JPRS-UCH-90-012
30 NOVEMBER 1990

FOREIGN
BROADCAST
INFORMATION
SERVICE

JPRS Report

Science & Technology

USSR: Chemistry

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL INFORMATION SERVICE
SPRINGFIELD, VA. 22161

Science & Technology

USSR: Chemistry

JPRS-UCH-90-012 CONTENTS *30 November 1990*

ANALYTICAL CHEMISTRY

CHEMICAL INDUSTRY

ELECTROCHEMISTRY

INORGANIC COMPOUNDS

LASER MATERIALS

ORGANOMETALLIC COMPOUNDS

ORGANOPHOSPHOROUS COMPOUNDS

PESTICIDES, HERBICIDES

PETROLEUM, COAL PROCESSING

POLYMERS, RUBBER

RADIATION CHEMISTRY

UDC 543.544

Studying Wine Polymers by Thermochromatography

907M0131A Tbilisi SOOBSHCHENIYA AKADEMII NAUK GRUZINSKOY SSR in Russian Vol 135 No 1, Jul 89 (manuscript received 30 Jun 88) pp 125-128

[Article by I. Sh. Shatirishvili, O. G. Gotsiridze, and G. Sh. Kutateladze, Georgian Agricultural Institute]

[Abstract] Thermochromatography is a new variant of pyrolytic gas chromatography that is used to determine compositions. Separation is carried out in a 25-m x 0.25-mm capillary column. Successive samples are fed into the system prior to the output of the preceding to provide a two-dimensional chromatogram of changes in the composition of decomposition products over a span of time that may be recorded in forward or reverse order. The method, originally developed to study fibers and polymers, was adapted in the present work to study the biopolymer make-up of sediments from four Georgian wines. Figures 2; references 3: 2 Russian, 1 Western.

UDC 543.253:546.77

Adsorption Preconcentration and Detection of Molybdenum in Complex/Compound Form With 8-Oxyquinoline by Using Catalytic BrO_3^- Currents

907M0164A Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 45, No 1, Feb 90 (manuscript received 22 Feb 89) pp 273-278

[Article by V. F. Toropova, Yu. N. Polyakov, I. I. Maltseva, and Ye. Yu. Mikryukova, Kazan State University imeni V. I. Ulyanov-Lenin]

[Abstract] To enhance mercury-detection selectiveness, catalytic currents in the system Mo(VI)—8-oxyquinoline—BrO_3^- were measured with a PU-1 polarograph on a dropping mercury electrode (DME) and on a stationary mercury microelectrode (a drop of silver suspended on a silver contact) in a thermostatically controlled electrolytic cell. A silver chloride electrode served as the comparison electrode. The starting solution Mo(VI) (1 x 10_{-2} M) was prepared from a weighed quantity of chemically pure Na_2MoO_4. The analytical-quality 8-oxyquinoline was sublimation purified, and a 1 x 10_{-2}-M solution of reagent in 0.1 M HCl was prepared. The remaining salt and acid solutions were prepared from chemically pure or analytical-quality preparations in twice-distilled water. It was found that, in $KBrO_3$ solutions in the presence of Mo(VI) with 8-oxyquinoline, two catalytic waves appear on both the DME and the stationary mercury microelectrode: the first at more positive potentials than the Mo(VI) reduction potential and the second at Mo(VI) reduction potentials. It was suggested that the first wave arose from the reduction of Mo)BrO_3-, while the catalytic effect of the second wave was attributed to the activity of the Mo(V)—8- oxyquinoline—BrO_3^-. Using these data, the authors developed two methods of detecting molybdenum in steels and catalysts. Both methods are based on the preadsorption preconcentration of Mo(VI)—8-oxyquinoline on a stationary mercury microelectrode without external polarization by using catalytic BrO_3^- currents in the electrochemical solution step. Figures 4, tables 2; references 8: 7 Russian, 1 Western.

UDC 543.544

TLC Preconcentration of Rare-Earth Elements From Mineral Ores and Neutron-Activation Detection of Their Presence

907M0164B Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 45 No 1, Feb 90 (manuscript received 30 Dec 87) pp 279-288

[Article by V. A. Ryabukhin, M. P. Volynets, and B. F. Myasoyedov, Institute of Geochemistry and Analytical Chemistry imeni V. I. Vernadskiy, USSR Academy of Sciences, Moscow]

[Abstract] A simpler and quicker method of thin-layer chromatogrphic [TLC] preconcentration of rare-earth elements for γ-spectrometric analysis was developed. Mineral ore specimens weighing from 100 to 120 mg were decomposed with a mixture of HF and $HClO_4$, evaporation-concentrated to moist salts, and made into chlorides that were dissolved in 10 ml 2 M HCl. NH_3 hydroxides were precipitated from this solution, separated by filtration on a 20- mm paper disk, rinsed with a solution of NH_4Cl and water, placed in a 10- to 15-ml quartz beaker, and treated first with 1 ml and then with 2 ml of a concentrated 0.1-M HCl solution. The solutions were transferred to another beaker and evaporated to minimal volume. The residue was dissolved in 0.1 M HCl and placed in 10-ml quartz measuring flasks. Solution aliquots corresponding to 10-50 mg of ore were used to preconcentrate the rare-earth elements. The sample and eluant solutions were transferred in the following order onto the center of a 30-mm TLC disk made from Fixion-50X8 TLC plates: 0.1 ml of 0.1 M $H_2C_2O_4$ solution, sample solution, 0.2 ml of 0.1 M $H_2C_2O_4$ solution, 0.2 ml of 2 M NH_3Cl solution with 7.5-8.5 pH, and 0.2 ml water. The specimens, together with a layer of sorbent, were removed from the substrate and placed in ash-free filter packets 1 cm square, which were rolled together in aluminum foil and irradiated in a flux of 2 x 10^{18} neutrons/cm^2. After 3 hours, the specimens were removed from the foil, placed between two layers of adhesive tape, and analyzed γ-spectrometrically. In mineral specimens weighing up to 30 mg, 8-10 elements were detected. The detection thresholds were as follows(μg/g): 0.05 (Eu), 0.1 (Sm), 0.2 (Tb), 0.3 (Yb), 0.4 (La), 1 (Tu), 2 (Ce), and 10 (Nd). Figure 1, tables 4; references 27: 10 Russian, 17 Western.

UDC 543.25

Effect of Macrocomponents of Havana-Brand Drinking Water on Intensity of Atomic Emission Lines of Microelements in Plasma of Direct-Current Arc in Air and Argon Atmospheres

907M0164C Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 45, No 1, Feb 90 (manuscript received 13 Apr 88) pp 309-314

[Article by M. S. Pomares Alfonso, L. V. Simonova, A. V. Karyakin, and Yu. I. Belyayev, Geochemistriy and Analytical Chemistry Institute imeni V. I. Vernadskiy, USSR Academy of Sciences, Moscow, and Applied Nuclear Research Center, Havana]

[Abstract] In order to reduce detection thresholds, a study was done on how the macrocomponents of Havana drinking water affect the line intensity of normed microelements in a direct-current arc in air and argon atmospheres. Solution I contained a macrocomponent mixture of Ca:Mg:Na:K = 47:4:15:1, which is typical for this type of water, with a total macrocomponent concentration of 1 g/l, the maximum allowed for this type of water. Solution II did not contain any macrocomponents. The concentration of microelements in both solutions was identical. The Ornstein method was used to measure the effective plasma temperature with ion lines of 303.7, 304.7, 305.7, 305.9, 306.7, and 307.5 nm. Electron concentration in the plasma was measured by using two ion lines of 322.7 and 305.7 nm. In air, the intensity of the Mn, Be, and Fe ion lines diminishes, while those of the Ti and V do not change. A similar picture emerges for the atomic lines of the microelements. In the argon atmosphere, the intensity of both the ion and atomic lines of the microelements increases. The large calcium concentration in the waters is primarily responsible for these effects, which occur during the atomization stage of the sample as a result of the change in the effective plasma temperature and the transfer of energy when the second-order atoms and ions of the microelements collide with the atoms of the macrocomponents and the plasma- forming gas. These results were used to develop atomic emission methods employing direct current arc plasma to detect Fe, Nm, Mo, Co, V, Zn, Cu, Ba, Ni, Al, Cr, Pb, Sr, Cd, and Ti microelements in Havana drinking waters. Detection thresholds ranged from 0.05 to 0.01 mg/l. Tables 4; references 10: 7 Russian, 3 Western.

UDC 543.8:543.257.1:547.26'118:547.436

Ionometric Detection of S-Aminoalkylthiophosphates by Using Silver, Mercury, and Palladium Salts as Reagents

907M0164D Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 45, No 1, Feb 90 (manuscript received 13 Jan 89) pp 345-348

[Article by M. M. Buzlanova, I. V. Karandi, N. M. Karimova, and N. N. Godovikov, Institute of Elementoorganic Compounds, USSR Academy of Sciences, Moscow]

[Abstract] A study was done to determine the possibility of ionometrically detecting S-aminoalkylthiophosphates by using Ag, Hg, Pd, and Pb salts as reagents. Potentiometric titration was done with an OR-211/1 pH-detector made by the Radelkis company. A 0.01-M solution of $AgNO_3$, a 0.01-M solution of $Hg(NO_3)_2$, a 0.01-M solution of $PdCl_2$ in a 0.1-M solution of KCl, and a 0.02-M solution of $Pb(CH_3COO)_2$ were used. A 0.01-M solution of NaCl was the titrant for the $AgNO_3$ and $Hg(NO_3)_2$, and an OR-S-711 sulfide-selective electrode served as the indicator electrode. The K_2PdCl_3 solution was titrated with a 0.01-M solution of KI by using an OR-I-7112 D I-selective electrode, and a 0.005-M solution of Na_2SO_4 and a Pb- selective 82-27 electrode made by the Kriter company were used for the $Pb(CH_2COO)_2$ solution. It was found that S-aminoalkylthiophosphates easily react with Ag, Hg, and Pd salts. The most satisfactory results were obtained with Ag and Hg salts, so they were recommended for use in detecting S- aminoalkylthiophosphates. (No reproducible results were obtained when using the lead salts.) The method entailed the following: Put 3.4 mg of material, 10 ml of distilled water, 5 ml of 0.01 M $AgNO_3$, or an $Hg(NO_3)_2$ solution in a titration vessel beaker. After several minutes, titrate with a 0.01-M solution of NaCl and an S-selective electrode. This method is quick, simple, and accurate, and it can be recommended for use in detecting basic substances in pharmaceutical preparations. Figures 2, tables 1; references 8: 3 Russian, 5 Western.

UDC 543.253:549.41:547.831

Extraction-Voltammetric Detection of Gallium and Indium in 8- Mercaptoquinolate Form in Minerals

907M0164E Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 45, No 1, Feb 90 (manuscript received 12 Dec 88) pp 349-354

[Article by N. A. Ulakhovich, G. K. Budnikov, L. G. Shaydarova, and S. V. Mashkina, Kazan State University imeni V. I. Ulyanov-Lenin]

[Abstract] The extractive and voltammetric behavior of Ga(III) and In(III) complexes with methyl-substituted 8-marcaptoquinoline were studied, and the results were used to develop a selective voltammetric method for detecting these elements when both are present. Direct and variable-current voltammetric data were recorded on a PPT-1 polarograph in a thermostatically controlled (25.0 + 0.2) three-electrode cell. The control electrode was a saturated drip electrode, and the anode was a platinum wire. Aqueous solution pH was monitored with a pH-340 detector. The inert electrolyte was a 0.1-M solution of $(C_4H_9)_4$ $NClO_3$. Sublimated analytical-quality Chemapol naphthalene was used as the low-melting-point extractant. The detection method was as follows. A 0.5-g specimen was placed in an Erlenmeyer flask, treated with an HF and HNO_3 mixture, heated to remove the SiF_4, and allowed to cool. The pH level was set at 1, and a 5-ml $5x10^{-2}$ M aqueous solution of Na

8-mercaptoquinoline and 10 ml of chloroform were added. Extraction proceeded for 2 minutes, the organic phase was separated, and the pH of the aqueous phase was raised to 5 by adding a citrate buffer solution, heating to 80°C, and adding 0.2 g of naphthalene. The cooled extract was dissolved in a dimethylamide solution, which was transferred to an electrolyzer with a dropping mercury electrode and the variable-current polarograph recorded between -1.0 and -2.0 V. The I_p was measured at E_p=1.44 V, and the indium concentration was determined graphically $I_p=(0.98+0.02)c_{In}$. To determine the Ga concentration, the pH level in the remaining solution was brought to 8 and the procedure repeated. This method was found to be precise and highly selective and to have low detection thresholds. Figures 2, tables 4; references 10: 8 Russian, 2 Western.

UDC 543.253:541.49

Extraction-Voltammetric Detection of Chromium in Agricultural Substances

907M0164F Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 45, No 1, Feb 90 pp 355-360

[Article by N. A. Ulakhovich, G. K. Budnikov, L. G. Shaydarova, and I. V. Postnova]

[Abstract] The extraction and complexing kinetics of Cr(III) were utilized to optimize the extraction-voltammetric detection of Cr(III) in agricultural substances. The method entails the following stteps. A specimen weighing 1 g is placed in an appropriate vessel, 10 ml of HCl is added, and after 10-20 min, 3 ml of HNO_3 is added. The mixture is slowly heated until the reaction finishes, and the temperature is raised to 200°C. The solution is carefully evaporation-concentrated to 2 ml, cooled, and (after 10-15 ml water has been added) filtered through a large-pore filter prerinsed with acid. In the separatory funnel, 5 ml of an 0.5 M aqueous solution of 8-mercaptoquinoline and 15 ml of chloroform are added to the solution, which is shaken for 2 minutes, and the extract is separated. The aqueous solution is transferred to an Erlenmeyer flask and heated to 80°C. Extraction is done with 0.5 g naphthalene and 0.0025 g Na 4-methyl-8-mercaptoquinolinate. The solid extract is dissolved in a background solution, and the differential pulse polarogram (PU-1 polarograph) is recorded from -0.5 to -1.5V. The Cr content is determined graphically. The procedure takes 30 minutes. When this method is used, chromium in the form of 4-methyl-8-mercaptoquinolate can be detected in agricultural substances in the presence of Cr(VI), Mn(III), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), d(II), Mo(VI), and Pb(II). Figures 2, tables 3; references 13: 12 Russian, 1 Western.

UDC 542.61:545.54.86

Gas Chromatographic Detection of Chlorophenols in Waste Water

907M0164G Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 45, No 1, Feb 90 (manuscript received 11 Jan 89) pp 367-371

[Article by T. S. Kylbich and V. S. Kozlova, Kiev Scientific Research Institute of General and Public Hygiene, Kiev Department, State Scientific Research and Design Institute of the Chlorine Industry]

[Abstract] A gas chromatographic method of detecting maximum allowable concentrations of chlorophenols in waste water was developed. A Tsvet-100 gas chromatograph was used to determine optimal separation conditions for chlorophenylacetates (acyl derivatives of the chlorophenols). Separation was done at temperatures programmed to rise 2°/min from 50 to 160°C. The temperature of the chromatograph's electron capture detector that was used to lower the detection thresholds was 240°, and that of the evaporator, 210°. Optimal values for the length and temperature of the chromatograph's glass column were determined. Optimal acylation and extraction conditions were established by adding 1-6 g of Na hydrocarbonate, 0.1-1.5 ml of chromatographically pure acetic anhydride, and 30 ml of extractant (diethyl or petroleum ether, butanol, toluene, or hexane) to 1 l of water or model solution; performing the extraction process (described below); and analyzing the specimen yielded. The detection method method used is as follows: 5 g Na hydrocarbonate, 30 ml hexane, and 1 ml chromatographically pure acetic anhydride are added one after the other to 1 liter of water. The mixture is vigorously shaken for 3 minutes in a separating funnel. The organic phase is separated, and extraction is repeated twice by using 30 ml hexane with 1.0 and then 0.5 ml acetic anhydride. The extracts are combined, dried with dehydrated Na sulfate, filtered, and steamed dry on a water bath at a temperature of 80-90°C and the residue dissolved in 0.2 ml hexane. A 4-μl specimen of the mixture was chromatographically analyzed under optimal conditions. The method was tested on paper plant waste water, and 0.026 mg/l of dichlorophenol and 0.0032 mg/l of trichlrophenol were detected. The following detection thresholds, in mg/ml, were achieved: n-chlorophenol, 0.007; 2.4-dichlorophenol, 0.004; 2,3,5-trichlorophenol, 0.0008; and 2,3,4,6-tetrachlorophenol, 0.0008. Figures 1, tables 2; references 8: 5 Russian, 3 Western.

UDC 543.257.1:357.7.035.4

Pesticide Detection Using Potentiometric Titration With Ion- Selective Electrodes

907M0164H Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 45, No 1, Feb 90 (manuscript received 31 Oct 88) pp 372-377

[Article by V. V. Kiyanskiy and V. A. Burakhta, Western Kazakhstan Agricultural Institute, Uralsk]

[Abstract] Potentiometric titration of pesticides with S, Cu, Cd, Br, and Pb ion-selective electrodes was studied to find fast, accurate, and possibly automated methods of pesticide detection. Carbathion, Zineb, Diquat, and Carbophos pesticides were tested by using an EV-74 universal ion detector. Semiconducting Ge, Si, C, and SiC electrodes were also used. In all cases, the comparison electrodes were a silver chloride electrode filled with a saturated KCl solution, a Zr metal electrode, and an ESK-63-07 glass electrode. The titrants were 10^{-1}- to 10^{-3}-M aqueous solutions of $AgNo_3$, $CuSo_4$, $CdCl_2$, and $Pb(NO_3)_2$. The pesticides were dissolved in ethanol, acetone, dimethylsulfoxide, and dimethylformamide. The detection method used is as follows. A model BA metering device based on a T-10 automated titrator is used to dispense 10 ml of pesticide solution into the titration cell. Next, 50 ml solvent is added and titration performed with a salt solution containing the potential-determining ion. The equivalence point is automatically stabilized. For Carbathion, well-defined potential jumps were obtained by using all the solutions and the S-, Cu-, Pb-, and Cd-selective electrodes, with the largest jumps yielded by the $AgNO_3$/S-selective electrode and $CuSO_4$/Cu-selective electrode combinations. For Zineb, good results were achieved with the same solution/electrode combinations that yielded the best results for the Carbathion, and also with the p-SiC electrode. For Diquat, the best combination is $AgNO_3$ and the Br-selective and p-SiC electrodes. Test results for the Carbophos were unsatisfactory. Each test takes 10-15 minutes and satisfies industrial requirements. The p- SiC electrode can be used as a universal detector of the active ingredients in Carbothion, Zineb, and Diquat. Figures 3, tables 1; references 11 (Russian).

UDC 543.42:550.89

Using Electrothermic Atomic-Absorption Spectrometry With Preextraction Concentration To Detect Tellurium, Arsenic, and Antimony in Fluid Quartz Inclusions

907M0164I Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 45 No 1, Feb 90 (manuscript received 2 Feb 89) pp 378-385

[Article by A. B. Volynskiy, N. N. Baranova, and T. G. Daryina, Geochemistry and Analytical Chemistry imeni V. I. Vernadskiy, USSR Academy of Sciences]

[Abstract] An extraction-atomic absorption method for detecting trace amounts of Te, As, and Sb in fluid quartz inclusions was developed. A quartz specimen with a grain size of 0.25-0.50 mm is rinsed first with a hot mixture (3:1) of concentrated HCl and HNO_3 and then five times with bidistillate, after which it is dried at 100-105°C and ground to powder. (Grinding may result in less Te loss than thermal stripping does.) A 0.3- to 0.5-g specimen is put into a quartz test tube into which 2 ml of 3 M HCl acid is poured. The mixture is agitated, allowed to sit for 10- 12 hours, and then spun in a centrifuge for 6-7 minutes at 5,000-6,000 rpm. The solution is poured into another test tube, its volume stabilized, and to each 0.1 ml solution, 0.01 ml of freshly made 10% solution of ascorbic acid and 0.05 ml of 3 M HCl are added. The ascorbic acid is used in order to minimize the effects of admixtures of ferrous minerals in the quartz. Extraction proceeds for 8 minutes with 0.15 ml of a 0.01 M solution of nickel diethylditiophosphate in CCl_4. Because the detection sensitivity was higher with the $Ni(DEDTF)_2$—CCl_4 extraction system, it was chosen over the system with the MBT (mercaptobenzotiazol) reagent. The resulting extract is sufficient for detecting As, Sb, and Te when there are high concentrations of Te in the specimen. If the Te concentration is low, 0.1 ml of ascorbic acid solution is added to the residual extract, and extraction is done with $V_v:V_o$ approximately 10:1. The detection thresholds for 0.5-g specimens of Te(IV), As(III), and Sb(III) are (%) 10^{-8}, $5(10^{-6})$, and $1.5(10^{-6})$, respectively. Figures 5, tables 1; references 16: 11 Russian, 5 Western.

UDC 543.544:543.7

Using High-Performance Liquid Chromatography To Detect Heavy Metals in Form of Dibutyldithiophosphates in Waters

907M0164J Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 45, No 1, Feb 90 pp 390-394

[Article by A. R. Timerbayev, Ye. N. Shapovalova, T. A. Bolshova, O. M. Petrukhin, I. G. Tsoy, and V. V. Tsoy, Moscow State University imeni M. V. Lomonosov and Moscow Chemical Technological University imeni D. I. Mendeleyev]

[Abstract] A high-performance liquid chromatography method was developed to detect heavy metals in water. Extraction chromatography on a Milichrom chromatograph is used to preconcentrate the metals (in this case, Cu, Hg, and Pb) in the form of dibutyldithiophosphates. From 0.02 to 0.07 g potassium dibutylthiophosphate is added to 100 ml of 0.1 M HCl and 0.2 M NaCl aqueous solution. The suspension is passed through a 2 x 200 glass column at 5 ml/min. The column is filled with 2 g Teflon impregnated with 1 ml toluene. The adsorbed chelates are eluted with 3 ml toluene. To separate the dibutyldithiophosphates, thin-layer chromatography is done on a KhZh-1305 chromatograph with an eluant feed line equipped with a pump from a Tsvet-306 chromatograph. A 10-µl specimen of the solution is eluted with 1 ml/min of a 7:3 mixture of toluene and hexane in a 2 x 62-mm steel column filled with Silasorb-600 silica gel (particle size, 10 µm). An SF-4 spectrometer with a wavelength of 300 nm is used to monitor the metal content in the eluate. By using this wavelength, all the sample metals can be detected simultaneously while optimizing the light absorption of the reagent. Absorption spectra are recorded on an American-made Varian DMS-70. The metal content is calculated from the graphs, which are linear from 0.01- 5 mg/l. Relative detection thresholds are 1.5, 4.2, and 10.9 µg/l for Cu, Pb, and Hg, respectively, in mineral, waste, and industrial process waters. The relative standard deviation is 0.01-0.03. The sensitivity of this method is comparable to that of atomic absorption, x-ray fluorescence, and x-ray emission methods, but is simpler, quicker, and cheaper and uses equipment that is more readily available. Figures 2, tables 1; references 5 (Russian).

UDC 66.065.52+541.12.012

Counterflow Crystallization Column for Deep Purification of Substances

907M0315C Moscow VYSOKOCHISTYYE VESHCHESTVA in Russian No 4, Jul-Aug 90 (manuscript received 6 Dec 89) pp 83-86

[Article by V. M. Vorotyntsev, V. M. Malyshev, and V. B. Karaksin, Institute of Chemistry of Highly Pure Substances, USSR Academy of Sciences, Moscow]

[Abstract] The influence of mechanical grinding of crystals on the effectiveness of purifying substances by counterflow crystallization from melt was studied on a crystallization column made of stainless steel 1,300 mm in height, inside diameter of 27 mm, and volume of 920 ml. The separation process was monitored by gas chromatographic analysis of samples collected from various parts of the column. There is an increase in the positive effect of grinding of crystals with an increase in the number of grinders used. Increasing the number of grinders significantly improved effectiveness of purifying substances by counterflow crystallization from a melt. Figures 3; References 10: 6 Russian, 4 Western.

UDC 541.135.8:546.78

Anode Photocurrents on Electrodes Having WO_3 Electrochrome Layer

907M0100B Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 55 No 11, Nov 89 (manuscript received 26 Jul 88) pp 1167-1171

[Article by Yu. S. Krasnov, I. V. Shiyanovskaya, F. N. Patsyuk, O. A. Sych, and A. T. Vasko, General and Inorganic Chemistry Institute, Kiev]

[Abstract] Amorphous layers of tungsten trioxide have outstanding electrochrome properties. Electrodes having such layers are characterized by intense coloration due to cathode potential shifting in the solid or liquid electrolytes supplying hydrogen, lithium, or sodium ions. Anode polarization of a colored electrode decolors it and causes a photocurrent to appear. In the present work a comparison was made of the anode photocurrents on electrodes having an amorphous tungsten trioxide layer applied by three different methods: (I) anode oxidation of sheet tungsten, (II) precipitation from aqueous solutions of tungsten-containing compounds, and (III) thermal vaporization of polycrystalline powder under vacuum. Method (I) gave the highest anode current, with that obtained by using methods (II) and (III) being two to three orders of magnitude lower. The character of the stationary distribution in potential skip within the structure of current-carrying substrate/amorphous tungsten trioxide/electrolyte systems during anode polarization is determined by the substrate and the characteristics of the electrochrome layer, which depends on its method of preparation. It is conjectured that electrochemical reactions occur at the SnO_2/WO_3 interface and involves water molecules adsorbed in the pores of the amorphous tungsten trioxide. Figures 3; references 8: 4 Russian, 4 Western.

UDC 541.13

Mass Transfer in Thin Layers of Molten Salts During Metal Refining Under Galvanostatic Conditions

907M0100C Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 55 No 11, Nov 89 (manuscript received 12 Jul 88) pp 1171-1176

[Article by V. V. Pototskaya and N. Ye. Yevtushenko, General and Inorganic Chemistry Institute, Kiev]

[Abstract] Liquid electrode thin-layer electrochemical reactors could be used in metal refining. The presence of a liquid interface between the electrode and the electrolyte and its interaction with heat and mass transfer processes from one phase to the other could lead to the existence of various types of interfacial convection resulting in the formation of dissociative structures similar to that of circulating cells (the Marangoni effect) to enhance a high rate of mass transfer as compared with natural convection. In many practical instances, transfer becomes the deciding role in the macrokinetics of heterogeneous conversions. In the present work a study was made of the mass transfer processes in thin layers of a molten three- component electrolyte with a liquid electrode during metal refining under galvanostatic conditions. Formulas were derived for the electric field potential in the thin layer and the distribution of component concentrations. Figures 3; references 9: 7 Russian, 2 Western.

UDC 541.135

High Temperature Electrochemical Synthesis of Intermetallic Titanium Iron Compounds

907M0100D Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 55 No 11, Nov 89 (manuscript received 21 Jul 88) pp 1176-1179

[Article by V. I. Shapoval, L. I. Zarubitskaya, V. I. Taranenko, and Yu. V. Korobka, General and Inorganic Chemistry Institute, Kiev]

[Abstract] Progress in the national economy requires the development of materials having special properties, especially that of being able to store hydrogen. This is manifested in the intermetallic compounds of titanium and elements of the iron subgroup, TiFe, TiCo, and TiNi. Although there are references in the literature on the solid-phase synthesis of TiFe and the electrolytic synthesis of some unstable alloys, dedicated research on the electrolytic preparation of intermetallides is lacking. In the present work electrochemical measurements were made, and potentials were determined for titanium and iron in salt melts at 700°C that contain both metals simultaneously. The data were then applied to conducting a series of electrolyses in refining baths where titanium and iron were coprecipitated. Figures 2; references 7: 4 Russian, 3 Western.

UDC 541.13:541.183

Kinetics of Reductive Sorption of Noble Metal Ions on Activated Charcoals

907M0100E Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 55 No 11, Nov 89 (manuscript received 12 May 89) pp 1179-1183

[Article by Yu. A. Tarasenko, S. P. Antonov, A. A. Bagreyev, and G. V. Reznik, General and Inorganic Chemistry Institute, Kiev]

[Abstract] Reductive sorption is a no-current electrochemical process for reducing metal ions as they are adsorbed from solutions on activated charcoals. Some specific features of this process have been described by using a mathematical model that made it possible to compute the parameters of the process under steady-state conditions. However, in cases of practical concern, reagent concentrations in the solution change during the course of the process, and it is therefore desirable to

develop an approach to describing a system in which the metal ion concentration diminishes with time as a result of reductive sorption, i.e., solve a kinetic problem. In the present work a closed system of equations for a no-current electrochemical reductive sorption process was constructed and solved. A numerical solution was derived for the reductive sorption of palladium on the exterior of an activated charcoal spherule. Comparison of computed results with experimental data show that the equations may be used as an algorithm to control a reductive sorption process. Figures 3; references 4 (Russian).

UDC 541.135.5

Electrocatalytic Properties of Carbonaceous Materials From Coke and Pitch

907M0101A Moscow ELEKTROKHIMIYA in Russian Vol 25 No 12, Dec 89 (manuscript received 15 Jun 88) pp 1658- 1660

[Article by Yu. A. Vetoshkin, A. N. Doronin, A. V. Yuzhanina, L. A. Mashkovich, and A. F. Kuteynikov, Graphite Building Materials SRI, Moscow]

[Abstract] Theoretical concepts linking the structure of carbonaceous materials to their electrocatalytic properties are presently lacking, and this relationship is studied experimentally. Thus, in the case of glassified carbon and carbon fibers, it has been demonstrated that the temperature at which these materials are treated has a great effect on their electrocatalytic properties. The addition of titanium to graphite lowers the hydrogen overvoltage in comparison to pure graphite, and the electrochemical behavior of the material is chiefly governed by the electrochemical properties of titanium carbide. Density, being a basic factor in the technology of carbonaceous materials, may be altered by either varying the conditions at which the initial material is treated or by adding various fillers. It is therefore of interest to examine the relationship between the density and electrocatalytic activities of carbonaceous materials derived from the same base but having different properties and treatment conditions. In the present work industrial-grade coke and pitch whose densities were altered by the addition of various fillers and by altering the treatment conditions of the initial materials were studied by measuring potentiodynamic cycles (volt-ampere curves). The data show that increasing the density by either adding fillers or changing the treatment conditions lowers the rates hydrogen and oxygen evolution. The addition of zirconium increases the current over the entire range of potentials, while the presence of silicon or boron decreases the oxygen desorption current. Figures 2; references 4 (Russian).

UDC 541.138.3

Electroreduction of Dioxygen Over Double Ruthenium and Lead Oxide Catalyst

907M0101B Moscow ELEKTROKHIMIYA in Russian Vol 25 No 12, Dec 89 (manuscript received 28 Jun 88) pp 1663- 1665

[Article by B. K. Almashev, S. N. Kit, G. A. Pushkareva, V. N. Kokunova, A. B. Fasman, and N. M. Sinitsyn, Kazakh Pedagogical Institute imeni Abaya, Alma-Ata]

[Abstract] Oxides are the most widespread nonmetallic electrocatalysts used. For electro-reduction of dioxygen, simple oxides and mixed oxides with spinel and perovskite structures have been used. It was also observed that certain ruthenates having a pyrochlore structure are active catalysts in the reduction of dioxygen in alkaline media. In a previous work it was demonstrated that the decomposition of a complex nitrosonitro ruthenium compound above 600°C results in the formation of a binary ruthenium lead oxide having a pyrochlore structure. In the present work a study was made of the catalytic activities of finely divided samples obtained by thermal decomposition of $Pb[RuNO(NO_2)_4OH]{\bullet}{\leq}_2O$ at 500, 600, 700, and 800°C in 7N KOH solution at 90°C. A pyrochlore sample having the composition $Pb_2Ru_2O_{7-x}$ and prepared at 600°C was the most active. Evidently, pyrochlore structuring is incomplete at lower temperatures, while particle aggregation takes place at the higher temperatures. Figures 3; references 8: 5 Russian, 3 Western.

UDC 541.138.3

Electrocatalytic Properties of Pt-Sn-Alloys in Oxygen Electroreduction Reaction

907M0101C Moscow ELEKTROKHIMIYA in Russian Vol 25 No 12, Dec 89 (manuscript received 6 Jul 88) pp 1666- 1667

[Article by A. B. Fasman, B. K. Almashev, S. N. Kim, G. S. Musabekova, and Ye. S. Shpiro, Kazakh Pedagogical Institute imeni Abaya, Alma-Ata]

[Abstract] Mixed metal electrocatalysts are frequently more effective as electrodes than are single metal electrodes. Using alloys makes it possible to increase the activity, stability, and selectivity of electrodes. Binary metallic systems are ordinarily used in oxidation processes, e.g., alloys of platinum with electronegative metals are used as anodes in methanol fuel cells. In the present work PtSn, $PtSn_2$, Pt_2Sn_3, and $PtSn_4$ catalysts were tested for effectiveness. The electrocatalytic properties of these catalysts depend on whether the tin is a solid solution in the platinum or whether it is an intermetallide. Chemical and x- ray analyses of the service lives of $PtSn_2$ and Pt_2Sn_3 catalysts shows that there is a rise in electocatalytic activity that gradually dissipates with time. Evidently, a new catalytically active phase is

formed during the first few hours, and with further operation, the active sites of this new phase become blocked with newly formed platinum and tin oxides. Figure 1; references 5: 3 Russian, 2 Western.

UDC 621.357.7.035.4:669.23425

Utilizing Chronopotentiometric Data in Palladium-Cobalt Alloy Electroplating Technology

907M0101D Moscow ELEKTROKHIMIYA in Russian Vol 25 No 12, Dec 89 (manuscript received 29 Jul 88) pp 1668-1670

[Article by Ye. V. Chumak, I. B. Yermolov, and L. I. Kadaner, Kharkov State Pedagogical Institute imeni G. S. Skovoroda]

[Abstract] A sulfamate electrolyte for electroplating palladium-cobalt alloys was developed at the electrochemical laboratory of the Kharkov Pedagogical Institute for use in preparing high-quality, 20-µm-thick coatings. Components coated with these alloys successfully withstood laboratory and industrial testing. The process for applying the coatings was developed during a study of studying the fundamentals of the electroplating process, including chronopotentiometric analysis. The potential-time curves (E-T) were obtained with an oscillograph under galvanostatic conditions for electrolytes containing palladium or cobalt only and palladium combined with cobalt. After a polarizing current was applied to palladium-containing electrolytes, the electrode potential reached a value somewhat greater than stationary and then dropped to the stationary value after 2-3 seconds. The course of the E-T curves and the stationary potential indicated that they vary as functions of the substrate material, time and density of the polarizing current, duration of pretreatment, and the delay between preliminary and operating current pulses. When palladium-cobalt coatings were electroplated onto the collector portions of disk-type electric motors fabricated from foiled, glass fiber printed circuit cards, it was observed that the alloy failed to be deposited in the metallized gaps joining the working surfaces of the plates, with intensive dissolution of copper resulting in contact failure. To suppress the anode current in the gaps, it was necessary to raise the mean current density to 3-4 A/dm^2, although this resulted in fusing along the edges. The fusing was circumvented by the addition of nitrite ions to the electrolyte. The overall potential of the alloy electroplating process was shifted to a more positive value to provide complete cathode protection and prevention of copper dissolution in the gaps, although the current yield of the alloy dropped significantly. Figures 2; references 2 (Russian).

UDC 541.135.5

Kinetics of Hydrogen Transfer Through Palladium Membrane Under Conditions of Electrochemical Injection and Extraction

907M0101F Moscow ELEKTROKHIMIYA in Russian Vol 25 No 12, Dec 89 (manuscript received 1 Mar 89) pp 1672- 1675

[Article by I. I. Kolesnichenko, A. A. Michri, and A. G. Pshenichnikov, Electrochemistry Institute imeni A. N. Frumkin, Moscow]

[Abstract] Hydrogen-permeable membranes may be effectively used in various processes and devices, such as gas separation, liquid- and gas-phase hydrogenation of organic compounds, and oxidation of hydrogen on gas-diffusion anodes in fuel cells. While the permeability of palladium-based membranes during hydrogen transfer between two gas phases has been well studied, data are still lacking on the relationship of the rate of stationary transfer of hydrogen through a palladium membrane during electrochemical injection and extraction of hydrogen as a function of the contact and diffusion potentials. In the present work a study was made of the kinetics of hydrogen transfer through a palladium membrane under the above conditions. The coefficient of diffusion of hydrogen within the palladium bulk was determined, and an estimate was made of the minimum rate of hydrogen transfer from the adsorbed state to the near-surface metal layer. A mathematical model for hydrogen transfer through a palladium membrane under conditions of electrochemical injection and extraction is presented. Figures 4; references 11: 6 Russian, 5 Western.

UDC 541.138

Potentiometric Study of Halide and Thiocyanate Complexes of Zinc in 1,2-Propylene Glycol

907M0131D Tbilisi SOOBSHCHENIYA AKADEMII NAUK GRUZINSKOY SSR in Russian Vol 135 No 1, Jul 89 (manuscript received 8 Sep 88) pp 149-151

[Article by V. V. Shavgulidze and L. V. Gegeshidze, Inorganic Chemistry and Electrochemistry Institute, Tbilisi]

[Abstract] Only a few references exist in the literature on the composition and stability of halide and thiocyanate complexes of zinc in aqueous solutions, and there arealmost none for inaqueous protic solutions. In the present

work a potentiometric study was made of the above complexes in 1,2-propylene glycol. Concentrations ofzinc nitrate as a function of electrode potential, and stability constants are presented.

UDC 541.13:546.11.01/05

Electrochemical Purification of Hydrogen in Systems With Solid Polymer Electrolyte

907M0315D Moscow VYSOKOCHISTYYE VESHCHESTVA in Russian No 4, Jul-Aug 90 (manuscript received 1 Feb 90) pp 87-89

[Article by A. V. Morozov and M. B. Rozenkevich, Moscow Chemical Technology Institute imeni D. I. Mendeleyev]

[Abstract] A study is made of the process of deep purification of gaseous hydrogen in a system containing a solid-polymer membrane electrolyte. Results are presented from the process of the purification of hydrogen. The method is said to allow deep purification of hydrogen at room temperature and atmospheric pressure, which distinguishes it from the diffusion method. Shortcomings of the method include its relatively high power consumption and the need for additional drying of the product. References 3: 1 Russian, 2 Western.

UDC 669.046.74'787'784:541.123

Reaction of MnO With Carbon

907M0131C Tbilisi SOOBSHCHENIYA AKADEMII NAUK GRUZINSKOY SSR in Russian Vol 135 No 1, Jul 89 (manuscript received 25 Jun 88) pp 137-140

[Article by G. G. Gvelesiani, D. I. Bagdavadze, D. Sh. Tsagareyshvili, D. M. Lanchava, and L. V. Tsamalaidze, Metallurgy Institute, Tbilisi]

[Abstract] Manganese oxide begins to react with carbon monoxide at 1,953 K, and at 1,578 K the reaction becomes reversible with separation of carbon black. Manganese carbide, Mn_7C_3, starts to form at an early stage between 1,343 and 1,473 K, and as the reaction develops, MnO reacts with the carbide to form metallic manganese. In the present work a complete thermodynamic analysis of the above reaction system was made for the temperature range from 1,000 to 2,500 K and atmospheric pressure at 50° intervals by using a previously described algorithm and a computer. Solid solution compositions, gas phase extraction of manganese, and energy consumptions were determined. Figures 4; references 6: 5 Russian, 1 Western.

UDC 541.1:546.19:66.011

Physicochemical Principles of Extraction of Arsenic From Arsenopyrite

907M0315E Moscow VYSOKOCHISTYYE VESHCHESTVA in Russian No 4, Jul-Aug 90 (manuscript received 22 Mar 90) pp 102-107

[Article by A. S. Pashinkin, V. A. Muratova, and V. A. Fedorov, Institute of General and Inorganic Chemistry imeni N. S. Kurnakov, Moscow]

[Abstract] Partial pressure diagrams of the systems Fe-As-S at 923 K and Fe-As-O at 1,200 K in logarithmic coordinates are used to develop the physical and chemical principles of the production of elementary arsenic from arsenopyrite by dissolution of arsenic trioxide in hydrochloric acid, subsequent purification by fractional distillation, adsorption on carbon, and reduction with hydrogen. It is demonstrated that the arsenic produced by thermal dissociation of arsenopyrite contains sulfur that is difficult to remove. Figures 3; References 24: 16 Russian, 8 Western.

UDC 621.391.029.7

Production of Optical Fibers From Highly Pure Quartz Glass by Internal Precipitation

907M0315A Moscow VYSOKOCHISTYYE VESHCHESTVA in Russian No 4, Jul-Aug 90 (manuscript received 19 Mar 90) pp 18-32

[Article by G. G. Devyatykh and A. N. Guryanov, Institute of Chemistry of Highly Pure Substances, USSR Academy of Sciences, Gorkiy]

[Abstract] The MCVD method is the most widely used method for the production of optical fibers since it eliminates environmental contamination and allows easy production of optical fibers with any desired profile of the index of refraction. This article discusses the problem of producing optical fibers from highly pure quartz glass with very low optical losses by the MCVD method. Mechanisms of optical losses in optical fibers are discussed, and the influence of the purity of the initial volatile substances is discussed. Methods are described for drawing of optical fibers, and the influence of the supporting quartz tubes on optical losses is analyzed. It is found that the purity of the initial materials used in the manufacture of optical fibers is limited by the content of hydrogen-containing substances, which must not be over $5 \cdot 10^{-5}$ mol%, with the oxygen content $1 \cdot 10^{-6}$ mol%. Gradient optical fibers are obtained with transmission bands up to 4.5 GHz·km. The core material used is quartz glass doped with germanium and phosphorus oxides with a variable germanium dioxide content. Figures 10; References 74: 32 Russian, 42 Western.

UDC 547.52:541

Mechanism of Catalysis of Arbuzov Reaction by Transition Metal Complexes. Part 2. Reaction of P(III)-Containing Ni(0) and Ni(I) Complexes with Aryl Halides

907m0107B Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 59 No 11, Nov 89 (manuscript received 1 Feb 88) pp 2508-2511

[Article by V. V. Sentemov, Ye. A. Krasilnikova, I. V. Berdnik, V. I. Moirozov, A. V. Ilyasov, F. Sh. Shagvaleyev and T. V. Zykova, Izhevsk Agroicultural Institute]

[Abstract] ^{31}P NMR, ESR, and electronic spectroscopy were utilized to demonstrate oxidative addition of aryl halides to P(III)-containing Ni(0) and Ni(I) complexes, resulting in the formation of $[ArPR_n(OR^1)_{3-n}]_2\cdot[NiX_2Y_2]$-type quasiphosphonium salts. Decomposition of the latter compounds leads to the formation of the final products of the Arbuzov reaction, represented by alkyl halides and $ArP(O)R_n(OR^1)_{2-n}$ compounds. Oxidative adduction of ArY to $Ni^0[P(OR^1)_3]_4$ results in the formation of P-containing Ni(I) complexes. References 24: 15 Russian, 1 Polish, 8 Western.

UDC 546.791.6+386

Coordination Features of Saturated Dicarboxylate Anions in Uranyl Complexes

907M0124B Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 6, Nov-Dec 89 (manuscript received 4 Jan 88) pp 10-11

[Article by M. T. Toshev, Z. R. Ashurov, N. A. Parpiyev, A. V. Sergeyev, V. E. Mistryukov, Yu. N. Mikhaylov, and R. N. Shchelokov, Bukharska Food and Light Industries Technological Institute]

[Abstract] In a previous work it was established that in uranyl complexes with simple carboxylate acido ligands the tendency for carboxylate ions to enter bidentate-cyclic addition to the uranyl group increases with the length of the alkyl group. It was then assumed that increasing the length of the methylene chain between the two carboxylate carbon atoms in dicarboxylic acids will result chiefly in bidentate-cyclic addition. In the present work x-ray structural analyses wer made of the crystal structures of uranyl complexes of succinate, glutarate, adipinate, and pimelate ions. Evidently, increasing the length of the methylene chain between the two carboxylate carbon atoms in dibasic carboxylic acids results in the formation of complex polymeric complexes, and the coordination function of the carboxylate group changes from that of a bidentate bridge (as in the succinate ion) to that of a bidentate-cyclic structure (glutarate, adipinate, and pimelate ions). Interatomic distances and valency angles for the four complexes are presented. Figure 1; reference 1 (Russian).

UDC 546.3

Regeneration of Metals From Electroplating Effluents Containing Chromium and Copper Ions

907M0131B Tbilisi SOOBSHCHENIYA AKADEMII NAUK GRUZINSKOY SSR in Russian Vol 135 No 1, Jul 89 (manuscript received 30 Sep 88) pp 129-132

[Article by L. V. Gabisoniya, N. M. Chikvaidze, and R. G. Tushurashvili, Inorganic Chemistry and Electrochemistry Institute, Tbilisi]

[Abstract] A radiation-chemical method is proposed for the treatment of electroplating effluents to extract chromium and copper ions in powder form. The effluents essentially contain dichromate ions, which are reduced to a lower valance state by γ-radiation to form an insoluble compound or the free metal. However, the radiolysis must take place in the presence of an OH-radical acceptor such as sodium hyposulfite. Copper sulfate is converted to the free metal. The method does not require costly reagents, produce large quantities of sludge, or require long periods of time. The powdered products could be recycled in powder metallurgy, while the phosphates and phosphites formed during the process could find applications as fertilizers. Figure 1; references 3 (Russian).

UDC 546.281

Dehydrocondensation of Silicon Hydrides With Transition Metal Complexes Present

907M0288H Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 60 No 5, May 90 (manuscript received 18 Jan 90) pp 1087-1091

[Article by N. K. Skvortsov, L. N. Burova, A. Ye. Trofimov, Ye. B. Vasileva, and V. O. Raykhsfeld, Leningrad Institute of Technology imeni Lensovet]

[Abstract] A study is made of the catalyic activity of soluble and fixed complexes of platinum, nickel, Rh, Ru, and Pd. The reactivity of various silicon hydrides was studied volumetrically in a solution of nitromethane after ensuring homogeneity of the reaction medium. The dehydrocondensation reaction is found to be a chelate process occurring through a nonpolar transition state. The overall reaction rate includes contributions of several elementary stages, which explains the variation in order of reaction and stereochemical result with the nature of the reagents and catalysts. The most important stage is activation of the bond in the silicon hydrides. Breaking of the OH bond makes no significant contribution to the rate-limiting reaction stage, and specific activation of alcohol or acid molecules by the catalyst does not occur. References 13: 3 Russian, 10 Western.

UDC 547.242.07(088.8)

Reaction of Aminoarsines with Carbon Disulfide

907m0107C Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 59 No 11, Nov 89 (manuscript received 21 Mar 88) pp 2520-2524

[Article by G. I. Kokorev, Sh. Kh. Badrutdinov, L. A. Almetkina and F. D. Yambushev, Kazan State Pedagogical Institute]

[Abstract] An analysis was conducted on the effects of As- and N-atom substituents on the outcome of reactions of aminoarsines with carbon disulfide. The reaction of arylbis(N-dialkylamino)arsines and of diaryl(N-dialkylamino)arsines (I) with carbon disulfide led to the formation of the corresponding dithiocarbamates. Reaction of arylbis(N-tert-butylamino)arsines and diaaryl(N-tert-butyrlamino)arsines with carbon disulfide resulted in the formation of arsine sulfides, tert-butylisothiocyanate, and hydrogen sulfide. Aryl(N-dialkylamino)haloarsines behave in a manner analogous to I, forming dithiocarbamates. However, aryl(N-tert-butylamino)haloarsines fail to react with carbon disulfide. Aryl(N-diethyl-N'-tert-butyldiamino)arsines react with carbon disulfide to form bis(arylarsine-N-diethyldithiocarbamato) sulfides as the final products. References 4 (Western).

UDC547.341

Reduction of Phosphoryl Acetaldehyde Oximes to Phosphoryl Hydroxylamines

907m0107F Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 59 No 11, Nov 89 (manuscript received 21 Dec 88) pp 2634-2636

[Article by B. G. Liorber, V. A. Pavlov and Z. M. Khamatova, Kazan Institute of Chemical Technology imeni S. M. Kirov]

[Abstract] The limited number of studies on phosphorylated hydroxylamines led to studies on their synthesis by reduction of phosphoryl oximes. 2-Diisopropoxyphosphorylethylhydroxylamine was synthesized by the reaction of diisopropoxyphosphorylacetaldehyde oxime with pyridine-borane in ethanol with 10% HCl. In analogous reactions 2-dipropoxy- and 2-diisobutoxyphosphorylethylhydroxylamine hydrochloride were produced, as well as 2-diisopropoxyphosphorylethylhydroxylamine. References 5: 2 Russian, 3 Western.

UDC 547.512:547.326'118

Addition of Dialkyl Dithiophosphoric Acids to 3-Methyl-3-Phenylcyclopropene

907m0107G Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 59 No 11, Nov 89 (manuscript received 29 Dec 88) pp 2636-2637

[Article by R. R. Khaliullin, V. V. Plemenkov, N. G. Khusainova and R. A. Cherkasov, Kazan state Medical Institute imeni S. V. Kurashov; Kazan State University imeni M. V. Ulyanov-Lenin]

[Abstract] Studies were conducted on the reaction of dialkyl dithiophosphoric acids—$(RO)_2PSSH$, where R = Et, i-Pr—with a 25% excess of 3-methy-3-phenylcyclopropene under argon at room temperature for 3-7 days, since such reactions have remained neglected. TCL studies and spectrometric analyses identified the products as O,O'-diethyl- and O,O'-diisopropyl-S-(2-metyl-2-phenyl)cyclopropyldithiophosphate. Both compounds were obtained in 90-92% yields. References 1 (Russian).

UDC 547.26'118

Reaction of Enaminones with Dimethylphosphorous Acid

907m0107H Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 59 No 11, Nov 89 (manuscript received 6 Sep 88) pp 2637-2638

[Article by A. A. Sobanov and A. N. Pudovik, Kazan state University imeni V. I. Ulynaov-Lenin]

[Abstract] Spectrometric studies were conducted on the products formed by the reaction of equimolar mixtures of dimethylphorphorous acid with 1-methylamino-1-buten- or 1-methylamino-1-penten-3-one at room temperature for one day. The resultant products were identified, respectively, as dimethyl-3-oxobutenylammonium methylhydrophosphonate and dimethyl-3-oxopentenylammonium methylhydrophosphonate. The yields were in the 85-89% range. References 3 (Russian).

UDC 547.26'118+547.494

Alpha-Phosphorylated Alpha-Chlorobenzyl Isocyanates

907M0288B Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 60 No 5, May 90 (manuscript received 29 Nov 88) pp 983-989

[Article by B. N. Kozhushko, A. V. Lomakina, and V. A. Shokol, Institute of Organic Chemistry, UkSSR Academy of Sciences, Kiev]

[Abstract] The authors have previously studied the synthesis of α-phosphorylated benzyl isocyanates and studied their diastereomer anisochronism and the diastereotopicity of the fluorene atoms and alkoxyl groups with the phosphorus atoms. The authors extend the reaction to α,α-dichlorobenzyl isocyanate, synthesize α-phophorylated α-chlorobenzyl isocyanates, study their physicochemical properties, and compare their spectral characteristics with those of the α-phosphorylated benzyl isocyanates. References 10: 9 Russian, 1 Western.

UDC 547.233:547.314.2:546.185

Synthesis of New Phosphorylated Acetylene Amines

907M0288E Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 60 No 5, May 90 (manuscript received 29 Nov 88) pp 1008-1011

[Article by A. D. Salimbayeva, B. Zh. Dzhiyembayev, S. K. Tukanova, and B. M. Butmin, Institute of Chemical Sciences, KaSSR Academy of Sciences, Alma-Ata]

[Abstract] It is know that the reaction of amines with dialkyl (diaryl) phosphites in the presence of triethylamine in CCl4 leads to the corresponding phosphoric acid amides. This reaction is thought to involve the intermediate formation of chlorophosphate. The authors have shown that this method is applicable for the synthesis of acetylene amides of dialkylphosphoric acids. The reaction is conducted in an excess of CCl4 with equimolar ratios of the reagents and with the HCl acceptor being triethylamine. The reaction occurs smoothly in all cases, with significant heating requiring cooling of the reaction mixture. The result is acetylene-containing amides of the dialkylphosphoric acids with yields of 81-96%. The possibility is demonstrated of the participation of acetylene-containing amides of dialkylphosphorous acids in the oxidative dimerization reaction. References 8: 5 Russian, 3 Western.

UDC 547.341

Condensation of Diarylphosphoric and Thiophosphoric Acid Ester Hydrazides With α-Diketones

907M0288F Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 60 No 5, May 90 (manuscript received 26 Dec 88) pp 1028-1033

[Article by F. V. Bagrov, Chuvash State University imeni I. N. Ulyanov, Cheboksary]

[Abstract] Continuing previous studies of the reaction of α-diketones with phenylhydrazine, the authors utilized diacetyl, acetylbenzoyl, and dibenzoyl to study the condensation of α-diketones with diarylphosphoric and thiophosphoric acid ester hydrazides in order to follow the influence of changes in the structure of the α-diketone and hydrazide component on the reactivity of the carbonyl groups in the initial diketone and on the tautomer configuration equilibrium of the reaction products. It was established that in a medium of absolute ethyl alcohol, regardless of the nature of the hydrazide, diacetyl reacts easily with an exothermic effect. Diacetyl monohydrazone can be obtained only by the use of a two- or three-times excess of the initial diketone with slow addition of the alcohol solution of the phosphoric acid ester diphenylhydrazide to the diacetyl solution. Condensation of hydrazides stops at the stage of formation of the monohydrazone or oxazone, depending on the reaction conditions and initial α-diketone used. The configuration and tautomer equilibria are studied by IR and NMR spectroscopy. Hydrazone-azo-tautomerism occurs in diacetyldiphenylphosphonyloxazones in polar solvents. References 3: Russian.

UDC 547.26'118

Phosphorylation of Azoles by Phosphoric Anhydride

907M0288I Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 60 No 5, May 90 (manuscript received 17 Jun 89) pp 1182-1183

[Article by P. M. Zavlin, D. A. Yefremov, and A. V. Gukayev, Leningrad Institute of Motion Picture Engineering]

[Abstract] A study is presented of the synthesis of phosphorylated azoles by direct reaction with phosphoric anhydride. It is found that when benzimidazole and its derivatives and benzotriazole react with phosphoric anhydride, a mixture of the corresponding phosphates and pyrophosphates is formed. The azoles were phosphorylated by phosphoric anhydride in the presence of tetrahydrofuran, which shifts the reaction in the direction of formation of the pyrophosphate. References 4: Russian.

UDC 547.341

Azaallyl Phosphites

907M0288J Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 60 No 5, May 90 (manuscript received 5 Jul 89) pp 1186-1187

[Article by D. M. Malenko, L. I. Nesterova, S. N. Lukyanenko, and A. D. Sinitsa, Institute of Organic Chemistry, UkSSR Academy of Sciences, Kiev]

[Abstract] It was found that when diethylchlorophosphite is reacted with the N-benzylamides of carboxylic acids in the presence of triethylamine under mild conditions, imidoylphosphites are formed with good yield. Heating of N-benzylimidoylphosphites to 100°C for 1 hour causes them to isomerize as a result of 1,3-prototropic migration to previously unknown azaallyl phosphites. References 3 (Russian).

UDC 541.183:632.938

Adsporption Refining of Cottonseed Oil From Pesticides

907M0124C Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 6, Nov-Dec 89 (manuscript received 15 Jul 88) pp 12-15

[Article by E. A. Aripov, N. F. Abdullayev, G. R. Narmetova, and Kh. A. Sharifikhodzhayeva, Chemistry Institute, Tashkent]

[Abstract] Natural mineral sorbents such as bentonite and foundry clays have a sufficiently high adsorption capacity to also remove dissolved pesticides from cottonseed oil during postrefining. In the present work the content of tributyltrithiophosphate (active ingredient of butafos) in cottonseed oil was determined before and after adsorption refining with askangel (Georgian bentonite clay activated with sulfuric acid). Thin-layer chromatography showed that this technique improves the clarity of the oil as well as removes traces of the pesticide. The polyphasic sorbent may be used for analytical control of pesticide in the cottonseed oil extract. Figures 3; references 6 (Russian).

UDC 541.68

Mechanochemical Interpretation of Coal Formation

907M0106A Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 6, Nov-Dec 89 (manuscript received 28 May 88) pp 41-43

[Article by G. P. Gordeyev, Leningrad Technological Institute]

[Abstract] A brief review is presented of mechanochemical factors important in coal formation, based on unequivocal data that tectonic processes play a key role in the genesis of coal. Tectonic forces are representative of virtually static stresses that lead to compaction, deformation, and comminution of coal deposits. According to current kinetic theory, mechanical restructuring is thermally activated, while thermal restructuring is mechanically activated. Analysis of energy of activation and structural parameters has shown that maximum coalification is to be expected in those segments of a deposit where coal exhibits low strength and maximum brittleness. References 12 (Russian).

UDC 541.128:662.642

Catalytic Characteristics of Oxidized Brown Coal of Kansk-Achinsk Deposits

907M0106B Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 6, Nov-Dec 89 (manuscript received 23 Sep 88) pp 44-47

[Article by S. S. Stavitskaya, I. A. Tarkovskaya and A. G. Voloshin, Institute of Physical Chemistry, Ukrainian SSR Academy of Sciences]

[Abstract] The existence of large deposits of oxidized coal in the Kansk-Achinsk basin that are unsuitable for use as fuel has led to studies on their utilization as a raw material for chemicals and as inexpensive catalysts. Trials with several systems have shown that samples of the coal catalyze formation of butyl acetate, decomposition of hydrogen peroxide, and electroreduction of oxygen on electrochemical electrodes. In the case of hydrogen peroxide decomposition, the cationic forms ranked as follows in efficiency: $Fe^{3+} > Cu^{2+} > Ni^{2+} > H^+$. Finally, electrochemical electrodes prepared from two samples of the Kansk-Achinsk coal developed a potential of 0.19-0.2 V under a 50 mA/cm current. Figures 2; references 11 (Russian).

UDC 662.794

Oxidative Destruction of Brown Coal

907m0106C Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 6, Nov-Dec 89 (manuscript received 23 Mar 88) pp 48-51

[Article by A. M. Syroyezhko, A. A. Vikhorev and S. N. Bakulina, Leningrad Technological Institute]

[Abstract] An analysis was conducted on the outcome of oxidative destruction of brown Kansk-Achinsk coal, semi-coke, and oxidized soot using an ozone-air mixture with 4 vol % ozone. The results demonstrated that as a result of ozonolysis the samples sustained loss of carbon and hydrogen, while the concentration of oxygen and nitrogen increased, as did the ash content. Chemical analysis demonstrated formation of saturated mono- (C_2-C_{21}) and dicarboxylic (C_2-C_{15}) acids. The yield of aliphatic dicarboxylic acids reached 49.8% and that of benzene polycarboxylic acids 44%, with the highest levels seen in soot, followed by essentially equivalent levels in semi-coke and commercial coal. References 2 (Russian).

UDC 541.183.5+622.831.32

Coal Breakdown by Carbon Dioxide

907M0106D Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 6, Nov-Dec 89 (manuscript received 14 Nov 88) pp 56-61

[Article by A. V. Astakhov, Ye. B. Vinokurova, M. S. Gasoyan and A. I. Ketslakh, Moscow Mining Institute]

[Abstract] Based on the observation that CO_2 treatment of coal leads to loss of strength, a kinetic analysis was conducted on this process in order to arrive at better understanding of the physical factors underlying this phenomenon. Analysis of the plots of methane release from CO_2-treated anthracite samples demonstrated that a CO_2 pressure of 3-4 MPa at room temperature in the anthracite leads to structural breakdown. Breakdown is attributed to condensation of CO_2, and in turn leads to the release of additional methane. The further release of methane and the related greater penetration of CO_2 serve to perpetuate the breakdown process. Figures 2, references 14 (Russian).

UDC 622.278

Transitional Combustion Phases in Underground Burning of Coal

907m0106E Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 6, Nov-Dec 89(manuscript received 23 Aug 88) pp 79-82

[Article by Ye. I. Gluzberg and A. N. Zasulskiy, Karaganda Polytechhnical Institute]

[Abstract] Mathematical analysis was conducted on the transition phases in underground coal combustion to correlate the rate of oxidation with temperature and concentration of oxygen. The basic approach consisted of solution of a two-dimensional equation describing turbulent diffusion and absorption of oxygen in the process of gasification. Correlation of the macroscopic rate of heterogenous combustion with macroscopic weight loss led to an equation applicable to underground coal combustion. As formulated, the equation may now

be used to model transition states in underground combustion of coal. Figures 3; references 4 (Russian).

UDC 662.61

Experimental Study of Release of Volatile Components from Coal Particles Subjected to Rapid Laser Heating

907m0106F Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 6, Nov-Dec 89 (manuscript received 17 Sep 87) pp 91-96

[Article by A. T. Pyatenko, S. V. Bukhman, V. S. Lebedinskiy, V. M. Nazarov, I. Ya. Tolmachev and E. E. Shpilrayn, Institute of High Temperatures, USSR Academy of Sciences]

[Abstract] An analysis was conducted on the effects of laser intensity on the release of volatile subtances from approx. 100-300 μm coal particles in vacuo due to heating with high-intensity laser beams (LG-43, 10.6 μm wavelength). Analysis of the emission times versus particle size in response to 0.71 and 2.12 MW/cm^2 laser beams showed that the emission times increased linearly with particle size, while the slope of the plot was inversely proportional to the power output. The emission times corresponded to the time required to heat the coal particles to T_m, which in the case of heating with a 2.12 MW/cm^2 laser reaches 1600-1700 K. The specific molar yield of the volatile components was observed to increase as the particle size decreased, with a sharp increase at particle sizes of $<$ 150 μm. Most of the volatile components are released before the temperature of the coal particles reaches 1000°C [sic], regardless of the temperature to which the particle may be heated. On mass basis, the data also demonstrated that the total mass of emitted volatile substances, including tar, was invariate vis-a-vis particle mass. In qualitative terms, the accrued data were interpreted to indicate that as the size of the coal particles diminishes the average MW of the emitted volatile molecules also decreases. Figures 4; references 9 (Russian).

UDC 622.33:66:061

Effects of Autoclave Treatment on Physicochemical Properties of Kansk-Achinsk Brown Coal

907M0106G Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 6, Nov-Dec 89 (manuscript received 24 Jan 88) pp 97-104

[Article by S. S. Budayev, I. V. Aleksandrov, Yu. B. Voytkovskiy, A. G. Yanovskiy and I. I. Kossov, Comprehensive Scientific Research and Engineering Institute of Enriched Solid Combustible Deposits]

[Abstract] The effects of autoclave treatment on the physicochemical properties of Kansk-Achinsk coal were investigated with a view toward improving this source of domestic fuel. The results demonstrated that autoclaving in the case of one sample increased the temperature of combustion from 15.7 to 20.7 MJ/kg, while reducing the moisture content from 33% to 15-18%. Lumpiness was not affected, but there was some increased tendency to self-ignition of the improved coal. Thermal and physicochemical analyses demonstrated phase transition changes in iron-containing components indicative of extensive redox processes and activation of the organic and mineral components. The net effect was the formation of pyrophoric substances that predispose to spontaneous ignition. Figures 1; references 7: 4 Russian, 3 Western.

UDC 613.633:622

Toxicity of Polycarboxylic Acids Produced by Coal Oxidation

907M0106H Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 6, Nov-Dec 89 (manuscript received 20 Dec 88) pp 109-110

[Article by Sh. S. Sarymsakov, R. P. Koroleva, T. A. Litvinenko and T. A. Kukharenko, Institute of Organic Chemistry, Kirghiz SSR Academy of Sciences]

[Abstract] Toxicity studies were conducted on outbred mice (20-22 g) to assess polycarboxylic acids (PCA) in two samples of oxidized coal: brown coal PCA (14.2% mixture of benzene carboxylic acids, 16.7% naphthalene carboxylic acids, 15.3% aliphatic [C_2-C_8] acids, and unidentified components), and lean coal PCA (37.8, 8.3, and 9.9%, respectively.) In addition, a third group of mice was treated with mellitic acid. The animals were injected with 10% aqueous solutions in doses ranging from 700 mg/kg to 2500 mg/kg. The general response pattern was similar in all cases, consisting of an initial stage of excitability and aggressiveness, to be eventually replaced by lassitude and death. Mellitic acid was observed to be the most toxic agent. All animals succumbed over a 7-day period from mellitic acid in a dose of 1500 mg/kg. All animals also succumbed from the brown and lean coal PCA mixtures in a dose of 2500 mg/kg. However, the dose-death relationship demonstrated that the lean coal PCAs were somewhat more toxic than the brown coal PCA. References 7 (Russian).

UDC 662.66:543.227:661.939

Coal Pyrolysis in Inert Atmosphere. Part 2. Broadening Possibilities of Thermogravimetric Analysis

907M0130A Moscow KOKS I KHIMIYA in Russian No 1, Jan 90 pp 2-5

[Article by V. P. Ignashin, N. D. Rusyanova, and A. V. Tenina, Eastern Coal Chemical SRI, Sverdlovsk]

[Abstract] While some regard thermogravimetric analysis as a satisfactory method for determining moisture,

ash, and volatile matter in coals, others feel that it is not as reliable as the more traditional methods. In the present work the capabilities of this method were evaluated in respect to some of the more important characteristics of solid fuels. Coals from various deposits and strata were tested on a DuPont TGA-951. A comparison of the results with those obtained by traditional means indicates that the thermogravimetric method may be used only to determine volatile matter. References 7: 2 Russian, 5 Western.

UDC 662.741.3.001

Effect of Petroleum Products on Shaping Properties of Coke From Mildly Caking and Noncaking Coals

907M0130B Moscow KOKS I KHIMIYA in Russian No 1, Jan 90) pp 15-18

[Article by I. M. Glushchenko (deceased) and O. F. Dolgikh, Industrial Institute, Dneprodzerinsk]

[Abstract] Until recently, petroleum products were selected as caking components for coking without taking into consideration their chemical composition, viscosity, or ecological consequences. Petroleum residues may be separated into two categories, namely, primary (bottoms stock) and secondary (distillates). In the present work the suitability of heavy petroleum products for coking coal was evaluated by taking into account their group chemical composition. The caking properties of primary source oil products may be altered significantly by heat treatment. Secondary source products enhance coking of charges having a high content of mature coals by making it possible to include a greater amount of grade T coal in the lean portion of the charge. Small amounts of primary products may be used in coking grade G coals. Figures 2; references 15 (Russian).

UDC 662.764.074.371

Method for Increasing Level of Hydrogen Sulfide Purging From Coke Oven Gas

907M0130C Moscow KOKS I KHIMIYA in Russian No 1, Jan 90) pp 25-26

[Article by N. K. Smolyakov, Yasinovka Coke Chemical Plant]

[Abstract] In 1988 the quality of coke oven gas produced at the Yasinov Coke Chemical Plant complied with current standards under which the hydrogen sulfide content could not exceed 5 g/m^3. However, the plant's major customer, the Metallurgical Combine imeni S. M. Kirov, did not accept this standard, nor did the Donetsk Ecological Inspection, which issued an order to curtail coke and coke oven gas production unless the hydrogen sulfide content fell below 3.5 g/m^3. This was corrected by installation of scrubbers and a pump to treat the gas with a soda-potash solution at a low pH level to provide adequate contact time for hydrogen sulfide, carbon dioxide, and hydrogen cyanide removal.

UDC 662.741.3.022:622.333

Increasing Effectiveness of Blending Run-of-Mine Coals and Enrichment Plant Concentrates

907M0130E Moscow KOKS I KHIMIYA in Russian No 1, Jan 90 pp 40-43

[Article by A. I. Pluzhnikov, Z. A. Vlasova, L. M. Turchenkov, and M. M. Konarev, Karaganda Metallurgical Combine]

[Abstract] Averaging out the quality of coals by blending at mines and enrichment plants is required to meet established norms. While blending at the mines provides uniform quality to most consumers, practice indicates that the ash content in coals entering coke chemical enterprises varies greatly, which makes it difficult to produce uniform-quality coke unless corrective steps are taken. A study was made of the blending taking place at the Karaganda Metallurgical Combine on run-of-mine coals KZh and G6, which differ significantly from each other with respect to ash content and other indicators. Averaging out of coal properties could be improved by increasing the number of silos in number 1 bunker to 18 and in number 2 bunker to 10. References 3 (Russian).

UDC 662.74:628.56

Reverse Osmosis in Effluent Treatment Processes

907M0130F Moscow KOKS I KHIMIYA in Russian No 1, Jan 90 pp 43-44

[Article by S. A. Grin, Moscow Coke Oven Gas Plant]

[Abstract] Currently available domestic industrial membranes are incapable of providing the required level of separation of cyanides, benzene, or phenol, nor is it likely that reverse osmosis will be effective for this purpose.

UDC 662.74:666.972.162

Coke Chemical Wastes as a Raw Material for Producing Technological Additives Used in Construction

907M0130G Moscow KOKS I KHIMIYA in Russian No 1, Jan 90 pp 44-46

[Article by Yu. P. Chernyshev, L. A. Kozlova, Donets Industrial Building Project, and N. I. Gurzhiy, Phenol Plant]

[Abstract] A schematic is presented for producing an oligomeric additive from naphthalene refining wastes. The additive may be used as a supplement to Dofen, a super plasticizer for concrete used in construction. Figure 1; references 5 (Russian).

UDC 541.1:547.27:542.9

Correlation Between Structure of $C_6H_5CH_2$—O—Ar Ethers and Their Reactivity

907M0269A Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 3, May-Jun 90 pp 25-26

[Article by V. Yu. Korobkov, Ye. N. Grigoryeva, V. I. Bykov et al.; IVTAN]
e dependence between rate constants of thermolysis of ethers (k) and reactivity indicators (N_t), calculated by the Dewar method, was established on the example of $C_6H_5CH_2$—O—AR. At 300 degrees C, $\lg k_{300}=-3.25 N_t+5.29$. This good correlation dependence makes it possible to extend this regularity to any substitutes in the $C_6H_5CH_2$—O—AR structure. Reactivity of the ethers changes within wide limits. Figure 1; references 10: 6 Russian; 4 Western.

UDC 662.66.092

Structure of Kansk-Achinsk Basin Brown Coals, Used to Produce Synthetic Liquid Fuel

907M0269B Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 3, May-Jun 90 pp 3-11

[Article by T. M. Khrenkova and I. B. Krichko; Institute of Combustible Minerals]

[Abstract] A study of Kansk-Achinsk coals to establish the interconnection of their structural parameters and basic indicators of the hydrogenation process (degree of conversion of the organic mass of the coal) by quantitative infra-red spectroscopy involved investigations of 36 samples of brown coal from Itatsk, Berezov, Nazarov, Irsh-Borodinsk and Aban deposits. The study revealed the general regularities and some specific features for coals from these deposits. Data obtained revealed the basic structural parameters of the coals, reflecting specific features of their structure including the level of carbon belonging to aliphatic (methylene and methyl) groups, phenol groups, carbonyl groups, carboxyl groups and the carbon content in condensed aromatic form and the carbon content in undetermined form. Reactivity of the brown coals during liquefaction correlated with the overall fractions of their basic structural parameters. Figures 3; references 13: 12 Russian; 1 Western.

UDC 662.75

Effect of Iron-ore Catalysts in Processes of Hydrogenation of Coal and Polycyclic Hydrocarbons

907M0269C Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 3, May-Jun 90 pp 48-52

[Article by V. I. Sharypov, P. N. Kuznetsov, Ye. D. Korniyets et al.; Institute of Chemistry and Chemical Technology, USSR Academy of Sciences, Siberian Department]

[Abstract] A study of the effect of iron-containing ore catalysts on processes of hydrogenation of brown Kansk-Achinsk coal in a hydrogen-donor solvent, Tetralin, and hydrogenation of model polycyclic hydrocarbons used brown coal mark B-2. Model polycyclic compounds used included naphthaline, anthracene and commercial Tetralin. Oxide and pyrite ore catalysts accelerated hydrogenation of the polycyclic aromatic hydrocarbons. Activity increased in the sequence pyrite)catalysts. The ore catalysts did not reduce hydrogen-donor properties of the solvent in the process of hydrogenation of brown coal in Tetralin. Their catalytic action was attributed to hydrogenation of polycyclic aromatic molecules of thermal destruction of the coal with formation of more active hydrogen donors than Tetralin. The high activity of the pyrite systems in hydrogenation of the coal was attributed to the fact that, besides hydrogenation on pyrrhotine, hydrogenation proceeds with participation of H_2 S. References 15; 1 Russian; 14 Western.

UDC 662.75

Features of Action of Methanol During Liquefaction of Coals of Different Types

907M0269D Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 3, May-Jun 90 pp 53-59

[Article by P. N. Kuznetsov, N. A. Belskaya, T. A. Tomilova et al.; Institute of Chemistry and Chemical Technology, USSR Academy of Sciences, Siberian Section]

[Abstract] A study of liquefaction of some samples of coals differing in origin and stage of metamorphosis and of the reaction of interaction of methanol with model individual inorganic compounds (naphthaline, anthracene, diphenyl) was performed in an autoclave containing 15 g of dry coal with particle size of 0.08-0.20 mm, 20 ml of methanol or toluene at an initial pressure of hydrogen of 5 MPa. The reaction continued for 60 minutes at 380 degrees C. The product yield after liquefaction in methanol differed according to the type of coal used. Sapropelic coals liquified most readily. Alkylation of the aromatic fragments accompanied liquefaction of humus type coals with the degree of alkylation increasing with a decrease of the stage of metamorphism. The type of solvent used had little effect on the degree of conversion of coal. A study of the alkylation reaction of the model substances showed that intermediate particles forming during thermal destruction of coal are alkylated. Figures 2; references 25: 3 Russian; 22 Western.

UDC 661.183.123

Carbon Adsorbents From Products of Solid Fuel Processing

907M0269E Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 3, May-Jun 90 pp 80-85

[Article by Yu. V. Pokonova, L. I. Zavertkina and A. I. Grabovskiy; Leningrad Technological Institute imeni Lensovet]

[Abstract] A study of formation of the porous structure of new crushed adsorbents at all stages of production and study of the sorption properties with different degrees of combustion losses used shale phenols and cracking residue. Analysis of the effect of the ratio of initial components of synthesis of polycondensation on formation of the porous structure of the adsorbents showed that an increase of multi-functional cracking residue in polycondensation and polymerization processes produced an adsorbent with a denser spatial-cross-linked structure with the highest volume of micropores and the lowest volume of macropores. A uniform rate of loss of mass during heat treatment of this polycondensate promoted formation of a porous structure with uniform distribution of the volume of pores in effective radii in the region of mesopores and micropores and narrower distribution of volume of pores in the region of micropores (at high combustion losses). The adsorbent's physical and mechanical properties equalled those of commercial granulated raw material AGS-4, which requires additional production stages. The adorbents surpassed industrial adsorbents in the adsorption properties studied. Figures 4; references 7 (Russian).

UDC 661.183.123

Production and Study of Carbon Adsorbents From Shale Products

907M0269F Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 3, May-Jun 90pp 86-89

[Article by Yu. V. Pokonova, A. I. Grabovskiy and M. S. Oleynik; Leningrad Technological Institute imeni Lensovet]

[Abstract] Some carbon adsorbents based on shale tar and phenols and used as charge components or bonding agents were produced and studied. The products of polycondensation of furfural of shale phenols and resins can be used as basic carbon-containing materials or serve as bonding agents in production of carbon adsorbents with predetermined properties. Use of the liquid products of shale processing ensured production of adsorbents with specific properties of porous structure and surface polarity. The carbon adsorbents produced from shale products may be used for sorption of vapors of organic solvents and gases sorbed only with difficulty from air and sorption of precious metals from solutions. The adsorbents are superior in sorption characteristics to commercial adsorbents. References 6 (Russian).

UDC 678.067.7:66.094.3

Effect of Thermo-oxidation on Properties and Microstructure of Highly-porous Carbon Heat-insulating Material

907M0269G Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 3, May-Jun 90 pp 107-112

[Article by S. V. Garmash, S. D. Fedoseyev, G. M. Butyrin et al.; Moscow Chemical Technology Institute]

[Abstract] A study of the possibility of increasing oxidative resistance and strength of highly-porous carbon heat-insulating material in order to improve the operational characteristics by packing it with pyrocarbon packing was described and discussed. Samples were packed with pyrocarbon packing at 1005 degrees C for 200 hours. Packing of the material improved its operational properties and increased the strength and thermo-oxidate resistance. The study of thermo-oxidation resistance of highly-porous thermal insulation material + pyrocarbon packing, changes of its strength, porosity and microstructure upon oxidation indicated a difference of mechanisms of oxidation at different temperatures. Figures 3; references 10: 6 Russian; 4 Western.

UDC 661.66.2

Features of Multiple Packing of Medium-grained Graphites by Impregnation by Coal Pitch

907M0269H Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 3, May-Jun pp 113-115

[Article by Ye. G. Trofimova, V. A. Chernykh, S. A. Surkov et al.]

[Abstract] Assessment of means of increasing the effectiveness of multiple impregnations and firings involved experiments on industrial blanks of medium-grained graphites of 2 standard sizes, on experimental 80 mm by 120 mm blanks and on 20X20X20 mm cubical samples. Impregnation was performed in industrial autoclaves or on an experimental device by heat treating in special containers fired in commercial kilns. The study determined the change of density, porosity, coke residue and degree of filling of pores for 4 kinds of semifinished articles. Impregnation became less effective when larger blanks were used. The use of a graphitized base for impregnation with impregnation being performed at high pressures was recommended. Decrease of the degree of filling of the pores greatly decreased the effectiveness of packing. Figure 1: references 3 (Russian).

UDC 662.74:546.26

Conductivity of Coal Pitch Melt

907M0269I Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 3, May-Jun 90 pp 116-118

[Article by V. Ya. Posylnyy, V. V. Vitkovskiy, A. M. Bezuglov et al.; Novocherkassk Polytechnical Institute; Shakhtinsk]

[Abstract] Determination of electrical conductivity of medium-temperature coal pitch with temperature of softening of about 65 degrees C in the range of temperatures from its melting point up to the beginning of mesophase transformation (from 130 degrees C to 430 degrees C) used a 4-probe method of measurement. The conductivity curve $\ln \sigma$ was plotted during a rather rapid increase of temperature of the pitch (about 2 degrees

C/minute) which removed, to some extent, the effect of destruction and polycondensation transformations on conductivity. The experimentally obtained dependence of conductivity of liquid pitch showed that σ in the temperature range studied drops by 3 orders of magnitude from 10^{-6} - 10^{-3} $Om^{-1}xm^{-1}$ in the premesophase region and was determined by processes of destruction and dissociation. Figures 2; references 3 (Russian).

UDC 574.32.1

Study of Thermal Conversions of Phenolformaldehyde Binders

907M0269J Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 3, May-Jun 90 126-129

[Article by G. V. Grebenshikova, A. A. Shubin, M. I. Rogaylin et al.; Institute of Combustible Minerals]

[Abstract] A derivatographic comparative study of thermal conversions of phenolformaldehyde resins involved experiments using a derivatograph in the 293-1273 K temperature range in an argon medium with constant rate of increase of temperature of 10 degrees per minute. The study included Novolak (mark SF-010) and thermosetting (SF-340A) phenolformaldehyde resins and carbon compositions based on SF-340A resins and finely dispersed carbon filler. The nature of thermal conversions and coke yields of Novolak and thermosetting phenolformaldehyde resins was practically identical which justified the recommendation of Novolak resin as a substitute for thermosetting resin when the composite subjected to heat treatment does not require rigid fixation of filler particles during pyrolysis of the component. Preliminary hardening of the binder was recommended to increase coke yield during use of thermosetting phenolformaldehyde resin. The use of a hardener was recommended in case of use of Novolak phenolformaldehyde resin. Heat treatment of composites with these phenolformaldehyde binders must be performed at low rates of heating in the 573-923 K range. Figures 4; references 3 (Russian).

UDC 661.66.2

Change of Specific Electrical Resistance of Impregnated Materials

907M0269K Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 3, May-Jun 90 pp 130-133

[Article by Ye. G. Trofimova, S. A. Surkov, V. A. Chernykh et al.;

[Abstract] Determination of the level and significance of change of specific electrical resistance of carbon materials impregnated with pitch showed that the impregnating agents used decreased electrical resistance for all samples. The difference in electroresistance values between impregnated and unimpregnated samples increased with an increase of softening and the level of high-boiling fractions in the pitch. The dependence of the relative change of specific electrical resistance of samples on the level of fraction α_1 suggested the presence of conducting connections in this fraction. The linear nature of this dependence and the high correlation coefficient confirmed the importance of this fraction in change of conductivity. Figure 1; references 4 (Russian).

UDC 549.21

Structure of Plasmochemical Carbon Black

907M0269L Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 3, May-Jun 90 pp134-136

[Article by V. G. Nagornyy, V. F. Pleshakov, V. T. Popov and N. A. Idinov]

[Abstract] Model representaions and calculations used to explain the presence of period 4.26 Angstroms in plasmochemical carbon black involved a study of carbon black produced on a plasmochemical device in a ceramic isothermic reactor by thermal dissociation of benzene in an argon plasma flow and subsequent quench hardening by cold argon. A bivacancy model of the graphite layer similar to an anulene polyconjugated system explained the presence of the 4.26 Angstroms period in the plasmochemical carbon black. A model diffractogram adequately described the actual structure of the plasmochemical carbon black and confirmed the findings of the study. Figures 2; references 5 (Russian).

UDC 338.4:662.732

Technical and Economic Indicators of Processes of Production of Hydrogen

907M0269M Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 3, May-Jun 90 pp 137-140

[Article by O. M. Korolkova, V. M. Antonova, Ye. A. Kolobova et al.; Institute of Combustible Minerals]

[Abstract] Examination of hydrogen production processes based on steam-oxidation and plasma gasification of coals and a thermo-oxidative method revealed the technological advantages and deficiencies of the methods. The studies were conducted in order to reduce energy and material and capital expenditures in hydrogen production and promote development of a process which can compete with natural gas reforming. Economic indicators of hydrogen production by these methods were presented and discussed. The national-economic effectiveness of production of hydrogen from coal by these methods was tabulated and discussed. Profitability from production by the thermo-oxidation method and the plasma gasification method was 20-30 percent lower than profitability from steam-oxidation gasification. Expenditures involved in the methods were ranked as follows (in percent): thermooxidative - 72.2, plasma gasification - 76.7, steam-oxidation gasification - 100 percent. Plasma gasification was most economical in regard to raw material (5.9 tons of coal to 1 ton of hydrogen) but this method requires greater energy expenditure. References 5: 4 Russian; 1 Western.

UDC 661.832.457.541.127

Effect of Ionic Equilibria in Phosphate Solutions on Kinetics of Anode Synthesis of Perphosphates

907M0124A Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 6, Nov-Dec 89 (manuscript received 8 Apr 88) pp 5-7

[Article by B. M. Beglov, Yu. G. Frolov, O. B. Khachaturyan, and I. Yu. Sugurova, Chemistry Institute, Tashkent]

[Abstract] Phosphate salts hydrolyze in aqueous solutions, the degree of hydrolysis varying with the pH. It has been demonstrated that the potassium perphosphate yield diminishes as the duration of electrolysis increases, while the concentration of active oxygen increases continuously. The reasons for this phenomenon, which is characteristic for all peroxide compounds, have been clarified, and one of the basic conditions is electrochemical decomposition of the perphosphate at the anode. In a continuing study of the kinetics of anode oxidation of phosphoric acid salts in electrolytic cells, it was demonstrated in the present work that a high pH value (13.8-14.0) precludes the shifting of hydrolytic ion equilibria and enhances high anion concentrations, thereby increasing the current yield of perphosphate to near the theoretical value. A probable mechanism for the formation of peroxophosphates is presented. Figures 2; references 5: 4 Russian, 1 Western.

UDC 647.8-41

Hydrolytic Stability of Modified Ureaformaldehyde Resin

907M0124D Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 6, Nov-Dec 89 (manuscript received 23 Nov 88) pp 29-31)

[Article by T. M. Mirkamilov, A. A. Abdurakhimov, G. A. Babakhanov, R. Sayfutdinov, and T. Tursunov, Order of People's Friendship Polytechnical Institute imeni Aby Raykhana Beruni, Tashkent]

[Abstract] Polymer binders used in exterior-grade wood products have higher requirements in so far as resistance to moisture is concerned. In the present work a study shows that ureaformaldehyde resins modified with gossypol resin (fatty acid bottoms stock) significantly improves the hydrolytic stability of the resin. Heat treatment of the modified resin increases its resistance to moisture still further. Figures 2; references 4 (Russian).

UDC 541.64+532.135

Effect of Fillers on Anion-Activated Polymerization of ε- Caprolactam

907M0124E Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 6, Nov-Dec 89 (manuscript received 23 Nov 88) pp 31-34

[Article by T. M. Khusanov, A. B. Akhmedov, N. R. Ashurov, and V. N. Volkov, Chemistry and Physics of Polymers Institute, Tashkent]

[Abstract] Reaction casting of large-sized articles by anion-activated polymerization of ε-caprolactam is a modern, cost-effective method of fabricating composition polymeric materials for building purposes. The process is exothermal and has a high polymerization rate, which makes it difficult to employ traditional methods to study the kinetics of formation. In the present work the kinetics of this process was studied by dynamic mechanical spectroscopy and the temperature change during polymerization and crystallization. The compositions contained polycaproamide filled with finely dispersed modified and unmodified ash and wollastonite. γ-Aminopropyltriethoxysilane served as the modifier. The results demonstrated that modification of the filler surface significantly affects the crystallization. Figures 2; references 5: 4 Russian, 1 Western.

UDC 677.4.371.3:532.74

Rules in Preparation of Fibroin Solutions and Their Structuromechanical Properties

907M0124F Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 6, Nov-Dec 89 (manuscript received 23 Nov 88) pp 34-37

[Article by A. L. Khamrayev, D. B. Khudayberdyyeva, S. D. Kamilova, and I. Z. Zakirov, Order of People's Friendship Textile and Light Industries Institute imeni Yu. Akhunbabayeva, Tashkent]

[Abstract] Efficient utilization of nontextile wastes from natural silk production is an important national economic problem. Study of the possible utilization of fibroin waste from natural silk production has followed two basic trends: adding the wastes to fiber-making solutions during the preparation of nitron fiber and dissolving them in a suitable solvent to make artificial fibroin fiber. While natural silk fibroin is soluble in concentrated acids, salt solutions, and other solvents, these solvents are not entirely suitable owing to the drop in molecular weight of the fibroin when in solution. For this reason, aqueous solutions of sodium thiocyanate were used in the present work to study solvation of fibroin as a function of concentration and composition of the solvent, temperature, and time. Rheological properties, surface tension, and fiber-forming abilities of the solutions were determined and optimum process parameters selected for both preparation of artificial fibroin fiber and modification of nitron fiber. Figures 3; references 3 (Russian).

UDC 662.74:628.543.12

Suction Pump Slurries and Ways To Utilize Them

907M0130D Moscow KOKS I KHIMIYA in Russian No 1, Jan 90 pp 37-39

[Article by N. S. Vinarskiy and I. A. Malaya, Coke Chemical SRI]

[Abstract] In addition to phenolic wastes, there are also the suction pump slurries from the coal preparation, coke grading, off-gas treatment, and dust-free coke production operations to consider. Frequently, operation of the suction pump systems is encumbered by clogging in the slurry pipes or the system itself becoming an effluent source. A study was made of the characteristics and quantities of slurries and the particle sizes of the coal and coke slurries to investigate the causes of deposit formation and to develope a closed water supply system. Data from five coke chemical plants are presented and analyzed. Slurries from coal washing and settling tanks could be closed cycled and enriched with technical-grade water. The slurries resulting from coke grading require different types of treatment, depending on the coke quenching method used. If the dry method is used and water hardness is increased, the recycled water must be treated, while if the wet method is used, biochemical treatment of phenolic wastes is possible. Figure 1.

UDC 541.129.13:541.127:546.11.3

Kinetics of Liquid-Phase Heterogenous Protium-Tritium Isotope Exchange in Gaseous Hydrogen. Part I. Experimental Methods and Data Treatment

907m0107A Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 59 No 11, Nov 89 (manuscript received 11 Feb 88) pp 2401-2406

[Article by Yu. L. Kaminskiy, G. P. Akulov, V. G. Kayumov and E. A. Gutina, Radium Institute imeni V. G. Khlopina, Leningrad]

[Abstract] An analysis was conducted on heterogenous isotope exchange of the $RH + {}^3H = R^3H + H^3H$ type of reaction via monitoring of the gaseous hydrogen phase, using negligible concentrations of the labeled reactants in a large excess of hydrogen. This approach favored virtually complete transition of the tritium into the gas phase, simplifying data treatment. Evaluation of isotope exchange between deoxy-D-[1-^{3}H]ribose and hydrogen over 5% PdO/Al_2O_3 catalyst in phosphate buffer, pH 7.0, at 20°C led to a graphically derived rate constant of $(1.72 +/- 0.08) \times 10^{-4}\ sec^{-1}$ (P 0.95). An essentially identical rate constant was obtained by computerized data processing relying on the iterative Gauss-Newton algorithm, with r = $(1.74 +/- 0.04) \times 10^{-4}\ sec^{-1}$. This approach is applicable to a variety of labeled compounds capable of tritium exchange with molecular hydrogen. Figures 2; references 12: 9 Russian, 3 Western.

UDC 547.857.7:546.11.3:541.127

Kinetics of Liquid-Phase Catalytic Heterogenous Protium-Tritium Isotope Exchanges in Gaseous Hydrogen. Part II. Adenine Series Nucleotides

907m0107D Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 59 No 11, Nov 89 (manuscript received 10 Feb 88) pp 2555-2560

[Article by G. P. Akulov, Yu. L. Kaminskiy and N. A. Patokina, Radium Institute imeni V. G. Khlopin, Leningrad]

[Abstract] Kinetic studies were conducted on protium-tritium exchange in hydrogen gas involving the following adenine nucleotides: [8-^{3}H]adenosine-5'-monophosphate (I), [8-^{3}H]adenosine-5'-diphosphate (II), [8-^{3}H]adenosine-5'-triphosphate (III), [8-^{3}H]adenosine-5'-tetraphosphate (IV), di[8-^{3}H]adenosine-5'-tetraphosphate (V), and [8-^{3}H]denosine-3',5'-cyclomonophosphate (VI). The kinetic studies were carried out at pH 8 (phosphate buffer) and pH 10 (carbonate buffer) under 100 kPa hydrogen pressure over three types of palladium catalysts (5% $Pd/BaSO_4$, 5% PdO/Al_2O_3, 10% $PdO/BaSP_4$). The resultant data revealed significant differences in the rates of exchange, which in some cases showed a difference of two orders of magnitude. In the pH range of 8-10, regardless of the type of catalyst, the rates of isotope exchange varied as follows for the compounds under investigation: I < II < IV < V < VI. With low nucleotide concentrations the order of the reaction with respect to nucleotide was unity, while at higher nucleotide concentrations it was close to 0. Figures 3; references 11: 5 Russian, 6 Western.

22161
21
NTIS
ATTN: PROCESS 103
5285 PORT ROYAL RD
SPRINGFIELD, VA 22161

Foreign Broadcast Information Service (FBIS) and Joint Publications Research Service (JPRS) publications contain political, military, economic, environmental, and sociological news, commentary, and other information, as well as scientific and technical data and reports. All information has been obtained from foreign radio and television broadcasts, news agency transmissions, newspapers, books, and periodicals. Items generally are processed from the first or best available sources. It should not be inferred that they have been disseminated only in the medium, in the language, or to the area indicated. Items from foreign language sources are translated; those from English-language sources are transcribed. Except for excluding certain diacritics, FBIS renders personal and place-names in accordance with the romanization systems approved for U.S. Government publications by the U.S. Board of Geographic Names.

Headlines, editorial reports, and material enclosed in brackets [] are supplied by FBIS/JPRS. Processing indicators such as [Text] or [Excerpts] in the first line of each item indicate how the information was processed from the original. Unfamiliar names rendered phonetically are enclosed in parentheses. Words or names preceded by a question mark and enclosed in parentheses were not clear from the original source but have been supplied as appropriate to the context. Other unattributed parenthetical notes within the body of an item originate with the source. Times within items are as given by the source. Passages in boldface or italics are as published.

SUBSCRIPTION/PROCUREMENT INFORMATION

The FBIS DAILY REPORT contains current news and information and is published Monday through Friday in eight volumes: China, East Europe, Soviet Union, East Asia, Near East & South Asia, Sub-Saharan Africa, Latin America, and West Europe. Supplements to the DAILY REPORTs may also be available periodically and will be distributed to regular DAILY REPORT subscribers. JPRS publications, which include approximately 50 regional, worldwide, and topical reports, generally contain less time-sensitive information and are published periodically.

Current DAILY REPORTs and JPRS publications are listed in *Government Reports Announcements* issued semimonthly by the National Technical Information Service (NTIS), 5285 Port Royal Road, Springfield, Virginia 22161 and the *Monthly Catalog of U.S. Government Publications* issued by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

The public may subscribe to either hardcover or microfiche versions of the DAILY REPORTs and JPRS publications through NTIS at the above address or by calling (703) 487-4630. Subscription rates will be provided by NTIS upon request. Subscriptions are available outside the United States from NTIS or appointed foreign dealers. New subscribers should expect a 30-day delay in receipt of the first issue.

U.S. Government offices may obtain subscriptions to the DAILY REPORTs or JPRS publications (hardcover or microfiche) at no charge through their sponsoring organizations. For additional information or assistance, call FBIS, (202) 338-6735,or write to P.O. Box 2604, Washington, D.C. 20013. Department of Defense consumers are required to submit requests through appropriate command validation channels to DIA, RTS-2C, Washington, D.C. 20301. (Telephone: (202) 373-3771, Autovon: 243-3771.)

Back issues or single copies of the DAILY REPORTs and JPRS publications are not available. Both the DAILY REPORTs and the JPRS publications are on file for public reference at the Library of Congress and at many Federal Depository Libraries. Reference copies may also be seen at many public and university libraries throughout the United States.