/cm}^2$) on the process of hydration aging. They determined that the hydration aging process may be broken down into three characteristic stages: 1) a relatively slow change in the specimen's specific electric resistance (this stage lasts from 40 to 50 minutes); 2) a sharp increase in specific resistance during the time interval from 60 to 100 minutes; and 3) a stage of a slower but progressive increase in the specimen's specific resistance (that begins after 100 minutes and lasts several hours). In the second part of their study, the authors aged $YBa_2Cu_3O_y$ ceramic in an atmosphere of saturated steam at a temperature of $333 \pm 5 \text{ K}$. A current with a density of 2.32 A/cm^2 was passed through the ceramic for the first 13 hours. The current was then decreased sharply to $6.23 \times 10^{-2} \text{ A/cm}^2$. An intensive process of hydration aging of the test material began soon thereafter. For 2 hours, the specific resistance changed only slightly. It then began to increase sharply. This 2-hour period was interpreted as being an "induction" period. The experiment results led the authors to hypothesize that a current density of $\geq 2.3 \text{ A/cm}^2$ could virtually halt the process of the deterioration of a high-temperature superconductor's electrical properties. The authors further determined that if the current density does not reach the critical value (in this case, 2.3 A/cm^2), the rate of the hydration process decreases. The process still continues slowly over time, however. In tests conducted, the electrical resistance of a specimen held for 88 hours increased by a factor of more than 30. The results obtained were in good agreement with the authors' original hypothesis that processes of electrolytic or thermal dehydration of specimens of HTSC occur in parallel with hydration processes and that there is definite equilibrium between these opposing processes. Figures 3; references 9: 6 Russian, 3 Western.

The Chemical Degradation of Bismuth-Containing High-Temperature Superconductive Ceramic

927M0001H Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 57 No 7, Jul 91 (manuscript received 28 Aug 90) pp 705-707

[Article by S.A. Nedilko, M.N. Volovik, and N.V. Antonova, Kiev University]

UDC 621.315.612+546.87

[Abstract] Because research on the chemical degradation of bismuth oxide-based high-temperature superconductors [HTSC] has been extremely limited, the authors of the study reported herein examined the degradation of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ under the effect of water and carbon dioxide. They also examined the effect of selected chemical reagents on the said HTSC. The study ceramics were produced by two methods, i.e. by coprecipitation of strontium, calcium, and copper by a solution of oxalic acid followed by calcining of the resultant charge and the addition of corresponding amounts of bismuth oxides and by the ceramic technology of sintering bismuth and copper oxides with calcium and strontium peroxides. The specimens produced by coprecipitation were found to have a tetragonal lattice with the parameters $a = 0.3823 \pm 0.0005$ nm and $c = 3.081 \pm 0.002$ nm. The specimens obtained based on ceramic technology were found to have a virtually crystalline structure and crystal lattice parameters. Studies of the reaction of the said HTSC and solutions of sodium hydroxide and sulfuric, nitric, hydrochloric, and acetic acids reveals that all of them completely destroy the test specimens' superconductive properties. The degradation studies performed indicated that the rate of destruction of the HTSC phase varies in the following series: $\text{HNO}_3 > \text{HCl} > \text{H}_2\text{SO}_4 > \text{CH}_3\text{COOH} > \text{NaOH}$. The loss of the superconductive properties of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ in the aforesaid solutions was found to be linked to the dissolution and liquid-phase transition of the individual ions or all of the component parts of the HTSC materials. The test results were found to be in good agreement with results of a study of the degradation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. The degradation results presented apply to the specimens obtained by coprecipitation. The specimens obtained based on ceramic technology were found to be less resistant to the effect of water, carbon dioxide, and the other chemicals studied. The authors attributed this fact to the great inhomogeneity of the ceramics produced by sintering oxides. Figures 2; references 8: 3 Russian, 5 Western.

**A Study of Shear Stress During the
Decomposition of Peroxides Under High Pressure**

927M0004E Ivanovo IZVESTIYA VYSSHIKH
UCHEBNYKH ZAVEDENIY: KHIMIYA I
KHIMICHESKAYA TEKHNLOGIYA in Russian
Vol 34 No 5, May 91 (manuscript received 26 Feb 90)
pp 105-110

[Article by A.I. Dyatlov and V.S. Abramov, Department
of Food Production Technology, All-Union Food
Industry Correspondence Institute]

UDC 541.427:547.514:539.383

[Abstract] In a continuation of their previous research on the decomposition of various peroxides, the authors of the study reported herein examine the kinetics of the decomposition of four different peroxides and the interconnection between decomposition and shear stress during shear deformation under high pressure. Specifically, the authors focus their attention on peroxides of benzoyl, lauryl, cumyl, and disuccinic acid. Peroxides with a purity of at least 98% were used. The experiments were performed on a modified Bridgman anvil-type unit. The amount of nondecomposed peroxide was determined by iodometric titration. The experiments performed demonstrated that under shear deformation and high pressure, the peroxides studied all decompose under conditions of plastic flow. The minimal shear stress initiating plastic flow was found to differ for each of the different peroxides under one and the same deformation conditions. The authors hypothesized that this fact is, in all likelihood, attributable to the nature of the substituents at the -O-O- grouping. They substantiated their hypothesis by demonstrating a correlation between the rate constants of the decompositions of the peroxides under high pressure and shear deformation and the minimal shear stress. They concluded that the four peroxides studied may be ranked as follows with respect to resistance to breaking at the -O-O- bond in a mechanical stress field: peroxide of disuccinic acid > lauryl peroxide > cumyl peroxide > benzoyl peroxide. Figures 3, table 1; references 5: 4 Russian, 1 Western.

The Molecular Structure of $C_{14}H_{21}O_5Ca(NO_3)_2$ in Its Crystalline State and the Characteristic Features of the Structure of Complexes of Calcium Salts With Benzo-15-Crown-5 in Solutions

927M0013A Moscow KOORDINATSIONNAYA
KHIMIYA in Russian Vol 17 No 6, Jun 91 (manuscript
received 20 Jun 89) pp 762-769

[Article by V.V. Tkachev, O.A. Rayevskiy, V.P. Kazachenko, V.Ye. Zubareva, and L.O. Atovmyan, Chemical Physics Institute, USSR Academy of Sciences, Institute of Physiologically Active Substances, USSR Academy of Sciences, and Chemistry Institute, SSRM Academy of Sciences]

UDC 548.737:543.422.547.898

[Abstract] The membranotropic and psychotropic activity of benzo-15-crown-5 [B15C5] related to its ability to form complexes with "biometals" is well known. In view of this activity, the authors of the study reported herein decided to study the structure of complexes of B15C5 with alkaline and alkaline earth metals. Specifically, they conducted an x-ray crystallographic study of the complex $C_{14}H_{21}O_5Ca(NO_3)_2$. The crystals were determined to be monoclinic with a limiting boundary of $P2_1/a$ and with the following crystal parameters: $a = 14.208(3)$, $b = 18.154(3)$, and $c = 8.264(2)$ angstroms and $\beta = 115.08(5)^\circ$. All five oxygen atoms of the macrocycle and four oxygen atoms of the two NO_3 groups were found to participate in the complex $C_{14}H_{21}O_5Ca(NO_3)_2$ in coordination with the calcium atom. Both NO_3 groups were determined to be located on one side of the macrocycle. The coordination polyhedron was determined to be a highly distorted single-cap square prism. X-ray crystallographic and infrared spectroscopy studies performed on the complex $C_{14}H_{21}O_5Ca(NO_3)_2$ in a solid state and in solution revealed that equilibrium is achieved in 1:1 and 1:2 complexes of calcium nitrate and thiocyanate with B15C5. The studies also demonstrated that conformation of the ligand in a 1:1 complex in solution does not coincide with conformation of the ligand in an analogous complex in a crystal state. Figure 1, tables 3; references 23: 7 Russian, 16 Western.

The Crystalline Structure of $Bi(O_2CCH_3)_3$

927M0014A Moscow KOORDINATSIONNAYA
KHIMIYA in Russian Vol 17 No 7, Jul 91 (manuscript
received 13 Nov 90) pp 909-913

[Article by S.I. Troyanov and A.P. Pisarevskiy, Moscow State University imeni M.V. Lomonosov]

UDC 546.87'292-162.2

[Abstract] The authors of the study reported herein crystallized $Bi(III)$ in a monoclinic system of the cubic structure $P2_1/c$; $a = 12.082(4)$, $b = 10.858(3)$, and $c = 7.348(1)$ angstroms; $\beta = 10.5.83(2)^\circ$; and $Z = 4$ with a

limiting boundary of $P2_1/c$. All of the acetate groups had bidentate bonds with the bismuth atom. Each, however, played a different role in the formation of additional bridge bonds by which the $Bi(O_2CCH_3)_3$ molecules were combined into layers parallel to the plane (yOz) . The coordination polyhedron of the Bi atom was determined to be an incorrect nine-vertex body, all of whose 14 faces are triangular. The undivided electron pair of the Bi atom was discussed in relation to previous discussion of it in the literature and was found to manifest stereochemical activity. The authors conclude by analyzing the values of the interatomic distances and valence angles in the structure $Bi(O_2CCH_3)_3$ as compared with the distances obtained in previously researched structures. This analysis led the authors to conclude that the following correlation exists in all of the cases considered, including in the case of bismuth acetate: The greater the Bi-O distance, the smaller the respective C-O distance. Their analysis of valence angle data led the authors to further conclude that no anomalies exist in the case of bismuth acetate. Figure 1, tables 3; references 10: 3 Russian, 7 Western.

Complex Compounds of Platinum (II) With Derivatives of 2-Acyl-2-Imidazoline-3-Oxide

927M0014B Moscow KOORDINATSIONNAYA
KHIMIYA in Russian Vol 17 No 7, Jul 91 (manuscript
received 7 Aug 90) pp 950-953

[Article by L.F. Krylova, N.V. Dulepova, I.A. Seregina, L.B. Volodarskiy, Novosibirsk State University imeni Lenin Komsomol]

UDC 546.92:541.49+547.288

[Abstract] The authors of the study reported herein synthesized cyclic complexes containing both one and two molecules of a bidentate ligand. They did so by reacting K_2PtCl_4 with 2-benzoyl-2-imidazoline-3-oxides. A total of eight compounds were formed (the reaction mixtures and conditions are described in detail) and subjected to infrared and ultraviolet spectroscopy to confirm their structure. Six of the eight compounds studied were found to possess an additional absorption band in the range from 370 to 415 nm that is not present in the spectra of free ligands. This band was taken as proof of the bidentate coordination of derivatives of 2-imidazoline-3-oxide. The IR spectra of the first and second compounds synthesized were observed to contain a shift of the band $\nu(C=O)$ in a lower frequency range than is the case in the spectrum of LH. This was taken as confirmation of the bidentate coordination of the ligand in the two compounds. $\nu(C=N)$ and $\delta(H_2O)$ oscillations were also observed in this same range. The authors classified the band at $1,705\text{ cm}^{-1}$ in the spectra of the first two compounds synthesized as a $\nu(C=O)$ band of coordinated acetone. The IR spectrum of the seventh compound synthesized and studied was found to contain two $\nu(C=O)$ bands. One (at $1,675\text{ cm}^{-1}$) corresponds to a noncoordinated group, whereas the other (at $1,660\text{ cm}^{-1}$)

corresponds to a coordinated group. Only one band (at $1,660\text{ cm}^{-1}$) corresponding to coordinated carbonyl was observed in the IR spectrum of compound No. 7. Table 1; references 2 (Russian).

The Direct Synthesis of Ethylenediamine Complexes of Cu(II) From Copper Powder

927M0014C Moscow KOORDINATSIONNAYA
KHIMIYA in Russian Vol 17 No 7, Jul 91 (manuscript
received 09 Jul 90) pp 968-970

[Article by O.Yu. Vasilyeva and V.N. Kokozev, Kiev
State University imeni T.G. Shevchenko]

UDC 546.56-121+547.233.1

[Abstract] Using metal powders is one way of creating low- and no-waste processes of producing the coordination compounds that are enjoying increasing use in different areas of the national economy. In a continuation of the effort to develop suitable methods for the direct synthesis of such powders, the authors of the study reported herein studied the direct synthesis of ethylenediamine complexes of copper (II) from copper powder. The preparation of the starting substances, experiment methodology, and procedures used to analyze the compounds synthesized were analogous to those described elsewhere. Six complexes were produced: CuEnI_2 , CuEn_2I_2 , CuEn_3I_2 , $\text{CuEn}(\text{NO}_3)_2$, $\text{CuEn}_2(\text{NO}_3)_2$, and $\text{CuEn}_3(\text{NO}_3)_2$. The molar ratios of the starting components and composition of the compounds formed are detailed in table form, as are the results of an x-ray phase analysis of the compounds synthesized. Also presented are data on the infrared spectra, thermogravimetric analysis, and magnetic moments of several of the compounds listed above. Tables 2; references 3 (Russian).

An Investigation of the Adduct Formation of a Lutetium Ion and Its Complexes With 18-Crown-6 and Diaza-18-Crown-6

927M0014D Moscow KOORDINATSIONNAYA
KHIMIYA in Russian Vol 17 No 7, Jul 91 (manuscript
received 7 May 90) pp 994-998

[Article by V.S. Khomenko and L.I. Krasovskaya,
Physics Institute imeni B.I. Stepanov, Belorussian
Academy of Sciences]

UDC 543.51

[Abstract] Interest in adducts of rare earth elements with crown ethers has recently increased in view of their possible use as probes in chemistry and biology. In view

of this fact, the authors of the study reported herein examined the adduct formation of ions of lutetium (III) with 18-crown-6 and diaza-18-crown-6. In accordance with a method described elsewhere, they synthesized the following adducts: $\text{Lu}(\text{NO}_3)_3 \cdot 18\text{-crown-6}$, $\text{Lu}(\text{C}_3\text{F}_7\text{COO})_3 \cdot \text{diaza-18-crown-6} \cdot 6\text{H}_2\text{O}$, $\text{Lu}(\text{BTFA})_3 \cdot 18\text{-crown-6} \cdot 2\text{H}_2\text{O}$, and $\text{Lu}(\text{BTFA})_3 \cdot \text{diaza-18-crown-6} \cdot 2\text{H}_2\text{O}$, where BTFA is benzoyltrifluoroacetone. They demonstrated the role of the hydrogen bond in the formation of the adduct $\text{Lu}(\text{C}_3\text{F}_7\text{COO})_3 \cdot \text{diaza-18-crown-6}$, which manifests a tendency toward sublimation. They further demonstrated that the complexing of macrocyclic polyesters of rare earth elements to tris-benzoylacetate results in their improved screening from the effect of the solvent. The authors subjecting the complexes synthesized to mass spectrometry and paramagnetic resonance studies. By so doing, they were able to establish the routes of the said complexes' decomposition under the effects of electronic impact and to obtain data on the complexes' contents of various elements, the chemical shifts in their PMR spectra, and the ion peaks in their mass spectra. These data are presented in table form. Tables 3; references 10: 7 Russian, 3 Western.

The Synthesis, Structure, and Properties of Pr and Sm Proton Conductor-Sulfosalicylates With the Composition $\text{M}(\text{OHCOOH}(\text{C}_6\text{H}_3\text{SO}_3)_3 \cdot 9\text{H}_2\text{O})$

927M0014E Moscow KOORDINATSIONNAYA
KHIMIYA in Russian Vol 17 No 7, Jul 91 (manuscript
received 13 Apr 90) pp 999-1004

[Article by Z.G. Aliyev, T.A. Baranova, L.O. Atovmyan,
S.B. Pirkes, Ye.S. Nimon, and A.M. Mikhaylova, Chem-
ical Physics Institute imeni N.N. Semenova, USSR
Academy of Sciences, and Chemistry Scientific Research
Institute of Saratov State University]

UDC 546.659-386.02-546.656-386.02:539.261

[Abstract] The authors of the study reported herein synthesized and studied the structure and properties of sulfosalicylates with the composition $\text{M}(\text{C}_6\text{H}_3\text{OHCOOH}(\text{SO}_3)_3 \cdot 9\text{H}_2\text{O})$, where $\text{M} = \text{Pr}$ (compound 1) and Sm (compound 2). The two compounds were studied by a variety of methods, including infrared spectroscopy, thermal analysis, and x-ray crystallographic analysis. Special attention was paid to the electric conduction of the compounds synthesized. The x-ray crystallographic studies revealed that the structural units of the crystals investigated are complex cations i.e., $[\text{M}(\text{C}_6\text{H}_3\text{OHCOOH}(\text{SO}_3)_3(\text{H}_2\text{O})_8)]^{2+}$; anions of sulfosalicylic acid, i.e., $(\text{C}_6\text{H}_3\text{OHCOOH}(\text{SO}_3)_3)^-$; and crystallization molecules of water. Crystals of praseodymium sulfosalicylate were found to have the following crystal

parameters: $a = 19.833(3)$, $b = 12.571(2)$, and $c = 7.288(2)$ angstroms; $\alpha = 103.50(1)$, $\beta = 100.67(1)$, and $\gamma = 75.66(1)^\circ$; and $Z = 2$. Crystals of samarium sulfosalicylate were found to have the following crystal parameters: $a = 19.804(6)$, $b = 12.543(3)$, and $c = 7.254(1)$ angstroms; $\alpha = 103.36(2)$, $\beta = 100.54(2)$, and $\gamma = 75.51(2)^\circ$; and $Z = 2$. Crystals of both compounds were found to have a limiting boundary of P1. The coordinates of the atoms in a crystal of compound 2 are presented in table form, as are the frequencies of the maxima of selected principal absorption bands of 5-sulfosalicylic acid and 5-sulfosalicylates of rare earth elements. At 25° , praseodymium sulfosalicylate was found to have a conductivity of 5.3×10^{-2} S/m when determined by the direct-current method (vs. 5.2×10^{-2} S/m when determined by the pulse method). Samarium sulfosalicylate was found to have a conductivity of 3.5×10^{-2} S/m by the direct-current method. The electronic component of conduction for the two compounds studied was also determined. Its average value was found to be between 8×10^{-7} and 1×10^{-6} S/m. Because the electronic component of conduction was thus found to be negligible, they were deemed proton conductors. On the basis of the totality of their data on the structure and properties of the compounds they examined, the authors concluded that proton transport in the compounds synthesized likely occurs in a double infinite layer along a system of hydrogen bonds. Figures 2, tables 2; references: 6 Russian, 1 Western.

The Crystalline Structure of $(H_3O)_2(UO_2)_{12}(CrO_4)_{13} \cdot 12HCON(CH_3)_2$

927M0014F Moscow KOORDINATSIONNAYA
KHIMIYA in Russian Vol 17 No 7, Jul 91 (manuscript
received 14 Mar 90) pp 1005-1008

[Article by V.A. Blatov, L.B. Serezhkina, and V.N. Serezhkin, Samarskiy State University]

UDC 548.736

[Abstract] Only one complex of uranyl chromate with N,N-dimethylformamide [DMF] was known until now. While studying the reaction occurring in the system UO_2CrO_4 -DMF- H_2O , the authors of the study reported herein obtained the compound $H_2(UO_2)_{12}(CrO_4)_{13} \cdot 12DMF \cdot 2H_2O$. Because of the unusual relationship between the uranyl and chromate ions in it, the authors decided to study this new compound's crystalline structure. They did so on a CAD-4-SDP-55/t autodiffractometer system. The new compound was found to crystallize in a cubic system and have a skeletal structure of $[(UO_2)_{12}(CrO_4)_{13} \cdot 12DMF]^2$ complex groupings. The new compound was deemed the first representative of the crystalline chemistry group $A_{12}K_9T_4M_{12}$ of uranyl complexes (with A designating UO_2). Figure 1, tables 2; references 3: 2 Russian, 1 Western.

Industrial Research on Oil Additives and Transition to Market Economy

927C0016A Moscow *KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL* in Russian No 5, May 91 pp 2-4

[Article by A. S. Zhurba, G. G. Burlaka and A. A. Pravikov, 'Masma' Scientific Industrial Association; FID VOIR [expansion unknown]]

UDC 658.657.1:665.7.038.002.3

[Abstract] Transition to a market-driven economy and the need to conserve and extend natural petroleum resources has made it an imperative of Soviet economic planning to develop a strong industrial research base dedicated to oil additives. The dismal failure of centralized command-type economy in meeting the need for oil additives in the USSR made obvious the need for a responsible approach based on cost-effectiveness and self-financing. Accordingly, plans have been laid for the creation of specialized research facilities based on Western models, whose operations are driven by competitive market forces that provide maximum incentives for the enterprise and individual workers. Tables ; references 19 (Russian).

Trends in Automobile Lubrication Engineering

927C0016B Moscow *KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL* in Russian No 5, May 91 pp 5-6

[Article by A. R. Kravchenko, Z. P. Melnik and L. P. Pugacheva, 'Masma' Scientific Industrial Association]

UDC 621.892.5

[Abstract] In recent years automobile durability has been significantly improved by the development of lithium complex-, aluminum complex- and polyurea-based lubricants. These are gradually replacing the more conventional lithium-, calcium- and sodium-based lubricants used to date. The development of these novel lubricants is particularly advanced in Japan and the USA, where new formulations—many incorporating MoS_2 —meet the required specifications for a wide range of speeds, loads and temperatures. Yet another important criterion is that the new lubricants meet the more stringent environmental and health safety standards now in force. Figures 2; tables 3; references 15: 3 Russian, 12 Western.

Aqueous Oil-Based Film-Forming Corrosion Inhibitors

927M0016C Moscow *KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL* in Russian No 5, May 91 pp 7-9

[Article by Yu. N. Shekhter, O. V. Vasilenko, T. I. Bogdanova and N. I. Korokh, All-Union Scientific Research Institute of the Petroleum Industry]

UDC 620.197.6

[Abstract] A discussion is presented of the many advantages of aqueous oil-based film-forming corrosion inhibitors as agents deserving greater developmental efforts and wider use. Among the key considerations making the colloidal aqueous solutions, emulsions and dispersions desirable inhibitors are the fact that they do not pollute the environment, pose no risk of fire or explosion during manufacture or use, and have seemingly universal applicability on various metal surfaces under various operational conditions. Mathematical modeling and computer simulation have been utilized in the formulation of a novel Soviet corrosion inhibitor NG-224 (Akamin) which meets the performance criteria of competitive Western inhibitors in this class of formulations. Figures 3; tables 1; references 6 (Russian).

Computers and Robotics in Raw Material Handling and Production of Lubricating Oils

927C0016D Moscow *KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL* in Russian No 5, May 91 p 9-11

[Article by A. N. Rodnikov, Central Scientific Research Institute of Technical Information and Materials Supply]

UDC

[681.3+621.865.8.004.14]:658.78.06:621.892.002.3

[Abstract] An analysis was conducted on the utilization of computers and robotics in raw materials handling and production and delivery of lubricating oils by Western firms in order to derive information relevant to Soviet industry. The cases under study were represented by Italoil (Italy), SLEA (France) and the Esso plant in Hamburg. The data demonstrated the benefits of LANs, robotics and informatics in the efficient handling and distribution of resources and management of production processes. In the final analysis, the latter translates into greater profitability and conservation of raw materials and energy resources from which the Soviet lubricating oil industry could benefit. References 4: 2 Russian, 2 Western.

Removal of Electrolyte Solutions from Metal Surfaces by Corrosion-Inhibiting Oils: Mechanism of Action

927C0016E Moscow *KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL* in Russian No 5, May 91 pp 11-13

[Article by G. T. Vigant, A. B. Englin, N. N. Zakharova and I. V. Klimyuk, State Scientific Research Institute of Chemistry]

UDC 621.892.86:620.197.3

[Abstract] Displacement of corrosive electrolyte solutions from metal surfaces by corrosion-inhibiting oils

was tested by conventional and electrochemical techniques. The following effectiveness ranking of common Soviet agents was obtained: KAP-25 (alkenyl succinic acid) > Sab'Ca (calcium alkyl benzosulfonate) > SIM (alkenyl succinamide urea). The most efficient agent, KAP-25, was also compared against different corrosives yielding the following series: $\text{HBr} > \text{HCl} > \text{H}_2\text{SO}_4 > \text{HNO}_3$. Comparison with data on the efficacy of alcohols, fatty acids and ureides of alkenyldicarboxylic acids showed that efficiency of the inhibitors is dependent on diffusion factors and relative energies of interaction with metal surface and corrosive electrolytes. Figures 1; tables 3; references 15: 14 Russian, 1 Western.

Solvent Effects on Deasphalting and Detarring of Heavy Oils

927C0016F Moscow *KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL* in Russian No 5, May 91 pp 26-27

[Article by R. A. Galimov and V. V. Abushayeva, Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Branch, USSR Academy of Sciences]

UDC 665.668:665.662.3

[Abstract] Trials were conducted to determine optimum solvent systems for asphalt and tar recovery from heavy oil (960 kg/m³ density; 3.64% sulfur content). The studies were conducted with hexane, isopropanol, and hexane:isopropanol combinations at room temperature. The results demonstrated that the most efficient system for elimination of tar and asphalt was secured with a binary hexane:isopropanol = 3:1 solvent and a solvent:heavy oil ratio of 1:1.5. Figures 2; tables 1; references 12: 9 Russian, 3 Western.

Impact of Zeolite Silicon Modulus on Catalytic Processing of Coking Distillates

927M0016G Moscow *KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL* in Russian No 5, May 91 pp 28

[Article by Yu. A. Karatetskiy, V. G. Karakasehv and A. Z. Dorogochinskiy, Groznyy Petroleum Institute imeni M. D. Millionshchikov]

UDC 665.656.097.3

[Abstract] An analysis was conducted on the impact of the silicon modulus of SVK zeolite on catalytic processing of the 40-320degC distillate fraction obtained by slow coking. The results demonstrated that the ratio of aromatic benzene and olefin components in the products could be controlled by the zeolyte employed in the process. At 500-650degC and a zeolite with a silicon modulus of 26 the yield of the benzene fraction was 36.9% by wt. and of the olefin fraction 15.8%. Zeolites with a silicon modulus of 190 provided respective yields of 21.5 and 41.5% of the two fractions. Figures 2; tables 1; references 2 (Russian).

Rapid Lead Determination in Ethyl Gasoline by X-Ray Radiometry

927C0016H Moscow *KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL* in Russian No 5, May 91 pp 33

[Article by A. I. Razdorskiy, S. I. Gorelkinskaya and T. V. Arbuzova, Kazakh State University imeni S. M. Kirov, Novo-Ufa Refinery]

UDC 621.386.1:543.422.8:543.5

[Abstract] A rapid method for lead determination in ethyl gasoline was developed, based on x-ray radiometry. Studies conducted with an PPL-103 radiometer provided with a cadmium-109 source for inducing lead fluorescence reduced the analysis to 10 min. This represents a 25- to 35-fold reduction in the time required by conventional methods. In addition, the analytical precision of this method was 2- to 4-fold greater and the sensitivity was 0.01 g/dm³ with a 95% confidence level, exceeding 2-fold the sensitivity of the conventional method (0.02 g/dm³). References 1 (Russian).

The Effect of Monoethanolamine Derivatives on the Formation of Epoxy Resin Composites

927M0003I Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 57 No 8, Aug 91 (manuscript received 19 Apr 90) pp 889-894

[Article by K.V. Zapunnaya, T.S. Khramova, G.M. Semenovich, Ye.P. Levanova, and Yu.S. Lipatov, Institute of High-Molecular Compounds, UkSSR Academy of Sciences, Kiev]

UDC 678.686:543.425

[Abstract] The authors of the study reported herein examined the effect of monoethanolamine derivatives on the process of the solidification of epoxy resin composites. Specifically, they studied epoxy resin composites based on ED-20 diphenylolpropane oligomer, DEG-1 aliphatic diethylolpropane oligomer, and modifying additives of SKD-GTR low-molecular weight butadiene rubber under the effect of aminoethylvinyl ether and its sulfur-containing oligomer. The said compounds were subjected to nuclear magnetic resonance and infrared spectroscopy studies on a BS-467 spectrometer (at temperatures of 313 and 343 K) and a UR-20 spectrophotometer. A comparative analysis of the kinetic data obtained indicated that the monomer aminoethylvinyl ether has a higher reactivity than its sulfur-containing oligomer in reactions with epoxy groups. The effective constants of the rate of conversion of the epoxy cycles of the epoxy oligomers and double bonds of the rubber were determined. In the presence of sulfur additives, vulcanization of butadiene rubber occurs at a temperature between 313 and 343 K, which is 80 to 100 K below the conventional conditions for vulcanization of rubber by sulfur. Vinyl ether of monoethanolamine was thus found to act as an accelerator of the vulcanization of rubber by elemental sulfur, a process that begins at a specified concentration of hydrogen bonds between the amino groups and sulfur. The main result of the reactions occurring was the formation of a continuous reticular structure formed by two lattices, i.e., the vulcanization lattice of rubber and an epoxy lattice, that may be linked by sparse chemical bonds with one another. The data obtained led the authors to conclude that the structure of the composites examined represents a hybrid matrix with inclusions of a rubber phase. In this respect, it is analogous to the structure of interpenetrating polymer lattices in which phase separation during the course of solidification occurs in accordance with a nucleation mechanism. Figures 5; references 8 (Russian).

Effect of Thickness and Diameter of Filaments in Rubber Cord Fabric on Fatigue Life of Light Duty Radial Tire Casings

927M0007A Moscow KAUCHUK I REZINA in Russian No 5, May 91 pp 10-12

[Article by V. Z. Gandelsman, V. Ya. Melnikov, I. M. Chernyaga, and I. L. Shmurak]

UDC678.01:539.4.014:677.46.061.4.3

[Abstract] Fissures were observed to form at the textile cord-rubber interface, and in the rubber between the filaments of light duty, single ply, radial tire casings during road and bench testing, as well as in service. These fissures apparently result from the growth of micro-defects originating during formation of rubber-cord systems and remaining intact during vulcanization, and also from low fatigue resistance in the rubber and low strength of the rubber-cord adhesion bond. Lowering the deformation load on the inter-filament rubber during the production process, and during service could diminish the length and quantity of the fissures and thereby increase the fatigue life of the tire casing. In the present work the effect of the design parameters of cut cord (thickness and diameter of filaments) and their tolerances on the state of deformation of inter-filament rubber during tire production and during service was examined. Optimization of the coefficient of deformation overloading of the inter-filament rubber for a given low reserve static strength limit makes it possible to raise the fatigue life of light duty tire casings. Figures 2; references 5 (Russian).

Method for Estimating Service Capacity of Quarry Tires

927M0007B Moscow KAUCHUK I REZINA in Russian No 5, May 91 pp 12-13

[Article by V. M. Smelyanskiy, A. G. Smirnov, L. B. Nikitina, and Ye. A. Dzyura]

UDC678.4.065-181.2.001.891.57

[Abstract] Tire cost occupies a greater and greater share of the cost of transporting earth and ore, especially as the carrying capacity of vehicles keeps increasing (75-180 tons). To lower these costs, improved, extra large size tires capable of carrying greater loads at higher speeds and over greater distances must be developed. This, however, results in higher operating temperature, which then becomes a critical factor determining the longevity of quarry tires operating under extreme conditions. Since the heat resistance of tire materials is limited, and the operating temperatures of extra large sized tires often exceeds design specifications, tire failure, even on short runs, is possible. Therefore, to have quarry tires function without failure, it is necessary to determine the threshold load and speed conditions, especially in hot climatic conditions. In the present work a low cost, rapid method for testing prospective quarry tires based on idealized models was developed. Figure 1; references 9: 8 Russian, 1 Western.

Features of Fatigue Properties of Tread Rubbers for Various Automobile Tires

927M0007C Moscow KAUCHUK I REZINA in Russian No 5, May 91 pp 26-28

[Article by M. K. Khromov, N. L. Sakhnovskiy, T. A. Koroleva, and L. I. Stepanova]

UDC678.063.5.002.612:678.04

[Abstract] Since automobile tires are used over a variety of road conditions, tread rubbers must be resistant to wear and withstand damage from uneven pavement with no cracks in the tread pattern, and at the same time have low rolling loss and good traction. These requirements can be met by selecting the proper rubber composition. In the present work a study was made of the features of fatigue-strength properties of rubbers for various tire types and their effects on rubber behavior while in service. Physical mechanical properties of four grades of synthetic tread rubber used in vehicles, trucks, and buses are presented. In evaluating service quality, it is possible to use fatigue-strength figures determined after 10^3 to 10^6 cycles. Figure 1; references 6 (Russian).

Effect of Functional Groups of Adhesive and Rubber Modifiers on Degree of Bonding at Adhesive-Rubber Interface

927M0007D Moscow KAUCHUK I REZINA in Russian No 5, May 91 pp 28-30

[Article by I. L. Shmurak]

UDC678.063.678.029.4

[Abstract] Bond strength in rubber-cord systems and fatigue life of rubber-cord components are determined by the capability of adhesives and rubber modifiers to react interfacially at the contact zone, and by their effects on the mechanical properties of boundary areas. To improve adhesives and modifiers, a study was made of the effects of an adhesive on its co-vulcanization with rubber mixes, and that of an adhesive and modifier on the mechanical properties on bonding and mechanical properties in the boundary region of the adhesive. Adhesive activity was judged by electron-donor capability; co-vulcanization of adhesive with rubber mixes, by the quantity of adhesive polymer attached to the rubber; degree of bonding, by the degree of swelling in benzene and tensile strength. The results show that the composition of the adhesive and modifying groups in the rubber mix may be optimized by regulating the activity and concentration of vinyl pyridine linkages in the adhesive and in the rubber modifier. The degree of adhesive bonding and the cord-to-rubber bond strength increase with the electron-donor capability of the adhesive polymer. Figures 4; references 8 (Russian).

Polychlorobutadienes with Reactive Functional Groups - Adhesives for Hot Bonding Elastomers to Metals

927M0007E Moscow KAUCHUK I REZINA in Russian No 5, May 91 pp 34-35

[Article by G. A. Niazashvili, O. V. Lakiza, and N. V. Klementova]

UDC678.644:620.179.4

[Abstract] Polymers used for hot bonding elastomers to metals must have adsorption and diffusion properties as well as high reactivity to various substrates at high temperatures. For elastomer-metal components to have reliable adhesion bonds, the reaction rates of the adhesive with the metal surface and co-vulcanization rate with the elastomer must be equal to or higher than the cross-linking rate of the elastomer. These properties are manifested in polytrichlorobutadiene adhesives having various functional groups. The strength of the adhesion bond has an extremal relationship with the ratio of functional groups in the macromolecules of these polymers. Optimal adhesion properties depends on the type of functional group. Thus, when bonding rubber or cast polyurethanes to metals, polytrichlorobutadiene manifests optimal adhesion with 4-19 (mole) percent cyanoacryl, 5-25 percent peroxide, and 1-15 percent carboxyl groups present in the molecule. Other aspects of the adhesional properties of polytrichlorobutadiene having various function groups are discussed. References 3 (Russian).

Study of Effect of Wax Composition on Atmospheric Cracking of Radial Tire Sidewalls

927M0007F Moscow KAUCHUK I REZINA in Russian No 5, May 91 pp 36-39

[Article by S. M. Kavun, I. A. Mobenkova, and K. V. Alekseyeva]

UDC678.762.3

[Abstract] Increasing the resistance of radial tire sidewalls to atmospheric cracking is one of the most important trends in raising the reliability, quality, and competitiveness of domestic tires, as well as making them more suitable for re-treading. Recommendations on the compositions of components in tire protecting systems must include the possibility of compounding of severe factors, e.g. solar radiation which causes sidewall overheating, the presence of ozone, wind, and rain which accelerate leaching and evaporation of stabilizers. In the present work both laboratory and road tests were conducted to determine the effectiveness of various waxes to preventing sidewall cracking. The new domestically produced wax ZB-P was found to be superior to ZV-1 and Paralayt 17, approaching that of Antilyux 660. References 9: 5 Russian, 4 Western.

**Reaction of Sulfenamide Accelerators with Sulfur
Under Temperature Conditions Simulating
Vulcanization**

927M0007G Moscow *KAUCHUK I REZINA in Russian*
No 5, May 91 pp 39-40

[Article by D. V. Tarasov, I. I. Vishnyakov, and B. S. Grishin]

UDC678.762.3

[Abstract] Modern concepts of chemical processes which take place during the induction period of rubber vulcanization and which determine the effectiveness of polymer cross-linking are well established. Research has been published on the chemical conversions and kinetics

of rubber ingredients during the induction period, as well as the mechanisms of these processes. However, this research was conducted chiefly using tradition methods of chemical analysis, and limiting identification of all possible chemical conversion products. Instrumental analysis has developed to the stage where these limitations have been decreased. In the present work a study was made of the thermochemical processes taking place under temperature conditions approaching vulcanization with sulfenamides M and Ts, and their mixtures with sulfur. Experiments conducted using chromatomass spectrometry and thermoanalysis demonstrated for the first time the possibility of the formation of high molecular weight polysulfides in the above reactions. Further study to clarify the role of these polysulfides is recommended. Figures 2; references 3: 1 Russian, 2 Western.