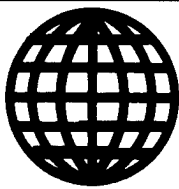


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# ***JPRS Report***

# **Science & Technology**

***USSR: Chemistry***

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# Science & Technology

## USSR: Chemistry

JPRS-UCH-90-009

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UDC 542.2

### Solid-State Sensors in Chemical Analysis

907M0305A Moscow ZHURNAL ANALITICHESKOY  
KHIMII in Russian Vol 45 No 7, Jul 90 pp 1279-1293

[Article by Yu. G. Vlasov, Leningrad State University]

[Abstract] The past decade has witnessed the intensive development of work in the field of researching, creating, and applying solid-state sensors. New sensitive materials have been created for conventional sensors, and new microelectronics-based sensors have been developed in response to the needs of industry, medicine, biology, and agriculture. The literature on sensors is voluminous. In addition to the numerous monographs that have been published worldwide, 340 reports were presented at the 1989 conference on solid-state sensors and actuators that was held in Switzerland. Chemical sensors, which are capable of selectively responding to a change in concentration of some component in liquid or gaseous phases, may be classified with respect to the type of particles they detect (electrons, ions, molecular compounds), the type of membrane used (liquid vs. solid, homogeneous vs. heterogeneous), and the type of material of which the membrane is made (glass, crystal, ion exchange, etc.). Solid-state sensors (those with solid membranes) constitute a significant portion of all existing types of sensors and have the greatest practical value in view of their extended service life, stable performance characteristics, and enhanced mechanical and chemical stability. Research on sensors generally proceeds from the premise that a sensor is a multiphase system including the given phase (solid or liquid) being researched, a sensor membrane, and a contact. Using chalcogenide glass to create the membranes of ion-selective electrodes is particularly promising owing to their structure and physicochemical properties, and their properties and production methods have been examined in detail. The first communication about the possibility of creating solid-state ion-sensitive sensors based on a field-effect transistor appeared in 1970. Since that time extensive work on such sensors has been conducted and reported. Another area that has been researched extensively is that of the mechanism of the functioning of chemical sensors (both chalcogenide glass ion-selective electrodes and ion-selective field-effect transistors). Particular attention has been paid to investigating the formation of a changed surface layer in these sensors by in situ measurements and to studying the mechanism of the functioning of ion-selective field-effect transistor-based sensors with membranes made of  $\text{Si}_3\text{N}_4$  and  $\text{ZrO}_2$ . Figures 15, flowchart 1, tables 5; references 43: 18 Russian, 10 Western, 15 Western works by Russian authors.

### Biosensors in Analysis of Environment

907M0305B Moscow ZHURNAL ANALITICHESKOY  
KHIMII in Russian Vol 45 No 7, Jul 90 pp 1304-1311

[Article by A. A. Tumanov and Ye. A. Korostyleva,  
Chemistry Scientific Research Institute, Gorkiy State  
University imeni N. I. Lobachevskiy]

[Abstract] Biosensors represent a new class of miniature analytical devices in which highly specific biochemical reactions condition an analytic signal related to the concentration of some specified component. As an analytical instrument, the biosensor consists of a sensitive biological element (biologically active substance or bioreceptor) and detection system (converter, detector). The literature describes a number of biosensor designs. Those in which the biological element is in direct proximity to the converter have definite advantages and provide the best metrological and other analytic characteristics. Microorganisms immobilized on a membrane connected with a converter to serve as the biological element of microbial sensors have been described. Amperometric sensors based on an  $\text{O}_2$ -sensitive electrode have been used to determine  $\text{CO}_2$  in wastewater. Other amperometric sensors with immobilized nitrifying bacteria have been developed to determine ammonia in wastewaters and to determine biochemical oxygen demand, which is an important indicator of the pollution of water by organic compounds. Enzymes are widely used as the sensitive elements of biosensors to determine the content of various substances in wastewaters. A new class of biosensor, the immunosensor, has been developed by using antibodies and antigens as the sensitive element in conjunction with electrodes and microelectronics devices. Electrochemical converters (amperometric, potentiometric, ion-selective, field-effect transistors) are the most promising for use in determining the pollution of natural waters, wastewaters, and the air medium in view of their simplicity to manufacture, low cost, and wide-scale accessibility. Microbial, enzyme, and immuno sensors are equally interesting as research objects since they promise to perform diverse analytical tasks. The need to obtain biological components of sufficient purity and in sufficient quantity is currently impeding the application of biosensors, as is the high cost of some biological sensor components. Figure 1; references 48: 11 Russian, 37 Western.

UDC 543.274

### Semiconductor Sensors for Monitoring Make-Up of Gaseous Media

907M0305C Moscow ZHURNAL ANALITICHESKOY  
KHIMII in Russian Vol 45 No 7, Jul 90 pp 1312-1316

[Article by N. P. Maksimovich, D. Ye. Dyshel, L. E. Yeremina, O. K. Kaskevich, G. I. Danyuk, and G. K. Klimenko, All-Union Scientific Research Institute of Analytical Instrument Making and Institute of Materials Science Problems, UkSSR Academy of Sciences, Kiev]

[Abstract] Metal oxide-based semiconductors are currently being widely used to monitor the make-up of the environment and process gases. Their advantages include their high speed, low mass, small overall dimensions, low power consumption, and long service life. They are, however, plagued by low selectivity and instability of their parameters over time. For this reason, the All-Union Scientific Research Institute of Analytical

Instrument Making set out to create a new semiconductor sensor to determine the content of various gases in air and inert media. They determined that tin dioxide alloyed with antimony is a promising material for semiconductor sensors intended to monitor the composition of gaseous media, including hydrogen, hydrogen sulfide, chlorine, and ethanol vapor in air. Figures 5, references 8: 4 Russian, 4 Western.

UDC 543.274

### Using MIS Structure-Based Sensor To Determine Hydrogen in Solids

907M0305D Moscow ZHURNAL ANALITICHESKOY KHMII in Russian Vol 45 No 7, Jul 90 pp 1317-1322

[Article by A. P. Babichev, N. Ye. Babulevich, S. D. Lazarev, S. S. Yakimov, Atomic Energy Institute imeni I. V. Kurchatov, Moscow]

[Abstract] Although chemical sensors are enjoying increasing use in obtaining and processing information about the content of different gases in liquid and gas mixtures, work devoted to researching and creating diagnostic systems based on such sensors is virtually nonexistent. This article describes the efforts made to develop a method for determining hydrogen in solids. The method revolves around using an MIS-sensor based on Pd-SiO<sub>2</sub>-Si as the primary converter. The mechanisms of the sensor's gas sensitivity are as follows. On a surface of catalytically active palladium, hydrogen molecules disassociate into atoms that, upon diffusion into the palladium layer, form a layer of dipoles at the Pd-SiO<sub>2</sub> interface. The action of this layer of polarized hydrogen atoms reduces the output from the palladium, which in turn leads to a change in the structure's capacitance. It is subsequently possible to determine the concentration of hydrogen in the medium not only on the basis of the amplitude value of the change in the grid bias of the C-U characteristic but also on the basis of the value of the derivative of the signal with respect to time  $\delta\Delta U/\delta t$  given only a short time of action of the hydrogen flow on the MIS-structure. The palladium layer gives the Pd-SiO<sub>2</sub> MIS sensor a good hydrogen selectivity. A unit for determining hydrogen in solids has also been developed. Its operability has been demonstrated in an analysis of UO<sub>2</sub> ceramic fuel. The most important of the method's parameters are its detection threshold ( $1 \cdot 10^{-11}$  g) and measurement time (about 15 seconds), which surpass the parameters of other methods conventionally used in performing analytical tasks. Figures 4; references 3: 2 Western by Russian authors, 1 Western.

UDC 543.08

### Piezoelectric Sensor for Determining Mercury Vapor

907M0305E Moscow ZHURNAL ANALITICHESKOY KHMII in Russian Vol 45 No 7, Jul 90 pp 1323-1325

[Article by A. N. Mogilevskiy, A. D. Mayorov, N. S. Stroganova, I. P. Galkina, D. B. Stavrovskiy, L. Spasov,

and D. Mikhaylov, Geochemistry and Analytical Chemistry Institute imeni V. I. Vernadskiy, USSR Academy of Sciences, Moscow, and Institute of Solid-State Physics, Bulgarian Academy of Sciences, Sofia]

[Abstract] The development of methods of determining small concentrations of substances harmful to human health, such as mercury vapors, is becoming increasingly important as ecological problems increase. One promising method of developing such sensors is to use the piezosorption method. This method is based on using the dependence of the natural frequency of a piezoquartz resonator on the mass of the electrodes. In this work the method is implemented by fashioning the quartz resonator's electrodes in the form of a metallic surface onto which a sorption coating is applied. A thin layer of gold serves as a sorption coating. Tests conducted on a large and small quartz resonator (respective resonator diameters of about 8 and 14 mm and respective electrode diameters of about 4 and 8 mm) indicate that such sensors may be used to determine small concentrations of mercury vapor in air all the way up to the limit allowable concentration. Both resonators tested were shown to have a frequency instability of about 0.5 Hz in 10 minutes; at the same time, the frequency fluctuations of the small resonators far exceeded those of the larger resonators. The likelihood of a fluctuation of 0.1 Hz in a measurement time of 10 seconds amounted to no more than 20% for a large resonator but was about 40% for a small resonator. The maximum frequency measurement speed for the measuring chamber used in the experiment was about 5 Hz/min at a mercury concentration of about  $1 \cdot 10^{-4}$  g/m<sup>3</sup>. Figures 3; references 5: 2 Russian, 3 Western.

UDC 541.183:541.128

### Semiconductor Sensors for Determining Different Forms of Oxygen

907M0305F Moscow ZHURNAL ANALITICHESKOY KHMII in Russian Vol 45 No 7, Jul 90 pp 1327-1332

[Article by E. Ye. Gutman and I. A. Myasnikov, Physical Chemical Scientific Research Institute imeni L. Ya. Karpov, Moscow]

[Abstract] Despite the positive experience accrued in developing semiconductor sensors for oxygen, detailed research in this field is still necessary in view of the specifics of determining different forms of oxygen (non-excited molecules and atoms as well as electron- and vibration-excited molecules). Semiconductor sensors for detecting different forms of oxygen that are based primarily on measuring the electrical conductance of metal oxides have found extensive use in scientific research and in various practical applications. The present work discusses the development of semiconductor sensors to determine oxygen molecules in different gases and oxygen atoms in the earth's upper atmosphere. Polycrystalline sintered metal oxide films are found to be the most suitable material for sensitive elements to detect different forms of oxygen. Their advantages include high



sensitivity, simplicity to produce, and operating reliability. Gas, vapor, and liquid methods of detecting nonexcited oxygen were tested. A continuous computer method and versions of sensor operation in saturated vapors of liquids with different dielectric constants at room temperature are proposed for determining nonexcited oxygen. Selectivity in determining one active form of oxygen or another is achieved in different ways. For example, differential sensors operating either on the principle of the different behavior of atoms and molecules in specimens of an adsorbent or on the principle of the reactivity of molecules and atoms during adsorption have been developed for separate determination of atoms and molecules. Selectivity in determining atomic oxygen in the presence of atomic hydrogen is achieved by the method of diffusion alloying of zinc oxide with zinc atoms coupled with continuous monitoring of selectivity as the alloying proceeds. Selectivity of the method of determining vibration-excited oxygen in an oxygen-containing medium entails using different oxygen particle-passing filters and restraining other possible active particles. Figures 4; references 8: 7 Russian, 1 Western.

UDC 543.426:543.37

#### Luminescence Sensors To Detect Oxygen in Gases and Water

907M0305G Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 45 No 7, Jul 90 pp 1333-1337

[Article by T. I. Grishayeva and A. I. Zakharov, Leningrad Technological Institute imeni Lensovet]

[Abstract] Various luminescence sensors for determining oxygen in gases and water currently exist. They represent a base into which a luminescing activator has been introduced, and their operation is based on the irreversible reduction in the intensity of the luminescence in the presence of oxygen. Solid disperse sensors in which the activate is introduced into sorbents with a developed specific surface, for example, into silica-based sorbents, are more promising for the sensitive and inertialess determination of oxygen. The silica sorbent-based sensors described in this article have a limit of detecting oxygen in gases amounting to several percent when the principle of the reduction in their fluorescence is used as the basis for the determination. This detection limit becomes  $10^{-7}$  to  $10^{-6}\%$  when their afterluminescence is used. The detection limit for oxygen dissolved in water can reach  $1 \cdot 10^{-1}$  mol/l when the afterluminescence of the immersed sensor is used. The oxygen sensitivity of the sensor developed may be controlled by changing the nature of the activator and the structure of the sensor matrix. Figure 1, tables 2; references 8 (Russian).

UDC 543.274

#### Determining Hydrogen Selenide in Gas and Liquid Media by Semiconductor Chemical Sensors

907M0305H Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 45 No 7, Jul 90 pp 1338-1347

[Article by S. A. Zavyalov, V. Ya. Sukharev, L. M. Zavyalova, I. A. Brovko, I. A. Myasnikov, and N. M.

Kuzmin, Physical Chemical Scientific Research Institute imeni L. Ya. Karpov, Moscow, Samarkanda State University imeni A. Navoya, and Geochemistry and Analytical Chemistry Institute imeni V. I. Vernadskiy, USSR Academy of Sciences, Moscow]

[Abstract] Controlling the content of gas microimpurities in process gases, air at industrial sites, and the air basin of cities is a most critical problem. Semiconductor chemical sensors are promising in this respect. This article reports the development of a method for determining hydrogen selenide in hydrogen. The method is based on the use of a semiconductor chemical sensor, i.e., a layer of zinc oxide applied onto a quartz base. Saturating the gas phase with vapors of a polar solvent (water is best) permits the production of irreversible signals from the sensor even at room temperature. It takes 1 minute to obtain an analytic signal in a kinetic determination mode. The limit of detecting hydrogen selenide in hydrogen saturated by water vapors is  $1 \cdot 10^{-5}$  vol%. The possibility of determining selenium in aqueous solvents by combining the technology of hydride formation and determination based on the change in the electrical resistance of a ZnO transducer is demonstrated. The lower limit of detectable concentrations of selenium in solution is 1.5  $\mu\text{g}$ . The sensitivity of the instrument developed to As, Bi, Sb, and Te, the hydrides of which are formed under the very same conditions as  $\text{H}_2\text{Se}$ , are also estimated. When 50  $\mu\text{g}$  of these elements is introduced into a solution (50-fold greater than the amount of selenium), no systematic errors are present. Figures 8; references 16: 14 Russian, 2 Western.

UDC 543.274

#### Gas-Sensitive Sensors Based on Bismuth Ferrites

907M0305I Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 45 No 7, Jul 90 pp 1349-1354

[Article by A. S. Pogosyan, G. V. Abovyan, V. M. Arutyunyan, P. B. Avakyan, and S. O. Mkrtchyan, Yerevan Polytechnic Institute and Yerevan State University]

[Abstract] A wide range of metal oxide semiconductors have been investigated as possible gas-sensitive materials for ceramic and film gas sensors.  $\text{SnO}_2$ ,  $\text{TiO}_2$ ,  $\text{ZnO}$ , and  $\text{Fe}_2\text{O}_3$  are used most frequently. The present article reports the results of experimental research on the gas sensitivity characteristics of three bismuth ferrites,  $\text{Bi}_2\text{Fe}_4\text{O}_9$ ,  $\text{Bi}_4\text{Fe}_2\text{O}_9$ , and  $\text{BiFeO}_3$ , which were examined from the standpoint of new materials for semiconductor gas sensors. The three bismuth ferrites were used as the material for sensors to determine ethanol, acetone, gasoline, and natural gas in air. Sensors made of the three bismuth ferrites were studied from the standpoint of the temperature dependence of their gas sensitivity, the dependence of their gas sensitivity on gas content, and their response time and stability. They were deemed promising materials on all counts considered. It was

hypothesized that the continuous occurrence of irreversible oxidation-reduction processes on the surface of the specimens, at the grain boundary, and on the surface of the ceramics's pores while the specimens are in an active gas atmosphere is responsible for the gas sensitivity of the ceramic specimens studied. Detailed study of the mechanism of the bismuth ferrites' gas sensitivity will require research on the kinetics of the reactions occurring on their surfaces and analysis of the products formed. Figures 5, table 1; references 9: 1 Russian, 8 Western.

UDC 541.135:547.29

#### Use of Lewis Acids as Anion-Selective Ligands in Membranes of Film Ion-Selective Electrodes

907M0305J Moscow ZHURNAL ANALITICHESKOY KHMII in Russian Vol 45 No 7, Jul 90 pp 1364-1371

[Article by T. Ya. Bart, V. S. Karavan, A. L. Grekovich, N.A. Ampilogova, V. Ye. Yurinskaya, and V. A. Nikoforov, Leningrad State University]

[Abstract] This article reports a study that was conducted to assess the possibility of using carbonyl compounds as hard Lewis acids for selective binding of anions in the organic phase of film ion-selective electrodes. A search was conducted for a specific solvent (ligand) suitable for the binding. During the study, 26 ligands were synthesized. Trifluoroacetophenone derivatives and ketonitriles in which the carbonyl carbon atom possesses significant electrophilicity were primarily investigated. Of the ligands investigated, hexyl ether of n-trifluoroacetylbenzoic acid (which is capable of plasticizing the membrane's polyvinylchloride matrix and is stable in solutions with different compositions) manifested the best electrode characteristics. It was demonstrated that the selectivity of anions to mono- and dibasic carbonic acids increases as the electrophilicity of the carbonyl group increases. The following composition (concentration in dioctylphthalate) was recommended as the optimal composition for the membrane of an acetate-selective electrode: 0.1 mol/kg ion exchanger (tetradecylammonium acetate) and 1 mol/kg of the ligand 20 in the study, which ensures linearity of the electrode function in the interval from  $5 \cdot 10^{-5}$  to 5 mol/kg  $\text{CH}_3\text{COONa}$  in the absence of an effect of pH in the range from 5.5 to 10. Tables 6; references 21: 18 Russian, 3 Western.

UDC 543.257.2

#### Lead- and Thallium-Selective Electrodes Based on Vanadium Oxide Bronzes

907M0305K Moscow ZHURNAL ANALITICHESKOY KHMII in Russian Vol 45 No 7, Jul 90 pp 1375-1380

[Article by T. V. Velikanova, V. L. Volkov, V. M. Zhukovskiy, and T. V. Sarapulova, Ural State University imeni A. M. Gorkiy and Chemistry Institute, Ural Department, USSR Academy of Sciences, Sverdlovsk]

[Abstract] Thanks to their relative chemical stability in solutions with a pH between 2 and 7, their high electronic conductance, and significant mobility of their interstitial ions, type  $\beta$  vanadium oxide bronzes with the general formula  $\text{M}_x\text{V}_2\text{O}_5$  are promising materials for manufacturing ion-selective electrodes. Completely solid ion-selective electrodes based on oxide vanadium bronze for determining H, Li, Ag, and Cu ions currently exist. The present article reports a study of Pb(II)- and Tl(I)-ion-selective electrodes based on type  $\beta$  oxide vanadium bronzes. The dependence of the potential of these electrodes on the concentration of potential-determining ions was studied in the concentration range from  $1 \cdot 10^{-6}$  to  $1 \cdot 10^{-1}$  M  $\text{Pb}(\text{NO}_3)_2$  or  $\text{TlNO}_3$ . When lead and thallium were determined in the presence of copper, results that were satisfactory from a precision standpoint were obtained with a Pb:Cu ratio of 1:50 and a Tl:Cu ratio of 1:10. The selectivity of the oxide vanadium bronze-based electrodes studied and their low sensitivity to the presence of Cu, Ca, Sr, and Ba makes them promising for analysis of high-temperature superconductors. It was also deemed possible to use the electrodes in both film and solid-phase versions as indicator electrodes during the potentiometric titration of lead (II) and thallium (I) alone and together, as well as in solutions containing copper (II). Figures 3, tables 4; references 6 (Russian).

UDC 541.135.5:543.257.1

#### Chalcogenide Glass Electrodes for Determining Lead, Cadmium, and Iodine Ions

907M0305L Moscow ZHURNAL ANALITICHESKOY KHMII in Russian Vol 45 No 7, Jul 90 pp 1381-1385

[Article by Yu. G. Vlasov, Ye. A. Bychkov, A. V. Legin, and M. S. Miloshova, Leningrad State University]

[Abstract] Crystalline composites based on a mixture of silver sulfides and a respective metal (cation-selective electrodes) and a mixture of silver sulfide and a respective halide (halide-selective electrodes) are the most popular materials for the membranes of the ion-selective electrode that are currently series produced. The chemical properties of such materials result in specific shortcomings in the ion-selective electrodes based on them, including the unsatisfactory stability of the performance characteristics and short service span of Cu-, Pb-, and Cd-selective membranes in acid and aggressive media and the low sensitivity of Cd-sensitive electrodes in the presence of doubly charged cations. Chalcogenide glass electrodes, on the other hand, are superior from the standpoint of their stability in aggressive media, their working pH range, and their selectivity. Work was therefore undertaken to develop and investigate the properties of new chalcogenide glass-based ion-selective electrodes for determining lead, cadmium, and iodine. The glasses were synthesized by using the method of vacuum melting in evacuated quartz ampules made of especially pure components and their compounds, and the electrodes were manufactured and tested in accordance with

a technique described elsewhere. The lead-selective electrodes developed on the basis of germanium glasses surpass existing electrodes with respect to their chemical stability and working pH range, the cadmium-selective electrodes developed have a selectivity to cadmium in the presence of discharged ions that is 10 to 1,000 times greater than that of existing electrodes, and the iodine-selective electrodes developed possess superior stability in strong acid and oxidizing media. Figures 3, table 1; references 12: 6 Russian, 6 Western by Russian authors.

UDC 541.61.183.12

### Polymer Coatings for Electrodes in Biosensors

907M0305M Moscow ZHURNAL ANALITICHESKOY KHMII in Russian Vol 45 No 7, Jul 90 pp 1401-1404

[Article by T. S. Lebedeva, A. A. Rakhnyanskaya, V. S. Pshezhetskiy, V. I. Yefremenko, S. V. Stolbin, and A. G. Timokhov, Moscow, Moscow State University imeni M. V. Lomonosov]

[Abstract] The operating reliability and stability of potentiometric-type sensors depends largely on the quality of the electrode on the surface of which the reaction occurs. Creating a polymer coating on an electrode's surface often improves the performance characteristics of such devices. A study was conducted to produce and study polymer coatings for biosensor electrodes manifesting the following: high adhesion to the metal, maintenance of contact with the liquid medium, lowest possible nonspecific adsorption of proteins and cells, and good dielectric properties. In addition, the surfaces of such films should contain reactive functional groups for immobilized proteins. The polymers for the study were produced by radical polymerization in solution in the presence of azobisisobutyronitrile and in a low-pressure plasma reactor. Their chemical make-up was determined by IR spectroscopy, and the number of immobilized proteins of the polymer surface was determined by measuring the level of surface radioactivity. The antigen-antibody reaction was registered on the basis of a secondary antibody labeled with  $^{125}\text{I}$  and in a potentiometric-type biosensor. Of the various classes of coatings synthesized, those obtained from polyacetals containing acetate and hydroxyl groups in addition to lactone cycles of varying nature were found to be best from the standpoint of high adhesion to metal and maintenance of contact with the liquid medium. It was not possible, however, to produce coatings that were uniform with respect to thickness or film quality. Coatings that, for practical purposes, met all of the aforementioned requirements were successfully obtained by polymerization of several monomers in high-frequency low-temperature plasma. The plasma polymerization method was used to produce coatings of polyacrolein, polyacrylic acid, and polyallylamine. The coatings developed possessed stable signal reproducibility, adequate reaction specificity, and sufficient signal-recording speed. Figures 4, table 1; references 2: 1 Russian, 1 Western.

UDC 541.13:577.15.004.14

### pH-Sensitive FET Transistor-Based Glucose Biosensor Dependence of Biosensor's Response on Composition of Solution Analyzed

907M0305N Moscow ZHURNAL ANALITICHESKOY KHMII in Russian Vol 45 No 7, Jul 90 pp 1410-1409

[Article by A. P. Soldatkin, A. K. Sandrovskiy, A. A. Shulga, N. F. Starodub, V. I. Strikha, and A. V. Yelskaya, Molecular Biology and Genetics Institute, UkSSR Academy of Sciences, Kiev, and Kiev State University imeni T. G. Shevchenko]

[Abstract] This article, which is an extension of a study published in early 1989, examines the effect of the composition of the solution undergoing analysis on the functioning of a pH-sensitive field-effect transistor [FET]-based glucose biosensor. The sensors in question are semiconductor chips with a differential pair of pH-sensitive FETs on each of them. Their design and assembly is described elsewhere. Sensors with membranes having different thicknesses were produced. In the first the membrane was about 30  $\mu\text{m}$  thick, and in the second it was less than 5  $\mu\text{m}$  thick. The response time of the latter was 30 to 40 times higher than that of the former. In the case of the thicker membrane, the nature of the effect of the ionic strength of the analyzed solution on the amplitude of the biosensor's response was nearly linear. In the case of the thinner membrane, the ionic strength of the solution had no effect. A procedure was recommended for using the sensor developed to measure the glucose concentration in whole blood. It entails diluting the whole blood to 1/20 to arrive at the glucose concentration range in a solution of 0.2 to 2.0 mM, which corresponds to the biosensor's working range. NaCl is added to a final concentration of 150 mM to create the required ionic strength in the buffer solution. There is no need for calibration of the sensor to obtain a strict pH value or to titrate the solution to a specified pH value. Figures 5, table 1; references 9: 3 Russian, 6 Western.

UDC 543.8

### Determining Galactosides by Using Potentiometric-Type Biosensor Based on Immobilized -Galactosidase

907M0305O Moscow ZHURNAL ANALITICHESKOY KHMII in Russian Vol 45 No 7, Jul 90 pp 1421-1425

[Article by A. V. Pshezhetskiy, T. S. Lebedeva, A. A. Rakhnyanskaya, V. M. Polushkin, and V. S. Pshezhetskiy, Moscow State University imeni M. V. Lomonosov]

[Abstract] In a number of cases it is impossible to use conventional analytical chemistry techniques when developing express and high-sensitivity methods of determining different biologically active substances.

This is especially true in clinical diagnosis, which frequently necessitates a determination of specific metabolism products against the background of preponderant quantities of their chemical analogues. This problem may be solved by using new-generation sensors, i.e., biosensors based on the unique capability of biological objects to recognize one another. The present study was undertaken to create a biosensor to determine  $\beta$ -galactosides, including those in  $\beta$ -galactose-containing disaccharides and glycolipids. The operation of the sensor in question is based on the change in the potential of the electrode on which  $\beta$ -galactosidase is immobilized as a result of the latter's reaction with the galactoside present in the solution.  $\beta$ -Galactosidase obtained from *Penicillium canescens* was used for the immobilization. The resultant enzyme manifested catalytic activity with respect to substrates of two different human enzymes,  $G_{MI}$ -galactosidase and galactocerebrosidase. Because of this activity, the enzyme and hence the method is suitable for use in diagnosing diseases related to congenital galactosidase insufficiency. Figures 3, tables 2; references 8: 4 Russian, 4 Western.

UDC 543.8:577.15.08

#### Characteristics of Enzyme-Containing Membranes for Biosensors

907M0305P Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 45 No 7, Jul 90 pp 1426-1431

[Article by L. P. Kuznetsova, L. I. Kugusheva, Ye. B. Nikolskaya, and O. V. Yagodina, Evolutionary Physiology and Biochemistry Institute imeni I. M. Sechenov, USSR Academy of Sciences, Leningrad]

[Abstract] The analytic characteristics of enzyme sensors, including enzyme electrodes and enzyme field-effect transistors, are essentially dependent on the properties of the enzymes immobilized on their surface. The changes in an enzyme's properties that normally occur during immobilization must be considered when using an enzyme for analytic purposes. Since including enzymes in gel membranes is one of the most popular methods of creating enzyme sensors, a study was conducted to examine the properties of gel membranes containing the following: monoaminoxidase from rat liver mitochondria (I), acetylcholinesterase from human blood erythrocytes (II), butyrylcholinesterase from equine blood serum (III), and cholinesterase from the heads of *Callifora vicina* L. blow flies (IV). The enzymes were immobilized according to a previously described method. The enzyme-containing membranes were placed in a thin capron mesh, the edge of which was secured between two rings that fit tightly into one another. The stirrer of a magnetic mixer was fastened to one side of the mesh, and the unit was placed in a buffer solution for 1 hour to swell the membrane and was then used in tests with substrates and inhibitors. The tests conducted revealed that immobilizing enzymes in gel membranes increases their stability during storage and use. This effect was most evident in the case of enzymes

(I) and (IV). Immobilization in gel membranes also changed the catalytic properties of enzymes and, hence, their analytic properties, and it attenuated the effect of irreversible inhibitors on the enzymes studied. The effect of irreversible inhibitors on immobilized cholinesterase was shown to depend not only on the nature of the enzyme and inhibitor but also on the nature of the substrate. These changes must be taken into account when gel membrane-immobilized enzymes are used in analytic applications. Figure 1, tables 3; references 11: 7 Russian, 4 Western.

UDC 543.21

#### Investigation of Gravimetric Biosensors

907M0305Q Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 45 No 7, Jul 90 pp 1446-1451

[Article by V. V. Yerokhin, R. L. Kayushina, P. N. Gorkin, I. N. Kurochkin, B. N. Popov, and S. F. Chernov,

[Abstract] It is known that the resonance frequency of the oscillations of a piezoelectric crystal shift upon a change in the mass on the resonator's surface. Piezoelectric resonator-based gravimetric sensors for determining different gases and other chemical compounds have been studied, and piezoelectric resonators have recently begun to be used as the detecting elements of biosensors. The key problem in creating biosensors in general and gravimetric biosensors in particular is that of the creation of a stable biospecific surface. One possible way of solving this problem is to apply oriented monomolecular films of antibodies, enzymes, and purified receptors onto the surface of the dielectric element. This article studies gravimetric biosensors using monomolecular layers of antibodies produced by the Langmuir-Blodgett and Langmuir-Shaffer methods on the surface of their piezoelectric resonators. It is shown that the formation of monomolecular layers of antibodies maintain their specificity and may be used in creating microgravimetric biosensors based on piezoelectric resonators. Investigation of the effect of the experimental condition on the contribution of nonspecific sorption to the shift in the sensors' resonance frequency shows that increasing the temperature of the incubation medium of a gravimetric immunosensor results in an increase in nonspecific sorption of the components of the buffer solution, increasing the temperature of washing in distilled water reduces the measured level of nonspecific sorption (an increase in the immunosensors' resonance frequency is observed at washing temperatures above 37°C), and increasing the washing time reduces the measured level of nonspecific sorption. Interaction between the respective antigens and monomolecular layers of antibodies significantly modulates the rate of nonspecific sorption in saline solution, thus permitting a significant increase in the sensitivity of gravimetric biosensors. Figures 4; references 9 (Western).

UDC 543.42.062:543.426.547.543

**Extraction-Fluorescence and Extraction-Photometric Determination of Disodium Salt of 4,4'-Dithiobisbenzenesulfonic Acids by Acridine Orange in Wastewaters From Electroplating Shops**

907M0322G Kiev *KHIMIYA I TEKHOLOGIYA*  
in Russian Vol 12 No 8, Aug 90 (manuscript received  
14 Feb 90) pp 721-723

[Article by T. L. Shevchenko, N. F. Falendysh, and A. T. Pilipenko, Colloidal Chemistry and Water Chemistry Institute imeni A. V. Dumanskiy, UkSSR Academy of Sciences, Kiev]

[Abstract] Sulfuric acid copper-plating electrolytes with a complex additive of the disodium salt of 4,4'-dithiobisbenzenesulfonic acid and the nonionogenic surfactant OS-20 are currently used in producing printed circuit boards. The goal of the study reported here was to develop a direct method for determining 4,4'-dithiobisbenzenesulfonic acid concentration in the electrolytes and wastewaters of copper-plating processes. The approach taken to developing a determination method was based on previous research showing that 4,4'-dithiobisbenzenesulfonic acid, which is a rather inert compound that does not react with most metal ions or organic dyes, does form a stable associate with acridine orange and that this associate may be used for photometric and fluorescence determination of 4,4'-dithiobisbenzenesulfonic acid concentrations. Aqueous solutions of  $1 \cdot 10^{-3}$  M acridine orange and 100  $\mu\text{g/ml}$  4,4'-dithiobisbenzenesulfonic acid were studied. Chloroform, benzene, toluene, and butylacetate were tried as extractive reagents. Studies showed that the greatest glow intensity and extract absorption occurred in the pH range from 1.6 to 2.0. The ratio of 4,4'-dithiobisbenzenesulfonic acid to acridine orange in the associate forced was 1:2. OS-20, when present in a 10-fold or greater amount with respect to 4,4'-dithiobisbenzenesulfonic acid, reduces the optical density and glow of the associate 4,4'-dithiobisbenzenesulfonic acid plus acridine orange. A direct relationship between the glow intensity and optical density of extracts was observed within the range of 4,4'-dithiobisbenzenesulfonic acid concentrations from 1 to 80 mg/l. This relationship was used to construct a calibration chart that was in turn used to determine 4,4'-dithiobisbenzenesulfonic acid concentrations in solutions of copper sulfate plating electrolytes and wastewaters from electroplating shops. The analysis was implemented as follows. An aliquot of electrolyte or wastewater containing 4,4'-dithiobisbenzenesulfonic acid in a concentration of at least 1 mg/l was placed in a

25-ml measuring flask, and 0.5 ml  $1 \cdot 10^{-3}$  M acridine orange solution was added. Distilled water was added to the specified mark, a pH of 1.6 was established, 7 ml chloroform was used as an extractive reagent, and either the fluorescence intensity was measured at 522 nm or else the optical density was measured at 500 nm. The concentration of 4,4'-dithiobisbenzenesulfonic acid was then determined by comparison with the calibration chart. The determination procedure developed had a detection threshold of 0.5 mg/l. Figures 2, table 1; references 5 (Russian).

UDC 546.426

**Determining Silicon in Deionized Water by Solid-Phase Spectrophotometry Method**

907M0322H Kiev *KHIMIYA I TEKHOLOGIYA*  
in Russian Vol 12 No 8, Aug 90 (manuscript received  
21 Feb 90) pp 723-726

[Article by A. T. Pilipenko, A. V. Terletskaia, and T. A. Bogoslovskaya, Colloidal Chemistry and Water Chemistry Institute imeni A. V. Dumanskiy, UkSSR Academy of Sciences, Kiev]

[Abstract] The existing photometric method of determining the  $\text{SiO}_2$  level in deionized water, which is based on the reduction of silicomolybdic acid to silicomolybdenum blue by stannous dichloride, permits the detection of more than 10  $\mu\text{g/l}$   $\text{SiO}_2$ . The study reported here improved this detection limit to 1.0  $\mu\text{g/l}$   $\text{SiO}_2$ . This was done by using a surfactant to separate a concentrate of silicomolybdenum blue on a membrane filter in a form suitable for direct photometric determination. The determination was conducted as follows. A quantity of 3.0 ml 1.0 N  $\text{H}_2\text{SO}_4$  and 2.0 ml 5% ammonium molybdate solution was added to 200 ml of the deionized water undergoing analysis. The solution was left for 10 minutes to form silicomolybdic acid. Added next were 8.0 ml 8.0 N  $\text{H}_2\text{SO}_4$  and 2.0 ml of a 4% solution of ascorbic acid. After 10 minutes, 0.5 ml of a 0.5% solution of cetylpyridinium chloride (or an analogous surfactant) was added to the solution of silicomolybdenum blue. The solution was vacuum-filtered through a membrane filter and washed with water until a weakly acidic reaction occurred (30-50 ml). The filter was dried out, and the coloration intensity of the spot was measured on a color comparator. The silicon content was determined on the basis of a calibration chart plotted by using standard silicon solutions. A detection limit of 1.0  $\mu\text{g/l}$   $\text{SiO}_2$  in a 0.2-l sample was achieved. From a sensitivity standpoint, the method of solid-phase spectrophotometry with membrane filtration surpasses all other methods of determining silicon concentration that are recommended for analysis of deionized water. Figures 3, tables 2; references 17: 9 Russian, 8 Western.

UDC 666.652.4:549.76

**Catalytic Properties of Polycation Forms of Type X Zeolites in Reactions of Alkylation of Isobutane by Butenes**

907M0303D Moscow *KHIMICHESKAYA  
TEKHOLOGIYA* in Russian No 4, Jul-Aug 90  
(manuscript received 26 Oct 87) pp 9-13

[Article by I. N. Tsupryk, P. N. Galich, K. I. Patrilyak, and I. A. Manza, Bioorganic and Petrochemistry Institute, UkSSR Academy of Sciences]

[Abstract] The process of producing isooctane (the high-octane component of gasoline) by alkylation of isobutane by butenes in the presence of solid catalysts has recently captured researchers' interest. Heterogeneous catalysts are, however, plagued by the flaw of nonselective occurrence of the process. This article examines the effect of the nature of exchange cations on the process of the alkylation of isobutane by butenes. The zeolite NaX, which was produced by the Grozno Scientific Research Institute without binders and which had a silicate modulus of 2.7, was used for the studies. The ion exchange was implemented by nitric acid salts of the respective metals in the following order: first potassium, then lanthanum, and finally (after calcining at a temperature of 500-600°C for an hour)  $\text{NH}_4^+$ . Cation-exchange forms

containing  $\text{NH}_4^+$  were placed directly in the reactor during the activation process, thereby producing a decationated form. The latter's catalytic properties were studied on a previously described unit by a method described yet elsewhere. The products were analyzed by gas-liquid chromatography. A total of 23 specimens were subjected to tests involving alkylation of isobutane by butylenes on cationic and on polycationic forms of type X zeolites (8 specimens were tested on cationic forms, and 15 were tested on polycationic forms). It was found that increasing the  $\text{Ca}^{2+}$  content by a corresponding reduction of the  $\text{Na}^+$  with the  $\text{NH}_4^+$  and  $\text{La}^{3+}$  contents remaining virtually unchanged had a positive effect on the catalytic properties of the specimens: the content of unsaturated hydrocarbons and the  $\text{C}_9^+$  in the alkylate decreased, and the ratio of trimethylpentanes to dimethylhexanes increased. The indicators of alkylation on zeolite decreased with the  $\text{Ca}^{2+}$  cation content from 40 to 18%. The process indicators improved as the  $\text{NH}_4^+$  content in the zeolite was increased to 30%. It was thus shown that introducing cations with different natures into the zeolite has a mutual effect or a unique type of synergetic effect on the formation of the catalytic properties of the polycationic forms studied in an alkylation reaction. This synergistic effect was found to depend on the chemical nature of the cations and on the specific order in which they were introduced into the zeolites. Figure 1; references 12 (Russian).

UDC 549.67-66.094.403

**Alkylation of Isobutane by Butenes on Zeolite Catalysts. I. Operating Mode of Catalyst Layer and Process Indicators**

907M0303A Moscow KHIMICHESKAYA  
TEKHNOLOGIYA in Russian No 4, Jul-Aug 90  
(manuscript received) pp 28-31

[Article by A. A. Galinskiy and V. I. Kashkovskiy, Bioorganic and Petrochemical Chemistry Institute, UkSSR Academy of Sciences, Kiev]

[Abstract] The process of alkylating isobutane by butenes is widely used in industry to produce strongly branched paraffin hydrocarbons, which are high-octane motor fuel components. One promising class of heterogeneous catalysts for the alkylation process is that of zeolites containing REA<sup>3+</sup> (REA being rare-earth elements), H<sup>+</sup>, Ca<sup>2+</sup>, Pd<sup>+</sup>, etc., cations. In the case of a homogeneous process, the main factors affecting the quality of the alkylate are agitation and a high molar ratio of isobutane to olefin in the zone in which the raw material makes contact with the catalyst. The latter may be increased significantly by circulating an isobutane-enriched hydrocarbon flow through the catalyst layer. In addition, removing the high-boiling reaction products that accumulate in the lower part of the reactor facilitates more complete transformation of the raw material, improves the quality of the alkylate, and extends the catalyst's stable operating life. This article reports on the development of a reactor device for use in alkylating isobutane by butenes on zeolite catalysts in various modes. The reactor unit developed consists of a reactor (a stainless steel tube with a length of 400 mm and an inner diameter of 22 mm) with a condenser-cooler (length, 100 mm; inner diameter, 8 mm) in its upper part and a lens sealing flange in its lower part. Inside the reactor is a glass tube (length, 350 mm; inner diameter, 14 mm) with a quartz packing on which the catalyst is placed. Thermocouples encased in a 5-mm-diameter steel tube measure the temperature in the layer. Placing the catalyst in different positions (over versus in the isobutane) and changing the point at which the butene was fed it caused the catalyst layer to operate differently. It was determined that the best alkylation indicators are achieved in modes with a suspended catalyst layer. This is evidently related to the intensive heat and mass transfer between the catalyst and raw material and to the even distribution of butenes throughout the volume of the contact, which increases the local isobutane-to-olefin ratio in the catalysis zone. Figures 3, table 1; references 10 (Russian).

UDC 541.183.661.662.73

**Effect of Different Properties of Activated Carbons on Quality of Resultant Chemical Ammonia Absorbers**

907M0303B Moscow KHIMICHESKAYA  
TEKHNOLOGIYA in Russian No 4, Jul-Aug 90  
(manuscript received 28 Aug 89) pp 47-51

[Article by I. A. Tarkovskaya, S. S. Stavitskaya, A. A. Larina, and Ye. A. Farberova, Physical Chemistry Institute, UkSSR Academy of Sciences]

[Abstract] Hydrocarbon absorbers are widely used in protecting the environment against pollution and in the

fine scrubbing of process gases. Despite the progress that has been made in increasing the effectiveness of technical-grade carbons by modifying them with different active substances to give them the capability of chemisorption, few data are available on the link between the quality of activated carbon-based chemical absorbers and the characteristics of the starting carbons. This study reports an examination of the effect of the chemical nature of the surface of activated carbons, the amount and means of introducing the active component, and selected other properties on the sorption activity of activated carbon-based ammonia absorbers. After conducting a series of tests, the authors concluded that the properties of activated carbon-based ammonia absorbers produced by modification with copper salts are largely dependent on the amount and form of copper and on the presence of acid functional groups. In the event of a rather well-developed porous structure, the nature of the initial carbon has relatively little effect on the chemisorption properties of the ammonia absorbers. For conventional activated carbons, increasing the content of water-soluble forms of copper, pretreating the surface with acid solutions, and partially or completely oxidizing it (which is accompanied by an increase in the content of acid functional groups) all help increase dynamic activity with respect to ammonia. In addition, the research conducted revealed that the processes occurring during impregnation of the hydrocarbon sorbents with copper sulfate are complex and ambiguous, thus necessitating further research in this direction. Tables 5; references 12: 13 (Russian).

UDC 666.973.6(088.8)

**Refractory Lightweight**

907M030C Moscow KHIMICHESKAYA  
TEKHNOLOGIYA in Russian No 4, Jul-Aug 90  
(manuscript received 17 Feb 87) pp 90-92

[Article by L. A. Sheynich, Kiev Construction Engineering Institute]

[Abstract] Existing refractory lightweights based on alumina and different sponging agents are characterized by a relatively high mean density, and the process used to manufacture them is rather complicated since it includes porizing the mass and subsequently fixing its structure by annealing at 1,600 to 1,700°C. This article reports research conducted to produce an alumina-containing refractory with a reduced mean density that does not require subsequent special annealing. Chemically pure gibbsite, lime, Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>, CaSO<sub>4</sub>, and commercial superphosphate were used. The ratio of soda solution and solid component in the mixture during the formation was 0.4. Five versions of the mixture were tested. Observations of the swelling of the mass after formation showed that the material's volume increased by a factor of 2 to 2.5. Its average density upon solidification under natural conditions ranged from 500 to 600 kg/m<sup>3</sup> with a

porosity from 70 to 65 percent. The swelling of the material was attributed to the reaction of the gibbsite with the  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ,  $\text{CaSO}_4$ , and soda, which resulted in the liberation of carbon dioxide. It was concluded that the material's average density could be further reduced by using it under conditions of elevated temperatures. The results obtained may be used in insulating equipment against the effect of high temperatures. Technical and economic calculations performed demonstrate that the proposed materials cost 250 rubles/m<sup>3</sup> less than do existing type Sh-0.4 (complexity category I) alumina low- and medium-silicate products. Table 1; references 2: (Russian).

UDC 543.42.62-784.23

### Determining Degree of Contamination of Air Basin By Toxic Substances by Spectrographic Analysis

907M0303G Moscow *KHIMICHESKAYA  
TEKHNLOGIYA in Russian No 4, Jul-Aug 90  
(manuscript received 20 Oct 89) pp 69-73*

[Article by L. A. Fadeyeva, T. V. Verkhoshapova, and Ye. N. Shapa, Physical Chemical Institute, UkSSR Academy of Sciences, Odessa]

[Abstract] This article reports a study undertaken to determine the quantity of solid aerosol components by the method of emission spectral analysis with a limit of detecting individual elements at a level of 0.5 the maximum allowable concentration. The components determined in the study were Cr, Mn, Ni, V, Zn, Co, Ca, Cd, Pb, Al, Cu, Mo, Ti, Zr, and Mg oxides. The main component was  $\text{Fe}_2\text{O}_3$ . The cineration product of AFA-VP-20 filters was analyzed for solid aerosol components. Standard equipment and materials were used for the study, including a DFS-8 spectrograph with a grid of 1,200 lines/mm, an MF-2 microammeter, and OSCh 8-4 graphite powder. Artificial and natural specimens were

found to enter the arc discharge in an identical manner, with the process essentially ending in 60-75 seconds. The analysis method developed entailed preparing reference specimens and a main specimen that represented the sum of the oxides of the components being determined (2.0 mass%) and graphite powder (added in the amount needed to reach 100 mass%), diluting (2- to 2.5-fold) the main reference specimen with graphite powder to produce a series (8 to 10) of reference specimens, mixing each in a 1:1 ratio with iron oxide and NaCl-containing graphite powder, mixing a quantity of no less than 0.005 g solid aerosol component with 0.045 g NaCl-containing graphite powder, and placing the specimens in the craters of six carbon rods. Spectrograms (one from each of the pairs of carbon rods) were then obtained. Photometric measurements were made of the lines, and calibration graphs were plotted to obtain mean value  $x_n$  based on three parallel spectrograms and all the analytic lines. The content of a given element was converted from its mass percent to values in mg/m as described elsewhere. The correctness of the spectrographic analysis method developed to analyze solid aerosol components was assessed by using the "added-found" method and the method of additives. A mean-square error of 0.15 was found for six parallel determinations. For most elements, the maximum yield was in the range from 15 to 30 seconds. Only in the case of titanium was a second maximum observed (it could be explained by the diffusion of the element's atoms from the electrode walls). The spectrographic analysis method developed turned out to be capable of determining 15 impurity elements with a detection limit of  $n \cdot 10^{-3}$  to  $n \cdot 10^{-4}\%$  and a standard deviation of 0.15%. The upper determination threshold was no more than 1.0 mass%, and the lower threshold for most elements was at the level of 0.5 the maximum allowable concentration. The method developed permitted simultaneous monitoring of the environment for up to 13 harmful impurities and may be used when assessing the effectiveness of units being developed to remove solid aerosol components from air. Figures 2, tables 3; references 9 (Russian).



UDC 614.842.6-52.001.5

**Producing of Powder Fire-Extinguishing Powders  
by Mathematical Modeling Method**

907M0303F Moscow KHIMICHESKAYA  
TEKHNOLOGIYA in Russian No 4, Jul-Aug 90  
(manuscript received 30 Jun 89) pp 82-84

[Article by V. A. Levitskiy and N. G. Lantsberg, Karbonat Scientific Production Association, Kharkov]

[Abstract] Powder fire-extinguishing compounds are finely dispersed systems consisting of main components, i.e., inorganic salts with flame-inhibiting properties, and additives that increase their fluidity and prevent caking. This work examines the relationship between chemical and granulometric make-ups and the parameters of the process of manufacturing fire-extinguishing powders. PSB-3 powder (manufactured in accordance with the specification TU 6-18-139-78), i.e., the one most widely used in domestic fire protection, served as the study object. Sodium bicarbonate accounts for 87 to 90% of its mass, additives improving its fluidity and reducing its tendency to cake (nepheline concentrate) account for 7.0 to 11.5% of its mass, and AM-1-300 modified Aerosil

accounts for the remaining 1.5 to 2.5% of its mass. The indicators selected for study were specific surface (in  $\text{cm}^2/\text{g}$ ) and amount of powder residue on a No 0071K sieve after sieving (mass%). According to the powder's specification, the former should range from 3,200 to 4,200  $\text{cm}^2/\text{g}$ , and the latter should not exceed 15 mass%. Test specimens weighing 1.5 kg were produced in an LB-101 laboratory ball mill (capacity, 5.0  $\text{cm}^3$ ). A linear mathematical model with paired interactions of factors was postulated for the specific surface, and an analogous model was adopted for the natural log of the residue in the sieve. The models were then analyzed to optimize the process of producing fire-extinguishing powders. Analysis of the dependencies found shows that the chemical make-up of a powder fire-extinguishing compound and its milling time affect the magnitude of its specific surface. The specific surface of the entire powder fire-extinguishing compound increases as its Aerosil content increases, and in the presence of Aerosil the milling of the component mix proceeds more intensively thanks to grafting of the additive particles onto the freshly formed surface of the sodium bicarbonate particles. Increasing the nepheline concentrate content reduces the indicator specific surface on account of poor erodability. The results obtained indicate the need to introduce the additional production stage of preliminary milling of the nepheline concentrate. Tables 2; references 4 (Russian).

UDC 541.138.3

**Alloy Formation in Case of Electrodeposition of Hafnium on Copper Cathode in Fused Salts***907M0304A Moscow ELEKTROKHIMIYA in Russian Vol 26 No 7, Jul 90 (manuscript received 22 Feb 88; after revision 09 Dec 88) pp 815-818*

[Article by S. A. Kuznetsov, S. V. Kuznetsova, Ye. G. Polyakov, and P. T. Stangrit, Institute of Chemistry and Technology of Rare Elements and Mineral Raw Material, Kolsk Scientific Center, USSR Academy of Sciences, Apatity]

[Abstract] Studying the processes of alloy formation on solid electrodes produces the data needed to implement surface alloying. In the study reported herein the chronopotentiometric method was used to study the alloy formation of hafnium with a copper base as it was electrodeposited from a melt of an equimolar mixture of sodium and potassium chlorides that contained potassium hexafluorohafnate. By using metallographic and x-ray spectral electron probe microanalysis together with scanning electron microscopy, the authors showed that it is primarily a compound with the make-up  $\text{HfCu}_4$  that is formed on the electrode surface in the case of cathodic introduction of hafnium into copper. Thus, alloy formation in the system Cu-Hf can occur not only due to electrochemical introduction but also due to mutual diffusion of the given vapor. It was further established that at a current  $>0.02 \text{ A/cm}^2$ , a hafnium phase is immediately formed on the surface of the copper cathode. A cathode current pulse was therefore fed for 2 minutes to prevent cathode intrusion into the copper base. X-ray spectral microanalysis of the bimetallic composition produced with the electrolysis parameters of the experiment showed the presence of three intermetallic compounds between the copper and hafnium. They were also easily visible on a photo of a transverse microsection of the bimetal taken by an REM-200 scanning electron microscope. Layer 1 (24  $\mu\text{m}$  thick) was close in composition to  $\text{HfCu}_4$ , and layer 2 (8  $\mu\text{m}$  thick) was close to  $\text{HfCu}_3$ . The composition of layer 3 could not be determined owing to its thinness (2-3  $\mu\text{m}$ ). Determination of the change in Gibbs energies of the formation of the intermetallic compounds of hafnium and copper (with the values calculated per mole of alloy at 1,023 K) indicated that the maximum Gibbs energy value occurs in the alloy  $\text{Hf}_2\text{Cu}_3$ . Figures 4, tables 2; references 9: 5 Russian, 4 Western.

UDC 541.138.3

**Initial Stages of Electrocrystallization of Copper Based on Electric Conduction of Precipitated Phase***907M0304B Moscow ELEKTROKHIMIYA in Russian Vol 26 No 7, Jul 90 (manuscript received 30 Jun 88; after revision 13 Oct 89) pp 824-830*

[Article by I. Ya. Kovarskiy, T. A. Arzhanova, and I. V. Kuzmin, Chemistry Institute, Far Eastern Division, USSR Academy of Sciences, Vladivostok]

[Abstract] Research on the electric conduction of coatings makes it possible to draw conclusions regarding

such factors as the nature and density of structural defects and impurities in crystals, the electrochemical behavior of impurities adsorbed on thin-film metal electrodes, and the recrystallization processes occurring during the formation and aging of a precipitate. This article describes the development of a specific method that would be suitable for using the electric conduction of a precipitated phase to study the initial stages of the electrocrystallization of copper and assesses its suitability for developing a more comprehensive description of the initial stages of electrocrystallization on a specific object. The process of the electrodeposition of copper on a type SU-10 carbon glass cathode was selected for study. The electrodeposition was implemented from a working electrolyte containing 1 M  $\text{CuSO}_4$  and 0.5 M  $\text{H}_2\text{SO}_4$  that was first purified according to the accepted method. Type MO copper foil served as the anode, and a copper electrode in working electrolyte served as the standard electrode. The authors examined the distinctive features of the growth and merging of three-dimensional nucleation centers in the conduction change and the dynamics of the change in the precipitate's conduction in thin layers. It was discovered that the time required for occurrence of the first conduction chains, i.e.,  $\tau_0$ , is approximately equal to  $1/i$  in the case of a galvanostatic regimen and approximates the constant  $k_2\eta$  in the case of a potentiostatic regimen. This confirms the fact that in the first case the nucleation centers grow primarily in a horizontal plane, whereas in the second case they grow evenly. The phenomenon of the statistical orderliness of the copper nucleation centers was shown to have an effect on the dynamics of the change in the curves characterizing specific electric conduction ( $\chi$ ) and electrolysis time ( $\tau$ ). Figures 5, table 1; references 9: 8 Russian, 1 Western.

UDC 541.135.5

**Calculating Characteristics of Actual Hydrogen Accumulator-Electrodes***907M0304C Moscow ELEKTROKHIMIYA in Russian Vol No 7, Jul 90 (manuscript received 7 Dec 88) pp 864-868*

[Article by Yu. G. Chirkov and A. G. Pshenichnikov, Electrochemistry Institute imeni A. N. Frumkin, USSR Academy of Sciences, Moscow]

[Abstract] The mass transfer in an individual grain of hydrogen adsorbent-metal has been studied previously. Yet another study has examined such mass transfer for the case of a porous electrode with consideration of the unevenness of the distribution of potential throughout the electrode's thickness. In view of the fact that real hydrogen accumulator-electrodes consist of sets of different-sized grains, the study reported here examined the behavior of models of electrodes with different-sized grains. It was assumed the electrode had  $n$  types of spherical grains and that, overall, it functioned in a

galvanostatic regimen. An absence of diffusion constraints was assumed. The following are among the conclusions drawn from the solutions of the 19 equations included in the article. The charges extracted from the grains are inversely proportional to their sizes. Hence, the smaller the grain, the less it is filled with hydrogen and the lesser the concentration of atoms in the adsorbed layer on the grain surface. The current densities in small-sized grains thus begin to decrease when compared with their initial density value, which is the same for all grains. This reduction becomes more significant as the grain radius decreases. In small grains, therefore, the process of charge extraction gradually slows down. In a galvanostatic charge mode, however, the total charge extracted from an electrode should be constant over time. The only way to compensate for the decrease in charge extraction from small grains is to increase the current density on the large grains. Thus, while the galvanostatic mode is propagated to each individual grain in an "ideal" electrode, in a model allowing for different-sized grains one cannot speak of a galvanostatic mode for individual grains since the current density changes over time. In multicomponent systems only the intermediate grains can have a density that is constant for practical purposes. It is thus demonstrated that determining current transfer requires using the value of the total grain surface, while only the large grains need be considered when determining the diffusion coefficient under quasistationary conditions. References 4 (Russian).

UDC 543.42

#### IR Spectroscopic Characteristics of Surface of Gold Electrode in Solutions With Different pH Levels

907M0304D Moscow ELEKTROKIMIYA in Russian Vol 26 No 7, Jul 90 (manuscript received 11 May 89) pp 869-873

[Article by A. F. Safronov and P. A. Kristensen, Irkutsk State University and Oxford University (Great Britain)]

[Abstract] Most electrochemical reactions occurring on a solid-liquid interface surface are very complex. Because of this there has been extensive discussion regarding the possibility of a technology that could help in obtaining direct information about particles on or around the electrode surface during electrochemical transformations involving the formation of oxygen-containing layers on the surface of noble metal electrodes. Infrared [IR] spectroscopy could be the ideal vehicle for this purpose since it permits in situ collection of data on the molecular specificity of bonds. This article reports a study that used modified commercial IR spectroscopy equipment to obtain information regarding the surface state of a gold electrode in dipeptide-containing alkali phosphate buffer solutions. A Digilab Qualimatic QS100 IR spectrometer with a Fourier transducer, wideband detector, and Global radiation source was used. The spectrometer's working chamber was specially equipped

to accommodate a Specac electrochemical cell. Serving as the working electrode was a gold disk (diameter, 7 mm) pressed into Teflon. A platinum wire mounted on the working electrode's Teflon casing served as the auxiliary electrode. The standard method was used to prepare buffer solutions for alkali phosphate buffer mixtures of  $\text{KH}_2\text{PO}_4$ ,  $\text{NaClO}_4$ , and  $\text{NaOH}$ . The dipeptide used,  $(\text{CysGly})_2$ , was manufactured by Serva. No spherical effects of the presence of the peptide and phosphate ions were observed in the spectrum. Increasing the solution's pH to 11.5 changed the spectrum in comparison with that of neutral solutions; as before, however, no peptide or phosphate ion was active. The external-reflection IR spectrometry method used thus made it possible to establish the key parameters of the formation of oxide layers on the surface of a gold electrode in the system researched under conditions of external polarization. Protonation of the alkali phosphate peptide buffer solution was found to occur only at potentials of 0.2 V or higher; in neutral and acid solutions it remained weak even at  $E = 0.4$  V. Under the conditions researched, the formation of an  $\text{Au}_2\text{O}_3$  layer on the gold electrode's surface may be considered active only at potentials of 0.4 V in alkali solutions. The steady increase in the intensity of the band at  $3,680\text{ cm}^{-1}$  confirmed the formation of an AuOH layer on the electrode surface throughout the entire range of potentials in alkali solutions and its presence (albeit lesser presence) in neutral solutions. Figures 4; references 7 (Western).

UDC 541.138.3:546.57

#### Features of Electroreduction of Cyanide Complexes of Silver

907M0304E Moscow ELEKTROKIMIYA in Russian Vol 26 No 7, Jul 90 (manuscript received 15 Aug 89) pp 876-878

[Article by G. A. Baltrunas, E. I. Morkyavichyus, and A. A. Dikchyus, Vilniyus State University imeni V. Kapuskasa, and Chemistry and Chemical Technology Institute, LiSSR Academy of Sciences, Vilniyus]

[Abstract] Electroreduction of cyanide complexes of silver is accompanied by partial passivation of the surface of the silver electrode. The degree of blocking of the surface under equilibrium conditions depends largely on the content of cyanides and reaches 82% when  $[\text{CN}^-] > 0.345$  M. The study reported herein examined the possibility of the electroreduction of cyanide complexes of silver on blocked sections of the surface. All measurements were taken at room temperature ( $19 \pm 2^\circ\text{C}$ ) by using reagents with the grades "pure for analysis" and "chemically pure." A silver wire that was coated with 6  $\mu\text{m}$  silver from the solution under investigation served as the working electrode. In the electrode polarization range studied the capacitance of the binary layer was varied from 40 to 70  $\mu\text{F}\cdot\text{cm}^{-2}$ , the adsorption capacity was varied from 25 to 45  $\mu\text{F}\cdot\text{cm}^{-2}$ , and the adsorption resistance was kept at about 2  $\Psi\cdot\text{cm}^{-2}$ . The presence of

two waves on the polarization curve of the electroreduction of cyanide complexes of silver was explained in terms of partial passivation of the surface of the electrode with different transfer currents and by the transfer coefficients on active and passive sections of the surface. It was hypothesized that the degree of blocking, particularly in the case of large polarizations, is a function of the electrode's potential, which in turn affects the dependence of  $i^{\text{block}}$  on  $\eta$ . It was acknowledged that the results obtained are very approximate since the small dimensions of the active and blocked sections (diameter, about 10  $\mu\text{m}$ ) result in a nonlinear diffusion of particles that in turn causes less blocking at the edges of a section than in the center. Figures 4; references 5 (Russian).

UDC 543.42

#### Laser-Stimulated Electrodeposition of Gold Onto Copper From Dicyanourate Electrolyte

907M0304F Moscow ELEKTROKHIMIYA in Russian  
Vol 26 No 7, Jul 90 (manuscript received 23 Nov 89)  
pp 888-891

[Article by Yu. V. Seryanov and M. V. Nesterenko, Saratov]

[Abstract] Local gold coatings are used in manufacturing electrical contacts with low resistance under low pressure, for providing surface conduction in microwave products, and as protective coatings for printed circuit boards and microcircuits in microelectronics equipment. The study reported herein sought the optimal conditions for local laser-electrochemical electrodeposition of gold in the form of spots or lines in order to form contact areas or images of the topology of integrated circuits. A laser-electrochemical unit based on an LTN-102 laser (wavelength, 1.06  $\mu\text{m}$ ;  $P \leq 125$  W) that has been described elsewhere was used in the experiments. A standard dicyanourate electrolyte was used for electrodeposition of the gold. Its make-up (in g/l) was as follows: potassium dicyanourate, 12; citric acid, 30; and potassium citrate, 40. It had a pH of 5 (additive, 0.1 N KOH). Copper foil (thickness, 50  $\mu\text{m}$ ) or thin strips of copper-metallized aluminum oxide ceramic (thickness of the metallized layer, 6  $\mu\text{m}$ ; thickness of the base, 1 mm) were used for the cathodes, which had an area of 1.5-3  $\text{cm}^2$ , and platinum foil served as the anode. Measurements were made of the current of the electrodeposition of gold inside the focused laser beam, the diameter of the spot and/or width of the line of gold deposited, and the distribution of the thickness of local deposits. A potentiostatic laser electrolysis mode in which  $E^* = -0.02$  V and  $W^* = 21$   $\text{kW}/\text{cm}^2$  were deemed optimal for selective local laser electroprecipitation of gold from a dicyanourate electrolyte. The yield was close to 100%. The half-width of the lines produced was close to the radius of the focused laser beam, and the latter was determined to be a sufficiently precise instrument for "sketching" the topology of integrated circuits with a linear resolution of about 125 lines/min, which conforms to the

requirements of microwave-range electronic devices. Figures 4; references 8: 7 Russian, 1 Western.

UDC 541.138.2

#### Photoelectrocatalytic Decomposition of Water on $\text{TiO}_2$ Anodes Modified by Metal-Containing Zeolites

907M0304G Moscow ELEKTROKHIMIYA in Russian  
Vol 26 No 7, Jul 90 (manuscript received 28 Nov 89)  
pp 891-894

[Article by Ch. A. Gasanov, A. S. Suleymanov, and D. B. Tagiyev, Inorganic and Physical Chemistry Institute, AzSSR Academy of Sciences, Baku]

[Abstract] In the past few years increasing attention has been paid to processes permitting the accumulation of solar energy by photoelectrochemical and photocatalytic decomposition of water into hydrogen and oxygen. Photocatalysts, i.e., semiconductor materials modified by different methods, are one type of promising and effective photoelectrode. The study reported herein examined the electrocatalytic behavior of polycrystalline  $\text{TiO}_2$  modified by metal-containing zeolites in the photoelectrochemical decomposition of water. A small quantity of ions of the metals Pt, Pd, and Ru (from 0.1 to 0.5 mass%) was added to the zeolite by ion exchange with the use of the respective ammonium complexes. Metal-containing zeolite photoanodes ( $S = 2$   $\text{cm}^2$ ) in the form of tablets made by pressing polycrystalline  $\text{TiO}_2$  with the respective zeolites were heat treated in a temperature interval that would not impair their zeolite structure. To make them conductive the tablets were reduced in a hydrogen atmosphere. Serving as the working electrolyte was 1 N  $\text{Na}_2\text{SO}_4$ . It was hypothesized that the role of the NaY zeolite in the electrode system is reduced primarily to increasing the system's absorbency with respect to water and its fragments on the electrode that participate in the limiting stage of the anodic process. It was further hypothesized that the role of the noble metals is to increase the electrode system's electric conduction and electrocatalytic activity. Both the polarization and capacity characteristics of  $\text{TiO}_2$  modified with metal-containing zeolites were found to differ significantly from those of  $\text{TiO}_2$  itself and the zeolites. The data confirmed that the kinetics and mechanism of the anodic processes occurring both during and without irradiation do not additively depend on the processes on the  $\text{TiO}_2$  and zeolites; instead, the specific features observed result from the interaction of the electrode system's components as reflected in the adsorption and electrodecomposition of water. The noble metals contained in the source zeolite thus had the strongest effect on the photoelectrocatalytic properties of the surface. Figures 4; references 16: 9 Russian, 7 Western.

UDC 541.138:547

### Low-Temperature Electrochemical Synthesis of Perchloric Acid With Stirring of Electrolyte

907M0304H Moscow ELEKTROKHIMIYA in Russian Vol 26 No 7, Jul 90 (manuscript received 24 Apr 89) pp 903-906

[Article by M. M. Flisskiy, Moscow]

[Abstract] Stirring the electrolyte is one of the most popular techniques for accelerating electrochemical reactions. Stirring the electrolyte when producing perchloric acid by oxidizing chlorine-and-acid solutions has not been discussed adequately in the literature. It is therefore examined in the study reported herein. All of the kinetic measurements and balance tests studying the make-up of the resultant anodic electrolysis products, as well as the capacity measurements, were taken under one and the same hydrodynamic conditions, i.e., while stirring the electrolyte in a turbulent mode. During the experiments, the electrolyte was stirred by a magnetic stirrer at 800 rpm. The anode and cathode spaces were separated by a glass diaphragm, and 1,440 coulombs was passed through a cell containing 40 ml of electrolyte. Calculations were made to determine the dependence of the current efficiency of the resultant anode electrolysis products on potential in a solution of  $5N HClO_4 + 0.45N HCl$  at a temperature of  $-30^\circ C$ . The current efficiency of the  $Cl_2$  and  $HClO_4$  were determined directly. The distinctive feature of electrolysis under the test conditions was that, in the range of potentials under investigation, the sum current efficiency of perchloric acid and chlorine was close to 100%, thus confirming the virtual absence of oxygen liberation. Below  $-40^\circ C$  the current efficiency of  $HClO_4$  increases linearly with temperature; below  $-40^\circ C$  the sum current efficiency of  $Cl_2$  and  $HClO_4$  is less than 100%, which indicates liberation of molecular oxygen under these temperature conditions. The interaction of the surface platinum compounds with the discharged chlorine ions was found to be the limiting stage in the anodic reaction of the formation of perchloric acid. It was proposed that at  $E < 2.6 V$  most of the applied jump in potential falls in the layer of adsorbed polarization dipoles not participating in electrochemical reaction at these potentials, whereas when  $E > 2.65 V$  the jump in potential is effective. Figures 3, tables 2; references 5 (Russian).

UDC 541.13.183

### Features of Electrocrystallization of Copper on Carbon Glass

907M0317F Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 63 No 7, Jul 90 (manuscript received 9 Jun 89) pp 1505-1509

[Article by V. A. Belonogiy, V. N. Storozhenko, and Yu. G. Olesov, Dnepropetrovsk Chemical Technological Institute imeni F. E. Dzerzhinskiy]

[Abstract] The high corrosion resistance of carbon glass in acid media makes it suitable for use as a cathode material in electroforming. This work studies the electrocrystallization of copper on carbon glass in sulfate solutions. Experimental  $E$  and  $\tau$  dependencies were derived by the galvanostatic pulse method by using the generally accepted method and measurement technology in a current density range from 0.4 to 20 mA/cm<sup>2</sup> at a temperature of 298 K. A specimen of type SU-2000 carbon glass pressed into Teflon was used as the electrode (cathode) for the study. Copper was electroplated onto its end, after which its surface was polished to a mirror finish. It was then treated in concentrated sulfuric acid for 20 minutes at 298 K and washed in bidistillate. It was discovered that the kinetic dependencies of the electrocrystallization of copper on a carbon glass surface, assuming three-dimensional nucleus formation in the interval from 0.4 to 20 mA/cm<sup>2</sup>, have discontinuities. It was also determined that the electrodeposition of copper at current densities above and below 2 mA/cm<sup>2</sup> occurs in surface sections having different energy states. Figures 4, table 1; references 12: 2 Russian, 10 Western.

UDC 541.135

### Investigation of Dissipative Structure of Processes of Mass Transfer in Electrochemical System With Interelectrode Chemical Reaction

907M0321 Moscow ELEKTROKHIMIYA in Russian Vol 26 No 8, Aug 90 (manuscript received 08 May 86; afterrevision 25 Oct 89) pp 965-970

[Article by N. S. Demidova, Moscow Aviation Institute imeni S. Ordzhonikidze]

[Abstract] A study examined the stability of a matrix electrochemical system that makes it possible to maintain a low partial pressure of  $CO_2$  in a sealed space. The electrode reactions occurring at the cathode and anode in an electrochemical system with an alkaline electrolyte were found to have the following respective forms:  $2H_2O + 2e$  form  $H_2 + OH^-$ , and  $2OH^-$  form  $1/2O_2 + H_2O + 2e$ . The adsorption of carbon dioxide in the interelectrode space was found to result from the  $OH^-$  ions formed and to occur in two stages:  $CO_2 + OH^-$  forms  $HCO_3^-$ , and  $HCO_3^- + OH^-$  forms  $CO_3^{2-} + H_2O$ . The kinetic approach was used to establish the bounds of the occurrence of the system's instability and to thereby classify the structures occurring in the electrochemical system. The dissipative function of an electrochemical system with an interelectrode chemical reaction, i.e., the rate at which entropy occurs, was plotted. The effect of generalized thermodynamic forces on the rate at which entropy occurs at different current densities was investigated. The problem was solved numerically by using a finite-difference approximation. It was proposed that the dissipative function developed be used for quantitative estimation of a rationality of setup that has been selected for a production process since using the function would

permit consideration of the interrelationship between the physical components of processes and external effects through the boundary conditions. Figures 4; references 16: 15 Russian, 1 Western.

UDC 541.138

### Nonstationary Electrochemical Dissolution of Metal in Binary Electrolyte

907M032B Moscow ELEKTROKHIMIYA in Russian  
Vol 26 No 8, Aug 90 (manuscript received 19 Jun 89)  
pp 990-996

[Article by G. R. Engelgardt, A. D. Davydov, and T. B. Zhukova, Electrochemistry Institute imeni A. N. Frumkin, USSR Academy of Sciences, Moscow]

[Abstract] Processes of mass transfer in nonstationary modes are important in many practically valuable areas of electrochemical technology and electrochemical analysis. It is very difficult to arrive at a quantitative description of nonstationary ion transfer under conditions where it is not possible to ignore migration, the concentration dependence of the transport properties of a solution, or other effects that are very important in the occurrence of electrochemical processes in concentrated solutions in the absence of an excess of indifferent electrolyte at high current densities. The study reported herein used several methods to calculate the concentration changes in the near-electrode layer of electrolyte during high-speed anodic dissolution of metals in a nonstationary mode after a specified current had been switched on. A comparison of the results obtained by calculation and by experimentation indicated that a concentration of metal salt exceeding the concentration of a saturated solution is reached at the end of the transition period (by the moment of the jump-like increase in the anode's potential). The degree of supersaturation cannot be precisely established on account of an absence of data regarding the transport properties of supersaturated solutions. It is, however, possible to estimate the minimal degree of supersaturation in a series of specific examples. The authors concluded that a numerical method that considers the distinctive features of the occurrence of ion-transfer processes in concentrated solutions at very high current densities provides the most reliable results regarding the concentration change in a diffusion layer when metals are dissolved under nonstationary conditions. Analytical methods that fail to consider such processes may result in significant errors. Figures 2, tables 4; references 13: 9 Russian, 4 Western.

UDC 541.138.3

### Mass Transfer in Alkali Galvanizing Electrolyte

907M0321C Moscow ELEKTROKHIMIYA in Russian  
Vol 26 No 8, Aug 90 (manuscript received 31 Oct 88)  
pp 1031-1034

[Article by A. G. Kapitonov, V. B. Obratsov, G. A. Ptashnik, and F. I. Danilov, Dnepropetrovsk Chemical Technological Institute imeni F. E. Dzerzhinskiy]

[Abstract] Previous works have shown that alkaline galvanizing electrolytes have a number of properties that make it possible to produce good-quality precipitates at anomalously high current densities. Some authors link this effect to the properties of the adsorption surfactant film formed on the electrode. According to others, zincate electrolytes have high performance indicators because of the formation of colloids and fine suspensions of their compounds discharged on the cathode. Yet others have shown that the electroprecipitation of metals from complex electrolytes at high current densities may be linked to the effect of migration of the reagent and acceleration of mass transfer owing to exaltation of the critical current with respect to the metal upon liberation of hydrogen. The study reported here examined mass transfer in a galvanizing electrolyte consisting of the following components:  $Zn(OH)_2$ ,  $Zn(OH)_3^-$ ,  $Zn(OH)_4^{2-}$ ,  $Zn(OH)^+$ ,  $Zn^{2+}$ ,  $H^+$ ,  $Na^+$ , and  $OH^-$ . The concentration profiles at different current densities were calculated, and it was shown that the  $OH^-$  and  $Zn(OH)_4^{2-}$  ions make the main contribution throughout the entire thickness of the diffusion layer. It was further concluded that, in alkaline galvanizing electrolytes, the role of migration effects is less significant than in systems examined previously. Only at high current densities do they have a negative effect. The main distinction of the system studied was the possibility of switching to kinetic control at high current densities in the absence of surfactants thanks to parallel gas liberation at the cathode (i.e., gas liberation that initiated strong convective currents preventing diffusion control). The critical kinetic current observed was linked with the chemical stage of penetration into the surface layer, which preceded the discharge and was accompanied by partial disassociation of the tetrahydrozincate ions. It was concluded that, under conventional conditions in the absence of strong agitation, the critical kinetic current is concealed owing to diffusion constraints. Figures 4, table 1; references 15: 9 Russian, 6 Western.

UDC 541.13

### Automated System for Electrochemical Measurements in Pulse Mode

907M0321D Moscow ELEKTROKHIMIYA in Russian  
Vol 26 No 8, Aug 90 (manuscript received 09 Jun 89;  
after revision 02 Jan 90) pp 1034-1037

[Article by V. E. Dauyotis, R. P. Raudonis, and G. S. Orshevski, Vilnius State University imeni V. Sapsukas]

[Abstract] A series of units permitting automated recording and processing of experimental data regarding electrochemical objects has been developed. The units, which are based on a DVK-2M microcomputer and CAMAC interface, have expanded the horizons of electrochemical research. In some cases, however, use of the equipment has been limited because of the limitations of the commercially produced PI-50-1 potentiostat that is used as a part of the automated system. The authors of the project reported here designed a potentiostat with a

directly grounded working electrode for use as a component of the aforementioned automated system. The new potentiostat is distinguished by several new components. A single oscillator has been developed to issue single, periodic, or sums of pulsed potentials. This generator was necessitated by the fact that the noise at the output of the module responsible for program control of one of the potential's fed to the adder makes the module difficult to use in individual measurements. The G6-28 oscillator used in the unit has been modified somewhat in view of the need for pulses 20 to 50 ns in duration with a controlled period between them. The system has a maximum digitization frequency of 20 MHz and a buffer capacity of 2 K, thus making it suitable for automating most electrochemical experiments. When the buffer has been filled, its data can be rewritten into a file on a floppy disk. The system's control program has been compiled in the algorithm language Quasic-2. Tests of the device on different circuits of equivalents of electrode processes indicate the capacitance and resistance values found by the new system differ from previously established values by less than 1.5%. The potentiostat developed can help extend the area in which currently available automated systems for gathering and processing electrochemical data may be used. Figures 3; references 11: 6 Russian, 5 Western.

UDC 541.135.2

#### **Predicting Operating Life of Platinized Titanium Anodes for Process of Electrodialysis of Natural Waters**

907M0321E Moscow ELEKTROKHIMIYA in Russian Vol 26 No 8, Aug 90 (manuscript received 9 Jun 89) pp 1037-1040

[Article by L. A. Mikhaylova, L. S. Ivanova, T. G. Bogatskaya, A. B. Rabinovich, and L. M. Yakimenko, Moscow]

[Abstract] Estimating the operating life of platinized titanium anodes when they are used as electrolysers to desalinate natural waters requires comprehensive investigation of the electrodes' corrosion behavior and the dependence of the rate of the platinum coating's dissolution on the following key electrolysis parameters: current density, the electrolyte's salt content, and the electrolysis temperature. Previous research has shown that during the electrolysis of diluted sodium chloride solutions there is a range of process parameters in which a strict correlation between oxygen liberation and dissolution of monolithic platinum or the platinum coating of platinized titanium anodes is observed. The existence of this correlation makes it possible, with a specified degree of precision, to use data regarding the rate of oxygen liberation in making a preliminary estimate of platinum's corrosion behavior. The study reported here used this method to examine the dependence of the wear of the platinum coating of platinized titanium anodes on three key parameters of the process of electrolysis of sodium chloride solutions. The following conclusions

were drawn: 1) the dependence of the wear of the platinum coating on current density is satisfactorily described by an equation of the form  $P = KI^\alpha$ , with the quantity  $\alpha$  depending on the concentration of sodium chloride in the electrolyte; 2) the dependence of the wear of the platinum coating on temperature and electrolyte concentration is exponential in form; and 3) the exponential dependence of the wear of the platinum coating on the electrolyte concentration has an alternate bend at  $c = 1.0$  mass% and is realized throughout the entire current density and temperature range studied. In the specific case studied, platinized titanium anodes used to demineralize waters about 3.4 mass% salt and with an overall chloride content of about 3.1 mass% at an electrolysis temperature of 20°C and a current density of 300 A/m<sup>2</sup>, the platinum coating will wear out at a rate of about 0.11 μm/y. Allowing for a platinum cladding 4 μm thick and a residual thickness of 2 μm, such an electrode will have a predicted life of about 20 years. At a current density of 150 A/m<sup>2</sup> its life will be extended to about 40 years. Tables, 2; references 9 (Russian).

UDC 621.359.7

#### **Electrodialysis of Boron-Containing Solutions Using MB-2 Bipolar Membranes**

907M0321F Moscow ELEKTROKHIMIYA in Russian Vol 26 No 8, Aug 90 (manuscript received 18 Jul 89) pp 1043-1045

[Article by A. T. Pilipenko, V. D. Grebenyuk, and L. A. Melnik, Colloid Chemistry and Water Chemistry Institute imeni A. V. Dumanskiy, UkSSR Academy of Sciences, Kiev]

[Abstract] Previous studies of the transfer of boron through heterogeneous and homogeneous ionite membranes (MK-40, MA-40, MK-41, MA-41L, MA-100, MK-100, MF-4SK, and MK-100M) have shown that boron can migrate through both cation- and anion-exchange membranes. Since the method of electrodialysis with bipolar and cationite membranes is used to cleanse boric acid solutions of the electrolytes present in them, the study reported here examined the laws governing the transfer of boron through bipolar membranes containing cationite and anionite layers. MB-2 bipolar membrane, which was produced by pressing MK-40 and MA-41 heterogeneous membranes, served as the test object. The experiments were conducted in a six-chamber electrodialysis device in which the individual chambers were separated by the following: cationite layer, anionite layer, cationite layer, bipolar membrane, and cationite layer. Five liters of starting solution containing 40 mg/dm<sup>3</sup> boron and 11.7 g/dm<sup>3</sup> sodium chloride was poured into the desalination chamber at a linear speed of 5 cm/s. The solution's pH was controlled by adding 10 mass% solutions of hydrochloric acid and sodium hydroxide. Transfer of boron through the MB-2 membrane was judged on the basis of its concentrations in samples periodically taken from the concentration chamber. The experiments confirmed the previously

published conclusion that transfer of boron through cationite membranes occurs in the form of a  $B^{3+}$  cation, which is the central atom of the complex compounds formed in the membrane phase as a result of the interaction of its functional groups with boric acid molecules. The previously described mechanism of the transformation of boron in sulfocationite membranes was also confirmed. The results obtained here indicate that one possible way of intensifying the process of using bipolar membranes when cleaning boric acid is to select membranes that reduce or virtually eliminate losses of the principal substance. Figure 1, tables 2; references 4 (Russian).

UDC 541.138.52

### Implantation-Modified Platinum and Platinotitanium Electrodes

907M0321G Moscow ELEKTROKHIMIYA in Russian Vol 26 No 8, Aug 90 (manuscript received 11 Dec 89) pp 1048-1050

[Article by L. N. Kulikova, V. N. Fateyev, V. P. Pakhomov, G. F. Potapova, and E. V. Kasatkin, Atomic Energy Institute imeni I. V. Kurchatov, Moscow]

[Abstract] Previous research has shown the effectiveness of using ion implantation, particularly implantation of oxygen ions, to increase the life of electrodes with a platinum coating and has demonstrated the possibility of thus increasing the electrodes' electrocatalytic activity. In a continuation of this avenue of research, the study reported here undertook potentiodynamic and structural studies of platinum electrodes and titanium-based electrodes that had been presprayed with platinum. They were subjected to implantation of  $O^+$ ,  $N^+$ ,  $Ar^+$ , and  $C^+$  ions on an ILU-4 unit. The test measurements were taken in a standard three-electrode cell in a solution of 1 N  $H_2SO_4$ . After anode-cathode activation, the electrode was oxidized at a specified potential for 15 seconds. Next the potential was switched at  $E = 1.5$  V, and cathode scanning was initiated after 2 ms. Auger electron and laser mass spectrometry indicated an oxygen enrichment of the electrode's surface layers during the ion implantation process with a close-to-gaussian distribution profile, with the maximum lying at a depth of about 30 nm. The increase in the near-surface concentration of oxygen

reached 20-30 atm%. The appearance of carbon impurities in the surface layers that was caused by the specific features of the ILU-4 unit (oil vacuum) was also observed. It was established that implantation of carbon ions results in significant passivation of the electrode's surface, a reduction of its activity during the oxygen liberation process, and a virtual disappearance of hydrogen and oxygen peaks in the potentiodynamic curves. Reducing the amount of implanted oxygen, on the other hand, had little effect on the form of the potentiodynamic curves or on the amount of chemisorbed oxygen. It was also demonstrated that the formation of Ti-Pt alloys and/or their oxides under the platinum layer during ion implantation primarily increases the electrode's life and has little effect on its electrocatalytic activity. Figures 4; references 8 (Russian).

UDC 541.135.2

### Formation of Peroxide Compounds During Electrolysis of Concentrated Solutions of Rubidium and Cesium Borates

907M0321H Moscow ELEKTROKHIMIYA in Russian Vol 26 No 8, Aug 90 (manuscript received 9 Oct 89) p 1051

[Article by A. A. Yakovleva and Ye. A. Nazhivin, Physical Chemical Scientific Research Institute imeni L. Ya. Karpov, Moscow]

[Abstract] It is known that the peroxodicarbonate anion formed on the anode as a result of the discharge of  $CO_3^{2-}$  ions is the source of active oxygen when the electrochemical method is used to produce sodium peroxoborate by electrolysis of a mixed carbonate-borate solution (140 g/l  $Na_2CO_3 + 7$  g/l  $B_2O_3$ ). It has also been shown that, under such conditions, the borate ion is not adsorbed on the surface of the platinum electrode and that its presence in the carbonate solution does not affect the kinetics of the anodic process or the structure of the interface. It has not, however, been possible to gather data on the electrosynthesis of peroxoborates by direct anodic oxidation of the borate ion. In an attempt to explain this inability, the authors of this article demonstrate the fundamental possibility of the electrosynthesis of peroxoborates by anodic oxidation of the borate ion in concentrated solutions of rubidium and cesium borates. References 3 (Russian).



UDC 628.162.533

### Using Phosphoric Acid To Clean Zinc-Containing Wastewaters for Fertilizer Production

907M0303H Moscow *KHIMICHESKAYA  
TEKHOLOGIYA* in Russian No 4, Jul-Aug 90  
(manuscript received 26 Oct 88) pp 92-93

[Article by A. I. Kudryavtsev, V. V. Pechkovskiy, and Ye. D. Dzyuba, Belorussian Technological Institute, Minsk]

[Abstract] Zinc microfertilizers have repeatedly been shown to be effective in agriculture. Production of such fertilizers can be increased by using industrial wastes, specifically zinc-containing wastewaters from the production of chemical fiber. The reagent method, which entails treating wastewaters with sodium carbonate solutions, that is used to extract zinc does not permit the use of zinc sediments for producing phosphorus fertilizers with microelements without additional processing. The authors of the present article have previously established that when wastewaters are cleaned by using phosphoric acid, the zinc-containing sediment formed may be used in the production of fertilizers with microelements. The study reported in the present article examined the stages of the settling of wastewater and the removal of zinc-containing sediment. They studied the colloid-chemical properties of the sediment formed in the process of cleaning wastewaters by using phosphoric acid. Specifically, they studied the pH dependence of the end volume of sediment ( $V_{\text{end}}$ ), the filtration coefficient ( $K_f$ ), and the electrokinetic potential ( $\xi$ -potential). During their experiments, they used a sediment formed during the cleaning of actual wastewaters and possessing the following make-up (mass%): Zn, 23;  $P_2O_5$ , 27; and Fe, 8.4 (with water constituting the remainder of the sediment). The sediment's density was  $2.3 \text{ g/cm}^3$ , and it consisted of particles ranging from 1 to  $50 \mu\text{m}$  in size (most in the 40- $\mu\text{m}$  range). The following conclusions were drawn: that reducing the pH of the medium reduces  $V_{\text{end}}$ , increasing the concentration of hydrogen ions reduces the value of the  $\xi$ -potential with respect to absolute value, and  $V_{\text{end}}$  and  $K_f$  are linked with the magnitude of the  $\xi$ -potential (the minimal  $V_{\text{end}}$  and maximum  $K_f$  are obtained at the lowest  $\xi$ -potential). These results confirm the hypothesis of the effect of acid-base equilibrium on the process of settling and filtering zinc phosphate sediment and the possibility of intensifying the processes of separating a suspension by adding high-molecular flocculants to the system. Figures 3; references 7 (Russian).

UDC 618.165.574

### Selecting Method of Cleaning Nickel-Containing Industrial Waters With Consideration for Economic and Ecologic Factors

907M0303I Moscow *KHIMICHESKAYA  
TEKHOLOGIYA* in Russian No 4, Jul-Aug 90  
(manuscript received 30 Apr 88) pp 94-96

[Article by G. S. Zarodin, M. Yu. Khazel, and T. B. Shchegoleva, Voronezh State University]

[Abstract] The use of protective and decorative galvanic coatings at machine building enterprises is responsible

for adding between 50 and 200 mg/l nickel to the washing water used during the process. The maximum allowable concentration of  $\text{Ni}^{2+}$  in discharged wastewaters is 0.1 mg/l. At Voronezh State University a technology was developed for local cleaning of nickel-containing industrial wastewaters by using ion-exchange materials. This article discusses the process of separating nickel on KB-4P-2 cationite in sodium form. The industrial wastewaters are averaged, and a medium for settling out the contaminants is created. The suspended substances are then separated out on mechanical filters.  $\text{Ni}^{2+}$  ions, if present, are extracted by passing the water through a layer of KB-4P-2 cationite in  $\text{Na}^+$  form, after which an equivalent quantity of sodium ions is added to the cleaned water to produce a softened water than can be used for steam boiler units without additional treatment. Capital outlay calculations presented demonstrate that using the ion-exchange method (using the cationites Kb-4P-2 and KU-2-8) to clean nickel-containing industrial wastewaters provides a considerable economic gain over the reagent method since the cationite-based methods allow the extracted nickel compounds to be returned to the production process. From an economic standpoint, the two cationites are about equal. From an ecological standpoint, however, KB-4P-2 is superior since using KU-2-8 entails using evaporation devices and diverting part of the nickel for reagent neutralization. Figures 2, table 1; references 4 (Russian).

UDC 628.16.08;628.33

### Using Activated Carbons in Technology for Cleaning Water and Wastewaters

907M0322I Kiev *KHIMIYA I TEKHOLOGIYA*  
in Russian Vol 12 No 8, Aug 90 (manuscript received)  
pp 727-738

[Article by M. N. Timoshenko and N. A. Klimenko, Colloidal Chemistry and Water Chemistry Institute imeni A. V. Dumanskiy, UkSSR Academy of Sciences, Kiev]

[Abstract] A number of monographs published in the sixties and seventies examined the effectiveness of using sorption processes in cleaning water and wastewaters. The past 5 to 8 years have witnessed a significant number of works examining the theoretical and practical aspects of using activated carbons to remove different contaminants from water. This review examines the status of prospects for using activated carbons in four types of process flows related to cleaning and preparing water: 1) the technology for preparing drinking water from natural waters; 2) the technology for obtaining technical-grade water from a mixture of biologically purified municipal and industrial wastewaters for use as make-up water in the circulation cycles of closed-loop water supply systems or for other technical purposes; 3) the technology for local cleaning of toxic wastewaters on site at the enterprises where they are formed; and 4) the

technology for direct physicochemical cleaning of the averaged wastewaters of an enterprise or group of enterprises, including by adsorption, to permit reuse of the cleaned waters for industrial purposes. Studies related to using activated carbons for these four purposes that have been conducted in Socialist and Western countries is cited to show both the promise of using activated carbon in cleaning natural water and wastewater and the need to increase practical application of the technology. Table 1; references 138: 56 Russian, 82 Western.

UDC 628.34

### Features of Coagulation Cleaning of Wastewaters From Textile Enterprises

907M0322J Kiev *KHIMIYA I TEKHOLOGIYA*  
in Russian Vol 12 No 8, Aug 90 (manuscript received  
14 Feb 90) pp 738-740

[Article by A. A. Mamontova, Colloidal Chemistry and Water Chemistry Institute imeni A. V. Dumanskiy, UkSSR Academy of Sciences, Kiev]

[Abstract] Numerous research has confirmed the need to include a coagulation stage in the complex process flow for cleaning the wastewaters of textile enterprise. The study reported herein was intended to select and substantiate the technological conditions providing the maximum extraction of organic substances (surfactants and dyes) and  $\text{Cr}^{6+}$  with the minimum secondary fouling of wastewater during the process of its coagulation cleaning. The study was conducted with actual wastewaters from cotton and worsted combines (the wastewaters from these combines differ greatly with respect to the amounts of surfactants and dyes they contain and with respect to their chromium contents). It was determined that a two-stage coagulation treatment method was best for the wastewaters from both combines. The first stage of the cleaning process developed entailed complex coagulation in bulk at the pH levels of 5 to 7 that are typical of such waters, and the second stage involved contact coagulation with correction of the pH level. Figure 1, tables 3; references 10: 8 Russian, 2 Western.

UDC 661.183.1

### Cleaning Organic Impurities From AV-17-8 Anion Exchanger

907M0322K Kiev *KHIMIYA I TEKHOLOGIYA*  
in Russian Vol 12 No 8, Aug 90 (manuscript received  
20 Feb 90) pp 741-743

[Article by L. A. Melnik, I. A. Grafova, I. I. Penkalo, and V. D. Grebenyuk, Colloidal Chemistry and Water Chemistry Institute imeni A. V. Dumanskiy, UkSSR Academy of Sciences, Kiev]

[Abstract] All grades of ion-exchange resins contain organic impurities in the form of low-molecular weight products of incomplete synthesis, incompletely polymerized monomers, solvents, etc., as well as breakdown

products formed when they are stored. Different ion-exchange resins have different types and amounts of impurities depending on the method used to produce the ion exchanger, the purity of the initial monomers, and the presence or absence of a cleaning stage after the sorbent has been synthesized. The study reported here examined the possibility of cleaning organic impurities from AV-17-8 anion exchanger. Solutions of inorganic salts were used as the reagents. The cleaning was implemented by placing technical-grade AV-17-8 anion exchanger into a column 30 mm in diameter. First reagent was passed through the column from top to bottom at a rate of  $2 \text{ cm}^3/(\text{cm}^3\text{h})$  for 5 hours. This was followed by distilled water at a rate of  $5 \text{ cm}^3/(\text{cm}^3\text{h})$  for 2 hours. The content of organic impurities in the sorbent was checked by determining the bichromate oxidability of an extract obtained by treating the anion exchanger with a solution of sodium hydroxide in a boiling water bath. This method permitted a more reliable assessment of the anion exchanger's purity and was distinguished by its high sensitivity. Thanks to the method, even the content of organic impurities in high-purity AV-17-8 anion exchanger was reduced by about 70%. The study thus confirmed the method's effectiveness in cleaning both technical-grade and high-purity anion exchanger. Furthermore, the new method is less harmful to the environment than the existing method is. Figures 2, table 1; references 11: 9 Russian, 2 Western.

UDC 621.359.7

### Cleaning Zinc-Containing Wastewaters by Electromembrane Method

907M0322L Kiev *KHIMIYA I TEKHOLOGIYA*  
in Russian Vol 12 No 8, Aug 90 (manuscript received  
6 Feb 90) pp 743-745

[Article by T. T. Sobolevskaya, A. G. Makhno, and V. D. Grebenyuk, Colloidal Chemistry and Water Chemistry Institute imeni A. V. Dumanskiy, UkSSR Academy of Sciences, Kiev]

[Abstract] Most of the chemicals used in electroplating shops enter the rinse waters. The methods for cleaning these waters are mainly geared toward transforming these reagents into oil-soluble compounds. This does not, however, solve the problem of returning the cleaned waters to the production cycle; rather, it results in the formation of secondary wastes that end up polluting the environment. The study reported here examined the process of electro dialysis of zinc-containing solutions in order to return the cleaned water and zinc salts to the production cycle. The solution studied was cleaned in a multichamber electro dialysis device with a distance of 0.2 cm between membranes. The device contained five demineralization chambers formed by MK-40 ion-exchange membranes with ears of  $50 \text{ cm}^2$  each. A manganese dioxide-coated titanium plate served as the anode. The membranes were separated by a knotless net and were brought into equilibrium before the beginning of the experiment. A zinc chloride solution with an

initial concentration of 8 mg/l Zn (II) and a pH of 3.2-7.2 was used in the first series of experiments. In the second series, the zinc chloride solution had an initial concentration of 110 mg/l Zn (II). In both series of experiments the solution was passed through all the chambers at a speed of 1 cm/s. The experiments confirmed the possibility of conducting electrodialysis of zinc-containing solutions under conditions where a precipitate forms on the ion-exchange membrane. It was established that lowering the pH reduces the amount of energy consumed for the process, reduces the likelihood of the formation of zinc hydroxide, and improves membrane regeneration conditions. Figures 3, table 1; references 6 (Russian).

UDC 579.695

### Biological Cleaning of Wastewaters From Production of Anide (Nylon-66)

907M0322M Kiev KHIMIYA I TEKHOLOGIYA  
in Russian Vol 12 No 8, Aug 90 (manuscript received  
6 Mar 90) pp 748-751

[Article by P. I. Gvozdyak, V. U. Nikonenko, T. P. Chekhovskaya, and S. M. Fedorik, Colloidal Chemistry and Water Chemistry Institute imeni A. V. Dumanskiy, UkSSR Academy of Sciences, Kiev]

[Abstract] Highly toxic hexamethylenediamine-containing wastewaters are formed when the synthetic polymer anide (nylon-66) is produced. Sometimes the concentration of this aromatic amine in industrial wastewater reaches 4 g/dm<sup>3</sup>. When this happens, the water is said to be "dead" since no acceptable method of neutralizing it exists. The study reported here summarizes the results of a pilot installation for the microbial cleaning of wastewaters to remove hexamethylenediamine from them and assesses the possibility of using the water life affixed to activated sludge to separate the resultant bacterial biomass. The experimental unit was tested on wastewaters from anide production. These waters typically contain from 1.5 to 4.0 g/dm<sup>3</sup> hexamethylenediamine, traces of adipinic and acetic acids, and copper and iodine ions. Such waters have a chemical oxygen demand of about 3,500 mg/dm<sup>3</sup>, a pH between 9.3 and 10.2, and a temperature from 40 to 80°C, and they are sterile. The wastewaters were cooled to 28-30°C in two parallel heat exchangers with a capacity of 8 m<sup>3</sup> each and were fed into a closed-type bioreactor 2.2 meters in diameter and 6 meters high that contained three air lift tubes and a packing made of anide filament. The liquid being cleaned passed from the first bioreactor to a second and then a third bioreactor (each was analogous in design). The liquid in the devices was kept at 3 meters. A biomass of the genus *Arthrobacter* was seeded into the first bioreactor at its start-up. To sustain the microorganisms' normal vital activity and high destructive activity, 0.02 kg orthophosphoric acid, 0.05 kg MgSO<sub>4</sub>·7H<sub>2</sub>O, and 0.01 kg KCl were added for each cubic meter of wastewater undergoing cleaning. Compressed air was used to aerate the liquid. Formation of hydrobiocenosis in the cleaning corridors occurred over

the course of the 2 months of the unit's operation. Analysis of the qualitative and quantitative make-up of the biocenosis organisms populating the cleaning equipment established that, during the cleaning process, the types of water life are replaced in accordance with their feeding level (from lower to higher level of the food chain). The pilot installation and method developed were thus confirmed to be effective in cleaning hexamethylenediamine-containing wastewaters. Figures 2, tables 2; references 10 (Russian).

UDC 628.16.087:628.322.087

### Disinfection During Tap Water Preparation

907M0322N Kiev KHIMIYA I TEKHOLOGIYA  
in Russian Vol 12 No 8, Aug 90 (manuscript received  
26 Feb 90) pp 754-756

[Article by L. S. Alekseyev, All-Union Scientific Research Institute of Water Supply, Sewage Disposal, Water Development Works, and Engineering Hydrogeology, Moscow]

[Abstract] All-Union State Standard [GOST] 2761-84 stipulates that only first-class underground waters can be used for household drinking water without treatment (including without filtration). The same GOST virtually bans feeding surface water into the system without treatment. It has been noted, however, that since the surface waters of some population centers in the North have a turbidity that does not exceed 1.5 mg/l for most of the year, this water is only disinfected and not filtered before use, thus greatly simplifying the water treatment circuit. This water must, however, be decontaminated with elevated doses of disinfectants. Because water becomes more corrosive and its content of carcinogenic trihalomethanes increases markedly when the amount of chlorine and chlorine derivatives added is increased, sanitary reliability criteria must be developed for municipal water supply systems, and standards regarding the doses of different disinfectants, the length of water lines, water turbidity, and the water treatment circuit must be set. An index that is the product of the disinfectant dose (in mg/l) times the time taken for treated water to pass to the first water consumer (in minutes) is recommended as such a criterion for the sanitary reliability of public water supply systems. The standard values of this index, which have been accepted in practice in the United States since 1986, are presented. It is further recommended that if the U.S. standards are indeed adopted, measures be taken to accomplish the following: provide stricter monitoring of the content of the protected-water areas of the entire watershed of a water supply source, increase the qualifications of personnel manning water treatment facilities, and tighten monitoring of the nature and causes of possible outbreaks of diseases among the population using a given water supply line. Tables 3; references 3: 1 Russian, 2 Western.

UDC 631.8.004.12:677

**Producing Superphosphate and Ammophos Dyed With Different Microadditives**

907M0303E Moscow KHIMICHESKAYA  
TEKHOLOGIYA in Russian No 4, Jul-Aug 90  
(manuscript received 25 Nov 88) pp 18-21

[Article by L. Ya. Perminova, N. Ye. Kondakov, T. F. Prikhodko, and N. F. Buda]

[Abstract] Along with nitrogen, phosphorus, and potassium mineral fertilizers, microelements play an important role in increasing the yield of fields. Boron, molybdenum, manganese, and copper are among the most important microelements. Soviet industry is currently producing simple and binary granulated superphosphates with a boron additive. Test batches of fertilizers with zinc, copper, and manganese microadditives have been produced, and a wide range of fertilizers with different microadditives are slated for production. This article reports on research related to dyeing simple and binary granulated superphosphates and ammophos with separate introduction of microadditives. The tests were conducted on commercial fertilizer specimens and on specimens prepared under laboratory conditions. Khivinskiy apatite concentrate, extraction phosphoric acid based on it, and microelements in the form of several powder compounds (boric acid, zinc sulfate, manganese sulfate, and ammonium molybdate) were

used in laboratory preparation of the fertilizers to be used as the phosphorus-containing raw materials in all the tests. Commercial water was used as a dye solvent. Regardless of their type and make-up, all the fertilizers with the same microadditive had to have a specified coloring, e.g., light blue for boron, yellow for zinc, pink for molybdenum. The following were examined during the superphosphate-dyeing tests: the effect of the change in content of free acid in the 1.0 to 5.0% range (for ammophos, the  $\text{NH}_3\cdot\text{H}_3\text{PO}_4$  ratio within the 0.9 to 1.1 range); the product drying temperature; the amount of dye expended for intensity of coloration; and the effect of the dyes selected on the results of chemical analysis of the dyed product with microadditives. Dyed and undyed specimens were analyzed for their content of various compounds and microelements. The tests indicated that a large portion of the dyes change their coloration depending on the content of free acidity in superphosphate and on the change in the  $\text{NH}_3\cdot\text{H}_3\text{PO}_4$  molar ratio in ammophos. Some of the dyes were found to be unstable at the temperatures used in drying fertilizers, and many could not be used owing to their expense or problems in producing or importing them. Ten dyes were recommended for use in dyeing the boron, molybdenum, manganese, and zinc microadditives used in various superphosphates and ammophos. Their All-Union State Standard (GOST) or Specifications and Norms (TU) numbers, concentration, and color are detailed in a table provided in the article. Table 1; references 9 (Russian).

UDC 669.296:669.794

### Enthalpy of Formation of Ternary Nickel-Based Liquid Alloys

907M0317E Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 63 No 7, Jul 90 (manuscript received 13 Dec 89) pp 1497-1501

[Article by O. Yu. Sidorov, M. G. Valishev, Yu. O. Pletneva, Yu. O. Yesin, and P. V. Geld, Ural Polytechnic Institute imeni S. M. Kirov]

[Abstract] Transition metals currently have extensive practical applications. Specifically, nickel-based materials are used as refractories when manufacturing the components of engines intended for different purposes, and yttrium- and zirconium-doped amorphous alloys of nickel with iron, cobalt, and copper show promise for application as magnetically soft and resistive alloys. Developing rational ways of improving alloys' properties requires adequate systematic and reliable experimental information about their enthalpies of formation. Such information is very scarce for nickel-based ternary alloys. This article examines the integral enthalpies of the formation ( $\Delta H$ ) of ternary melts of Ni, Me, and Y (where Me designates Fe, Co, or Cu) from pure components at 1,873 K in the nickel-enriched concentration range. The data found by the authors during their experiments are discussed within the framework of the phenomenological models of Gromakov, Kohler, Toop, and Bonnier, which are based on information about the properties of respective binary systems. Rather good agreement between the experimentally and theoretically obtained calculations of the function  $\Delta H(x)$  is found. The authors thus conclude that, given a concentration of alloying components up to 5-10 mol% in the melts studied, all of the aforementioned phenomenological models make it possible to obtain suitable results for the quantity  $\Delta H$ . Figure 1, table 1; references 27: 21 Russian, 6 Western.

UDC 621.359.7

### Occurrence of Space Charge Region During Electrolysis Process

907M0322A Kiev KHIMIYA I TEKHOLOGIYA in Russian Vol 12 No 8, Aug 90 (manuscript received 15 Mar 90) pp 675-680

[Article by A. V. Listovnichiy, Colloidal and Water Chemistry Institute imeni A. V. Dumanskiy, UkSSR Academy of Sciences]

[Abstract] One possible way of intensifying electrolysis is to use a beyond-cutoff mode of concentration polarization of the ion-exchange membranes, during which a space charge region is formed at the membrane's receiving surface and the flow of  $H^+$  and  $OH^-$  through the membrane is sharply increased. The study reported

herein examines the qualitative distinctions of concentration polarization of a unipolar ion-exchange membrane in a mode in which a space charge is formed close to the membrane's surface. Also examined is the physical meaning of a series of approximations that make it possible to significantly simplify the mathematical description of this model. Thirty-five equations are included. The concepts "electroneutral diffusion layer," "diffusion layer," and "space charge region" are compared. It is concluded that since the difference between each of the three terms lies in the fact that different simplifying assumptions are made when concentration and electrical fields in the respective areas are described, each term has an equal right to exist. The effect that the transfer of water dissociation products has on the concentration polarization of a unipolar membrane is discussed. It is concluded that the concentrations of  $H^+$  and  $OH^-$  ions begin to have a significant effect on the structure of the space charge region when these concentrations reach the level of the square root of the water's ion product. Also examined is the concentration polarization of a system for the case where a space charge region of macroscopic dimensions is formed from the receiving side of the membrane. The results obtained may be used to describe the concentration polarization of the system examined throughout its entire range of parameters. Figures 2; references 19: 16 Russian, 3 Western.

UDC 621.593

### Calculating Flow of Water Vapor Through Porous Hydrophobic Membrane During Membrane Distillation With Allowance for Concentration Polarization

907M0322B Kiev KHIMIYA I TEKHOLOGIYA in Russian Vol 12 No 8, Aug 90 (manuscript received 15 Mar 90) pp 681-683

[Article by P. P. Zolotarev, Physical Chemical Scientific Research Institute imeni L. Ya. Karpov, Moscow]

[Abstract] The goal of the study reported herein was to develop a theoretical estimate of the effect of concentration polarization (i.e., the ratio of the concentration of dissolved matter at the membrane surface to its concentration in the solution being separated) on the process of membrane distillation in a flow-through regimen in solutions of nonvolatile matter. An approximate film theory of mass exchange in the vicinity of a membrane is used for the estimates. Approximate formulas (14 equations in all) are derived to examine the cases of contact membrane distillation and membrane distillation with a gas gap. The cases of long channels in a laminar flow mode and long channels in a turbulent mode are discussed. Figure 1; references 12: 7 Russian, 5 Western.

UDC 541.18.045+66.067.38

**Fouling of Reverse-Osmosis and Ultrafiltration Membranes**

907M0322C Kiev *KHIMIYA I TEKHOLOGIYA*  
in Russian Vol 12 No 8, Aug 90 (manuscript received  
23 Feb 90) pp 684-703

[Article by A. A. Baran, Colloidal Chemistry and Water Chemistry Institute imeni A. V. Dumanskiy, UkSSR Academy of Sciences, Kiev]

[Abstract] Fouling of the membrane is the principal problem in using membrane processes whose driving force is applied pressure, specifically filtration of multi-component systems. Fouling of the membrane is the most important obstacle to more extensive use of membrane processes in many branches of chemistry and biology. This review examines the main causes and mechanisms of fouling of semipermeable membranes and classifies the principal substances responsible for fouling them. Processes of physical and biological destruction as well as the pressure applied to membranes during reverse-osmosis and ultrafiltration processes all alter membranes' properties during operation. A number of foreign firms have proposed various composite membranes with an increased resistance to the effect of aggressive and/or biologically active media that would combat these changes. Concentration polarization is another important cause of fouling; it causes membranes to lose a great portion of their hydrodynamic permeability and changes their retaining characteristics. The literature includes information on two broad groups of strategies for reducing concentration polarization, i.e., methods of intensifying mass release from the membrane's surface into the nucleus of the flow of the solution being separated and methods based on establishing low permeability, in which case the concentration polarization cannot reach significant magnitude. The relationship between concentration polarization and gel formation has also been examined extensively; however, despite the good agreement between the gel polarization model that has been developed and experimental data, many aspects of this theory remain to be explained. While it has been determined that the effects of concentration polarization should be reversible, those effects resulting from "pure" fouling of membranes cause an irreversible reduction in the transmembrane flow. Among the types of membrane fouling that have been examined in the literature are fouling due to the formation of salt residues, colloidal particles, low-molecular weight organic matter, high-molecular weight matter, and biological sources of fouling. The literature contains numerous attempts at mathematical description of membrane fouling. The simplest describe the dependence of the volumetric flow on time or on the volume of permeate. Since these models are semiempirical, they say virtually nothing about the mechanism of the fouling process. Other types of models that have been developed include those that use the approximation "resistance in a

series" in an analogy with the problem of the transformation of heat and those that use an approximation of a "turbulent explosion." Despite their attempt to describe the phenomenon of fouling on firmer ground, these models are far more complex and require knowledge of a greater number of parameters. For this reason, the simple exponential models developed earlier are more useful in developing a simple description of the phenomenon and correlating it with working parameters. Figures 12; references 76: 26 Russian, 50 Western.

UDC 541.183

**Formation of Composite Inorganic Membranes and Their Properties**

907M0322D Kiev *KHIMIYA I TEKHOLOGIYA*  
in Russian Vol 12 No 8, Aug 90 (manuscript received  
23 Nov 89) pp 703-706

[Article by M. T. Bryk, A. P. Savitskiy, and V. M. Kochkodan, Colloidal Chemistry and Water Chemistry Institute imeni A. V. Dumanskiy, UkSSR Academy of Sciences, Kiev]

[Abstract] Polymer membranes, which have come to enjoy wide-scale use, do not always possess the properties required for a number of production processes. This has spawned the intensive development and study of new types of inorganic membranes possessing a number of advantages, including corrosion resistance, abrasive resistance, stability in the presence of bacteria, heat stability, the ability to function in a broad range of pH values, the capability of regeneration by steam and chemical reagents, and longer life. The study reported herein examined the structure and separation characteristics of composite inorganic membranes produced by modifying the surface of a microporous ceramic base with products of the polycondensation of silicic acid. The resultant thin silica gel layer was virtually insoluble in water, withstood heating to 800-900 K, and possessed a highly developed pore structure that could be controlled with the formation of modifying layers. Porous corundum strips (diameter, 25 and 64 mm; thickness, 2.5 mm) with an average pore diameter between 3.0 and 0.8  $\mu\text{m}$  and overall porosity of 37-43% were used as the base for forming the membranes. Tests examining the membranes' structural and separation characteristics indicated that they occupy an intermediate position between ultra- and microfiltration membranes and that they may be used in a number of processes related to cleaning aggressive wastewaters containing organic and high-molecular weight compounds. The presence of a thin silica gel layer on the surface of the membrane developed provides the capability of subsequent modification to reduce the average pore size and to give the membrane additional functions. Figures 3; references 9: 5 Russian, 4 Western.

UDC 628.34:668.474

**Possibility of Efficient Cleaning of Cationic Dyes From Wastewaters by Using Hydrolysis Lignin**

907M0322E Kiev *KHIMIYA I TEKHNLOGIYA*  
in Russian Vol 12 No 8, Aug 90 (manuscript received  
18 Dec 89) pp 706-710

[Article by I. S. Geles, N. A. Ponkina, and V. B. Litvinova, Forest Institute, Kareli Department, USSR Academy of Sciences, Petrozavodsk]

[Abstract] Hydrolysis lignin has been used as a sorbent in cleaning dyes from wastewaters. Owing to the low sorption activity of technical-grade hydrolysis lignin, however, the efficiency of the process is not very high. The study reported here examined the possibility of increasing the efficiency of the process of using hydrolysis lignin when cleaning cationic dyes from wastewaters. Hydrolysis lignin from the Segezha Paper and Pulp Combine was used as a test object. Samples were air-dried and sieved through a sieve with 3-mm-diameter holes. The lignin was subjected to alkali treatment in a solution of trisodium phosphate for 10-15 hours and in a solution of sodium hydroxide. Next, the lignin was separated from the solution, washed with water to an alkali concentration of 0.4-0.5 g/l, neutralized by hydrochloric acid to a pH of 8, and washed with water until a close-to-neutral reaction was achieved. A control experiment was conducted to test for secondary fouling of the cleaned wastewaters by water-soluble components of the lignin. Infrared and ultraviolet spectral analysis revealed that secondary fouling when hydrolysis lignin is used as a sorbent is a reality. It was discovered that increasing the efficiency of cleaning cationic dyes from wastewaters requires using activated hydrolysis lignin in two stages, with the first stage entailing partial sorption of the dye from highly concentrated wastewaters or solutions (1.7-2.5 g/l) until 15-25% of the lignin's total sorption capacity is reached. In the second state, the hydrolysis lignin with 75-85% of its sorption capacity remaining is

used to clean the dyes remaining in the now-less-concentrated (i.e., <1.3 g/l) wastewaters under non-equilibrium conditions. This method was found to increase the process by preventing secondary fouling. Figures 3, tables 2; references 14 (Russian).

UDC 621.187

**Na-Cl-Ionization of Mineralized Waters**

907M0322F Kiev *KHIMIYA I TEKHNLOGIYA*  
in Russian Vol 12 No 8, Aug 90 (manuscript received  
11 Mar 90) pp 712-715

[Article by K. M. Abdullayev, Kh. A. Dzhavadova, R. G. Mamedbekova, S. A. Shakhmarov, and R. M. Musayev, Azerbaijan Oil and Chemistry Institute imeni M. Azizbekov, Baku]

[Abstract] The technology of Na-Cl ionization is used in treating fresh waters in the preparation of make-up water for low- and medium-pressure steam generators and heating systems and to prevent carbonate deposits. The study reported here examined the capability of Na-Cl ionization technology with regard to preventing sulfate deposits during thermal and membrane softening of mineralized waters. Experiments were conducted on mineralized waters with three different concentrations (maximum, average, minimum) of the following:  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{HCO}_3^-$ . (The total salt contents of the waters ranged from 3 to 12 g/l.) A mixture of AN-31 anionite and KU-2 cationite was used during the softening. The ionite mixture was found to provide rather deep softening and desulfatization, with the residual content of hardness ions and sulfate ions not exceeding 1 mgEq/l. Regression equations were derived to calculate the exchange capacity of the  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ , and  $\text{Ca}^{2+}$  ions in the mixture and the hardness as functions of the composition of the initial water, the percentage of cationite in the mixture, and the regeneration and sorption conditions. The possibility of solving the problem of sulfate deposits during membrane and thermal softening of mineralized waters by preliminary Na-Cl ionization on a mixed layer of KU-2 cationite and AN-31 anionite was thus confirmed. Figures 5; references 7: 6 Russian, 1 Western.

UDC 535.21:621.375.826

**Modeling Phase Transitions in Semiconductors Under Laser Irradiation***907M0306A Moscow FIZIKA I KHIMIYA OBRABOTKI MATERIALOV in Russian No 4, Jul-Aug 90 (manuscript received 11 Apr 88) pp 14-18*

[Article by G. G. Gromov, S. V. Zhuk, and K. V. Rudenko, Moscow]

[Abstract] Mathematical modeling of the pulsed laser annealing of semiconductors has attracted the interest of a number of researchers. The present work examines the features of modeling the dynamics of the phase transition from melting to resolidification. The existing model of such transitions includes a unidimensional heat conduction problem that considers the melting-recrystallization phase transition together with the diffusion of charge carriers subjected to laser irradiation with consideration of the temperature dependencies of the semiconductor's parameters and the effect of nonequilibrium charge carriers on optical properties. Unlike a number of previous works, the present work examines the semiconductor's phase composition on the basis of the spatial distribution of its heat content, which permits a more correct description of the phase transition's dynamics. The distribution of the semiconductor's temperature and absorbed heat along the axis perpendicular to its surface are determined and divided into three regions (a melt, a transitional two-phase region, and a solid phase). The position of the melting front is determined, and the properties and state of the three regions altogether are described. Other models frequently ignore the temperature dependence of density, which results in a change in specific volume and, consequently, in the coordinate grid used in computations. For some semiconductors, ignoring this fact results in an error greater than the precision of the computations. For this reason, the specific volume change during melting is considered in the present work. The absorption and reflection of the radiation are also taken into account by using the characteristic matrices method, and the refraction and absorption indices are calculated with an allowance for the contribution of nonequilibrium charge carriers. These modifications make the model more realistic, and threshold values calculated for InSb on the basis of the proposed model show good agreement with experimentally obtained values. Using the proposed model makes it possible to discover new effects, specifically a change in the reflection factor that is nonmonotonic over time. Figures 3; references 10: 7 Russian, 3 Western.

UDC 535.21:621.375.826

**Nonsteady Processes in CdHgTe During Pulsed Laser Annealing***907M0306B Moscow FIZIKA I KHIMIYA OBRABOTKI MATERIALOV in Russian No 4, Jul-Aug 90 (manuscript received 5 Apr 89) pp 19-22*

[Article by G. G. Gromov, S. V. Seregin, S. V. Zhuk, V. B. Ufimtsev, Moscow]

[Abstract] This article investigates the redistribution of the components that occurs when complex semiconduc-

tors and solid solutions based on them are subjected to pulsed laser annealing.  $\text{Cd}_{0.2}\text{Ng}_{0.8}\text{Te}$  plates of the orientation (100) were subjected to dynamic chemical smoothing and then irradiated with a YAG laser ( $\lambda = 1.064 \mu\text{m}$ ;  $\tau = 100 \text{ ns}$ ). For comparison, the specimens were irradiated in air and in a liquid nitrogen medium. Relaxation processes in the postannealing period were studied by optical probing of the irradiated surface with an He-Ne laser beam ( $\lambda = 0.6328 \mu\text{m}$ ) and by measuring the reflection factor R. Annealing in air resulted in a jump in the reflection factor, with a relaxation of R occurring in the postpulse period. It may be hypothesized that the observed increase and subsequent nonstationarity of R in the postpulse period result from annealing the  $\text{Cd}_{0.2}\text{Ng}_{0.8}\text{Te}$  through the liquid phase. The rapidity of the relaxation processes and behavioral peculiarities of the  $\text{Cd}_{0.2}\text{Ng}_{0.8}\text{Te}$  make explaining the observed effect difficult. One possible reason for the phenomenon observed may be redistribution of the components of the  $\text{Cd}_{0.2}\text{Ng}_{0.8}\text{Te}$  in that area of the specimen that is recrystallized as a result of pulsed laser annealing with the formation of a surface layer enriched with a component having a greater reflection factor than the  $\text{Cd}_{0.2}\text{Ng}_{0.8}\text{Te}$  does. Airy's formula for the total amplitude of a reflected wave is used to construct an approximate optical model of the system air layer-base. R(t) curves are plotted for three possible relaxation processes. Annealing in a liquid nitrogen medium also resulted in a jump in the reflection factor; however, no postpulse relaxation occurred. This may be due to the rapid hardening of the nonequilibrium layered structure and low temperature for reverse diffusion equalization of the composition. The data obtained from experimentation and computation make it possible to hypothesize that pulsed laser annealing of  $\text{Cd}_{0.2}\text{Ng}_{0.8}\text{Te}$  results in complex, irreversible processes in the annealed layer of the semiconductor, including decomposition of the compound and redistribution of its components. Figures 2; references 9: 6 Russian, 3 Western.

UDC 621.375.826:678.01

**Thermal Mechanism of Laser Destruction of Polycarbonate***907M0306C FIZIKA I KHIMIYA OBRABOTKI MATERIALOV in Russian No 4, Jul-Aug 90 (manuscript received 8 Jun 89) pp 30-32*

[Article by S. G. Bychkov, A. A. Biketov, and N. A. Ramazanova, Alma-Ata]

[Abstract] The macrokinetics of the laws of the laser destruction of polycarbonate are investigated. The laser destruction of materials subjected to pulses of millisecond duration is interesting on two counts. First, the process is most efficient from the standpoint of precision machining. Second, the mode of free-running lasing with millisecond pulses permits realization of the maximum output energy of virtually all of the most technologically



promising types of lasers. The tests described were conducted on an experimental unit described elsewhere. The pulse energy of the ruby laser used (in a free-running mode) was varied from 0.5 to 1.2 J, the duration of the pulse was kept virtually constant at 0.35 ms, and the density of the beam's power on the specimen surface (after focusing the lens with a focal distance of 157 mm on a spot 0.85 mm in diameter) was varied from  $0.25 \cdot 10^6$  to  $6.05 \cdot 10^6$  W/cm<sup>2</sup>. The test polycarbonate cube (edge, 5 mm) was irradiated on all six faces. The areas subjected to the laser's effect were analyzed under an MMI-2 microscope, and the gaseous products of the destruction were analyzed on an MKh-1307 gas spectrometer. Under a microscope, the irradiated zone was shown to be a crater with a nearly cylindrical shape. Unlike in epoxy resins, no brittle destruction was observed. In other words, the mechanism of entrainment of mass from the irradiation zone is defined as complete gasification of the material. Traces of carbonization were found only at the crater's bottom. The quantity of solid residue was insufficient for IR-spectral or element analysis. The crater's diameter (0.62 mm when  $q = 0.25 \cdot 10^6$  W/cm<sup>2</sup>) indicated that gasification of the material did not occur throughout the entire irradiated surface but only in regions where the density of the power was greater than the threshold value. The crater's dimensions increase virtually linearly as  $q$  increases. No increase in the amount of coke was observed. Within the framework of the theory of the thermal destruction of materials by pulses of millisecond duration, it is proposed that the integral radiosity (I) and pulse of the mechanical efficiency (P) are directly dependent on the amount of gasified matter, i.e., on  $\Delta m$ . The component make-up of the gaseous products was maintained throughout the entire power density range, and this confirmed the invariant mechanism of the destruction of polycarbonate under the given conditions, with the most characteristic ratio of components (in vol.%) being as follows: H<sub>2</sub>, 2; CO, 54; CO<sub>2</sub>, 43.5; CH<sub>4</sub>, 0.3; unidentified compounds, 0.2. A definite correlation between the calculated and experimental blow-in velocities of the gasification products was observed. The test results indicate that the macrokinetic laws of the laser destruction of polycarbonate can be satisfactorily described within the framework of the thermal theory. Figures 2; references 9 (Russian).

UDC 64.373.821.038.825.2

#### Problem of Interaction of Laser Radiation With Polymer Materials

907M0306D Moscow FIZIKA I KHIMIYA OBRABOTKI MATERIALOV in Russian No 4, Jul-Aug 90 (manuscript received 27 Jun 89) pp 33-38

[Article by Yu. A. Bykovskiy, I. N. Dobrokhotov, A. S. Sokolnikov, Ye. P. Fetisov, Yu. D. Fiveyskiy, and A. A. Chistyakov, Moscow]

[Abstract] Laser treatment of nontransparent polymer materials requires a clear understanding of the interaction of laser radiation with organic molecular condensed

media, particularly polymers. This article presents an experimental study of the characteristics of the interaction of continuous-wave laser radiation with nontransparent polymers along with a theoretical description of the phenomena studied. Thin cylindrical specimens of two epoxy resin-based polymers with similar thermo-physical characteristics but different chemical structures were irradiated with a continuous-wave CO<sub>2</sub> laser ( $\lambda = 10.6 \mu\text{m}$ ). A chemical transformation front that moved along the specimen at some speed was formed as each specimen was irradiated. At the front, the macromolecules decomposed, and gaseous products and coke formed. The coke was peeled off the specimen. The speed at which the chemical transformation front passed along the specimen was determined by measuring its length before ( $l_0$ ) and after ( $l(\tau)$ ) irradiation for the period of time  $\tau$ . Analysis of a graph of the change in the polymer specimens' lengths as a function of the duration of the irradiation and density of the power of the incident radiation indicated that the interaction of continuous-wave laser radiation with polymers is not just one-dimensional but stationary in nature. The results of laser irradiation of the specimens with different chemical structures were very different. By viewing the destruction process in terms of the phase transition of the polymer into a gaseous state with subsequent destruction of the polymer's molecules in the gas phase it was possible to use specified thermodynamic relationships and obtain reasonable quantitative results. The values found for the speed of the specimens' destruction, coupled with values of the density of the power of the incident laser radiation and selected characteristics of the polymers and their destruction products, make it possible to obtain numerical values for a important characteristic of polymers—the specific heat of destruction. Figures 3; references 8: Russian 7, Western 1.

UDC 669:620.193.1

#### Effect of Oxygen on Erosion Stability of Ti, Ni, Cr, Mo

907M0306E Moscow FIZIKA I KHIMIYA OBRABOTKI MATERIALOV in Russian No 4, Jul-Aug 90 (manuscript received 13 Feb 89) pp 79-83

[Article by F. N. Borovik, V. N. Kovalevskiy, and A. S. Masakovskaya, Minsk]

[Abstract] One factor determining the erosion stability of metals is the change in interatomic interaction in the metal matrix as it relates to the effect of the gas atoms embedded in the electronic structure of the initial substance. During the gas erosion process, the surface working layers of the product's material are saturated with oxygen, nitrogen, hydrogen, and carbon. An assessment of the effect of interstitial oxygen on the nature of the interatomic interactions in Ti, Ni, Mo, and Cr is presented. The assessment is based on model calculations of energy structure that are in turn based on Hart-Fock-Slater self-consistent field equations in an approximation of Wigner-Seitz spherical shells. It was

discovered that the redistribution of the electron density in the vicinity of the interstitial atom has the nature of a bond between the atoms of the principal component, which, in the case of the metals Ti, Mo, and Cr, results in the formation (as these metals become saturated with oxygen) of local volumes with a high contribution of the ionic component of the bond, thus facilitating the generation and development of microcracks. In nickel, as the concentration of oxygen increases in the volumes, a weakening of the interatomic bond is observed. This weakening eventually leads to the formation of microcracks at reduced stress levels, and the presence of migrating oxygen increases the likelihood of their growth. Figures 2, table 1; references 5: 3 Russian, 2 Western.

UDC

### Investigation of Molybdenum-Hafnium Make-Up of Silicide Coating on 5VMTs Niobium Alloy

907M0306F *Moscow FIZIKA I KHIMIYA OBRABOTKI MATERIALOV in Russian No 4, Jul-Aug 90 (manuscript received 24 May 89) pp 90-95*

[Article by Yu. P. Zotov, Ye. K. Ivanova, N. P. Kushnareva, B. I. Podgorskiy, V. V. Tikhonovich, Kiev]

[Abstract] The method of x-ray microspectral analysis is used to investigate the layer-by-layer change in the make-up of a molybdenum- and hafnium-based silicide coating on the niobium alloy 5VMTs. When the coating is formed by the slip method, subsequent casting does not result in mutual diffusion of the material of the coating and the matrix. Intensive diffusion of niobium from the base to the coating or of hafnium, molybdenum, and silicon from the coating to the metal is observed only after annealing at 2,120 K. The coating formed after siliconization consists of four layers: an outer porous layer based on  $\text{Mo}(\text{Hf}, \text{Nb})\text{Si}_2$ ; more monolithic layers of  $\text{Nb}(\text{Mo}, \text{Hf})\text{Si}_2$  and  $\text{NbSi}_2$  on the interface with the matrix; and a narrow layer of  $\text{Nb}_5\text{Si}_3$ , with the exact make-up and width of the layers depending on the composition of the slip and the durations of the high-temperature annealing and siliconization. During the process of high-temperature holding in an oxidizing medium, it is hafnium that reacts most intensively with oxygen. It therefore seems advisable to optimize the hafnium content depending on the specific conditions of a given product's operation. Tables detailing the content of elements in the composite after high-temperature annealing and at a specific point on the coating after high-temperature heating are included. Figures 5, tables 2; references 6 (Russian).

UDC 677.529

### Thermophysical Characteristics of Carbon-Carbon-Type Composites

907M0317G *Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 63 No 7, Jul 90 (manuscript received 20 Oct 89) pp 1544-1550*

[Article by Ye. A. Tishina, G. I. Kurnevich, N. P. Radimov, Belorussia State University]

[Abstract] Practical application of composites presupposes knowledge of their thermophysical characteristics.

The present article therefore examines the heat conduction, heat capacity, temperature conduction, and thermal expansion of 12 carbon-carbon-type composites that differ from the standpoint of their reinforcing filler, matrix, reinforcing structure, and density. Analysis shows that the heat capacity of the composites studied is close to that of natural flake graphite and other artificial graphite materials. The heat conduction of these composites is determined primarily by their reinforcing filler, and it increases as the density of the material increases, with the nature of the temperature dependence of the heat conduction coefficient becoming more complicated as the reinforcing structure's complexity increases. The structure of the reinforcement, and hence the density, of these composites determines their thermal expansion. It is significantly lower than that of natural graphite. Included in the article are tables detailing the composites' heat conduction coefficients, matrices, and densities; the temperature dependences of their specific heat capacities for solid and powder forms, and their temperature conduction. Figures 2, tables 4; references 7: 6 Russian, 1 Western.

UDC 541.034

### Electrochemical Doping of Composites Based on Poly-(n-Phenylene) in Sulfuric Acid Solutions

907M0317H *Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 63 No 7, Jul 90 (manuscript received 5 Mar 87) pp 1554-1557*

[Article by Y. N. Danilchuk, A. F. Zuyeva, O. N. Yefimov, V. P. Tarasov, and V. I. Plakhsy, Chemical Physics Institute, USSR Academy of Sciences]

[Abstract] Poly-(n-phenylene) is among those polymers that become electroconductive upon doping with strong acceptors or donor electrons, and it has excellent thermal and chemical stability. It may be doped chemically or electrochemically. Electrochemical doping makes it possible to produce electrodes with a high degree of incorporation, which may be important from a practical standpoint. The authors of this article therefore conducted a series of experiments related to the electrochemical oxidation of poly-(n-phenylene) containing different additives in a 16 M solution of  $\text{H}_2\text{SO}_4$ . It was concluded that introducing plasticizing and current-conducting additives can result in the optimum combination of mechanical and electrochemical properties in an electrode mass based on poly-(n-phenylene). Of the six electrodes tested, the best one consisted of the following (in mass%): poly-(n-phenylene), 70; polychrome-1, 20; carbon black, 5; and graphite, 5. It is recommended for use in making a cathode in sulfuric acid current sources. Figures 2, table 1; references 8: 8 Western.

UDC 541.14:778.342

**Principles of Photochemical Recording of Information by Light-Sensitive Complexes of Transition Metals**

907M0317A Leningrad ZHURNAL PRIKLADNOY KHMII in Russian Vol 63 No 7, Jul 90 (manuscript received 23 Jan 90) pp 1441-1455

[Article by A. V. Loginov and G. A. Shagisultanova]

[Abstract] The photochemistry of complex compounds was demarcated as an independent branch of inorganic chemistry about 30 years ago. Since that time voluminous information has been accumulated regarding the properties of electron-excited states and the refined mechanism of the photolysis of complex compounds. The present article formulates general principles for use in designing photographic materials based on complex compounds with different types of actions and purposes. The approaches examined are based on the fundamental concepts of coordination photochemistry, analysis of developments described in the literature, and the authors' own developments. The following topics are examined: the types of electron-excited states and photostimulated reactions of complex compounds, ligand photosubstitution reactions, photoisomerization reactions, reactions initiated by phototransfer of an electron from a metal to a ligand and from a metal to the medium, and reactions initiated by phototransfer of an electron from a ligand to a metal and from a nucleophile to a metal. The materials examined show that the photochemical properties of complex compounds afford extensive possibilities for creating new photographic materials for different purposes. Progress in this area has been largely related to understanding of the mechanism of catalysis of processes of physical, chemical, optical, and thermal intensification of a hidden image by metal complexes and by their photolysis products. The following are among promising directions of developments using specific properties of complex compounds or individual classes of complex compounds: photochrome materials based on reactions of the substitution of ligands and isomerization of complex compounds in homogeneous layers of organic polymers; photopolymerized compounds in which photolysis products of a complex compound act as initiators and/or catalysts of polymerization; materials of direct blackening, where products of the photodecomposition of complex compounds act as initiators and/or catalysts for the formation of inorganic, organic, and organometallic dyes; materials for linear optics in which submicroheterogeneous metal particles (plasmons) function as active centers; liquid- and gas-phase light-sensitive compounds for low-temperature selective metallization of solid surfaces to produce microelectronics instruments; and photopolymerized organometallic materials to produce different optical elements and protective masks. References 111: 61 Russian, 50 Western.

UDC 541.49:547.551

**Reaction of Complex Compounds of Cobalt (III) With Silver Formed as Result of Reactions in Color Development Process**

907M0317B Leningrad ZHURNAL PRIKLADNOY KHMII in Russian Vol 63 No 7, (manuscript received 21 Jun 89) Jul 90 pp 1456-1459

[Article by Yu. B. Yakovlev, V. A. Fomin, L. V. Krayenny-Admoni, and Ye. N. Sirovinkina, Leningrad State Pedagogical Institute imeni A. I. Gertsen]

[Abstract] Silver formed during the reduction of silver halides by organic diamines used as color developers are self-catalysts of oxidation-reduction reactions in the color development process. The formation rate of the dye of a color image depends on the quantity and activity of silver particles that may serve as a source of fog on unexposed sections of photographic materials. During the development process chlorine-containing complexes of cobalt (III) oxidize metallic silver and change it into silver chloride. This article examines the kinetics of this reaction in the case where the silver reacting with the cobalt (III) compounds is that silver formed during the reduction of silver halide by organic diamine. Four cobalt compounds, i.e.,  $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$ ,  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ ,  $[\text{Co}(\text{Dp})_3]\text{Cl}_3$ , and  $[\text{Co}(\text{En})_3](\text{ClO}_4)_3$ , that were synthesized according to the respective, previously described methods were used as the study cobalt compounds.  $\alpha$ -Naphthol, a cobalt compound, and developing solution were added to a gel solution containing silver chloride with the formation of silver. The optical density ( $\lambda = 580 \text{ nm}$ ) was measured by an SF-26 spectrophotometer and recorded on an LKS-4-003 instrument. It was discovered that introducing cobalt compounds into developing solution reduces the dye formation rate, which helps reduce the fog level. Figures 3, table 1; references 6 (Russian).

UDC 541.139:771.72

**Catalytic Formation of Dye on Oxygen-Activated Silver Particles**

907M0317C Leningrad ZHURNAL PRIKLADNOY KHMII in Russian Vol 63 No 7, Jul 90 (manuscript received 21 Jul 89) pp 1459-1464

[Article by I. I. Mikhaleiko, Yu. A. Zubarev, L. V. Krasnyy-Admoni, and V. D. Yagodovskiy]

[Abstract] Using the process of catalytic dye formation to intensify a developed silver image is promising in the context of the implementation of photographic materials with a low silver content. The study reported herein examined the possibility of activating the silver particles catalyzing the catalytic dye formation process by preliminary heat treatment in an atmosphere of nitrogen and oxygen and by quenching. Silver particles were applied by the method of impregnation of a Silochrome S-80 carrier in a solution of  $\text{AgNO}_3$  in the amount of 1.5 mass% in relation to the S-80, followed by evaporation and decomposition of the  $\text{AgNO}_3$  at  $450^\circ$  and reduction of the Ag in a hydrogen current for 3 hours. Heat treatment was conducted in an oxygen (or nitrogen) flow

with a volumetric velocity of 5 l/h for 15 minutes. The specimen was then cooled in a gas flow at a rate of 10 deg/min (slow cooling) and 100 deg/min (fast cooling/quenching). Catalyst in the amount of 1 mg ( $3.57 \cdot 10^{-4}$  g Ag) was tested for its activity in the catalytic dye formation process in an intensifying solution with a pH of 7. The dye formation rate was calculated, and adsorption of the oxidizing agent from an aqueous solution on the silver catalyst was determined at 25° on the basis of the change in the solution's concentration. It was determined that heat treatment at 350-450° in oxygen increases the activity of silver particles in the catalytic dye formation reaction because of the formation of active forms of oxygen on the surface thanks to its dissolution and the restructuring of the metal surface. The silver's activity increases further when quenched from a temperature of 200-300° owing to stabilization of the active forms of oxygen. The kinetic laws governing the catalytic dye formation reaction when sodium peroxoborate is used as the oxidizing agent differ from those when ammonium pentachlorocobalt (III)-chloride (KSK-3) is used: for the former, the coefficient characterizing the shape of the kinetic curve decreases as the temperature of annealing in oxygen increases, whereas for the latter it passes through a minimum. The activity of the Ag-catalyst is comparable when the two oxidizing agents are used during high-temperature activation. During low-temperature activation, it is more active when the KSK-3 is used. Figures 3; references 9: 6 Russian, 3 Western.

UDC 541.49:541.183

#### **Complexing of Palladium During Sorption by Copolymer of Polyacrylonitrile Fiber With Poly-2-Methyl-5-Vinylpyridine**

907M0317D Leningrad ZHURNAL PRIKLADNOY KHMII in Russian Vol 63 No 7, Jul 90 (manuscript received 2 Feb 90) pp 1464-1470

[Article by S. A. Simanova, G. N. Molodkina, L. V. Kononov, N. M. Burmistrova, A. A. Lysenko, and A. V. Shchukarev, Leningrad Technological Institute imeni Lensovet]

[Abstract] A study examined the sorption of  $K_2[PdCl_4]$  on a graft copolymer of polyacrylonitrile fiber with

poly-2-methyl-5-vinylpyridine and the composition and structure of palladium complexes with a sorbent as the polymer ligand.  $K_2[PdCl_4]$  synthesized according to the existing method served as the starting compound. The amount of palladium sorbed by the fiber was determined on the basis of the difference in the palladium content in the solution before and after sorption or after burning the fiber. The sorption was conducted under static conditions with constant mixing (at 20 and 98°) from solutions of 0.1-2.0 M HCl and 0.1-1.0 M NaCl. The fiber weighed 0.1-0.2 g, and the volume of the solutions studied was 25 ml. The concentration of palladium in the solutions varied from  $5 \cdot 10^{-3}$  to  $2.5 \cdot 10^{-2}$  mol/l. The fiber was prewashed with a solution that did not contain palladium. Freshly prepared solutions of the starting compound were used in all cases. Equilibrium in the distribution of palladium between fiber and solvent in acid media at room temperature and during heating was established rapidly—in 10-15 minutes—as during the sorption of chlorine complexes of ruthenium (IV) and osmium (IV). Unlike chlorine complexes of Ru (IV) and Os (IV), a chlorine complex of palladium is markedly sorbed by polyacrylonitrile-poly-2-methyl-5-vinylpyridine fiber from close-to-neutral solutions, albeit more slowly. Under comparable conditions of sorption from acid media, the sorption capacity of polyacrylonitrile-poly-2-methyl-5-vinylpyridine fiber with respect to palladium (II) chlorine complexes turned out to be less than that with respect to chlorine complexes of Ru (IV) and Os (IV). It was thus concluded that fiber made of a copolymer of polyacrylonitrile and poly-2-methyl-5-vinylpyridine may be recommended for quantitative extraction of chlorine complexes of palladium (II) from both acid and neutral solutions. The mechanism of sorption extraction will, however, differ in each of these two cases. Sorption from acid solutions occurs primarily on the basis of an ion-exchange mechanism and entails the formation of onium chlorine complexes in the phase of the fiber, whereas in neutral solutions is associated with the formation of diamine-dichloro complexes with a polymer ligand in the fiber phase. Figures 3, tables 2; references 24: 22 Russian, 2 Western.

UDC 541.68

**Mechanical Properties of Mined Coals From Standpoint of Physicochemical Mechanics**

907M0307A Moscow KHIMIYA TVERDOGO  
TOPLIVA in Russian No 4, Jul-Aug 90 (manuscript  
received 21 Aug 89) pp 9-12

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

[Abstract] The genesis of the mechanical properties of mined coals may be explained in terms of "two-phase" concepts. The literature demonstrates that mined coals should, in virtually all stages of their genesis, be viewed as a porous skeleton impregnated to some degree or other by liquids, including highly viscous liquids. Surfactants are always among those products constituting the mobile phase of mined coal, and the most active surfactants are those that are close to solid sorbing bodies in nature. Thus, all of the principal changes in the mechanical properties of coals in a genetic series may be explained on the basis of capillary forces and the effect of adsorption reduction in the strength of solid bodies (Rebinder's effect), i.e., through the action of surface stress forces. The basis for this conclusion is that the deep mechanical destruction of organic matter gives rise not only to a mobile phase and chemomechanical restructuring of the immobile phase but also to enormous internal interface surfaces, thus causing coal to have a pronounced microheterogeneous structure. The intergrain contacts of this structure are in a process of constant rebirth and destruction. Rebinder and capillary effects alternate throughout the genesis of coal. The antibatic nature of the strength and compressibility dependencies for coals from one basin is confirmed by different published studies of coals from different basins. According to research by investigators of the Rebinder school, under the effect of surfactants, a body that was elastic will, as adsorption reduction of its strength occurs, become plastic and then brittle. In this context, types Zh, K, and OS coals, those with minimum strength, are brittle, whereas coals in higher and lower stages of coalification are plastic. This fact and others lead to the conclusion that capillary and Rebinder effects in surfaces can serve as an adequate model of so complex a system as mined coal. It is noted, however, that since the effect of surface forces in the subsurface layer of condensed matter is expressed at depths of hundreds of angstroms, mined coals with their enormous inner surface can hardly be assumed to consist entirely of such layers. Figure 1; references 15: 11 Russian, 4 Western.

UDC 543.813

**Yield of Volatile Matter From Coals of Pechorsk Basin at Different Temperatures**

907M0307B Moscow KHIMIYA TVERDOGO  
TOPLIVA in Russian No 4, Jul-Aug 90 (manuscript  
received 16 Jan 89) pp 17-18

[Article by A. I. Ptushko and I. N. Vylka, Vorkutaugol Production Association]

[Abstract] In recent years, International Organization for Standardization [ISO] standards have come to enjoy

increasing use in the Soviet national economy. Using them in methods of analyzing solid fuels will not result in problems if the analysis results obtained on the basis of international and national standards coincide within allowable limits. The study reported herein compared results of determining the yields of volatile matter in coals from the Pechorsk basin by using the method outlined in ISO 562-81, which calls for performing the determination at a temperature of 900°C, and that outlined in All-Union State Standard [GOST] 6382-80, which stipulates an analysis temperature of 850°C. During the comparison, seam samples were taken from fresh faces of working seams at mines of the Vokruta-Ugol and Untaugol production associations and from blast holes at six other deposits. A total of 110 samples of different types of enriched coals were examined. It was found that when the determinations were made at a temperature of 900°C (versus the 850°C called for in the GOST standard), the resultant yields for various coals were elevated by the following amounts (%): type D coals, 3.1; type GZhO, 2.1, type Zh, 1.9, type K, 1.6, type OS, 1.1, and type T, 3. Thus, despite the relatively small temperature difference between the two standards, the analysis results for some coals varied by up to 30%. This variation was evidently due to temperature-dependent differences in the degree of decomposition of organic matter. Statistical processing of the determination results did, however, indicate that the values for the yield of volatile matter determined by methods regulated by ISO 562-81 and GOST 6382-80 are in rather close correlation. It was thus concluded that the yield of volatile matter from the coals of the Pechorsk Basin may be determined on the basis of ISO 562-81 without regrading the coals. Figures 2.

UDC 662.74:551

**Make-Up of Liquid Products of Heat Destruction of Salt-Bearing Coals Processed With Alkaline or Acid Solutions**

907M0307C Moscow KHIMIYA TVERDOGO  
TOPLIVA in Russian No 4, Jul-Aug 90 (manuscript  
received 28 Mar 89) pp 26-32

[Article by V. A. Tamko, V. I. Saranchuk, V. N. Shevko-plyas, and L. A. Plotnikova, Physical and Organic Chemistry and Coal Chemistry Institute, UkSSR Academy of Sciences]

[Abstract] The laws governing the process of the heat destruction of brown coals that have been pretreated with solutions of inorganic matter have already been investigated, and the positive effect of these solutions on the quantitative yield and qualitative make-up of the resultant liquid products has been established. The study reported herein demonstrates the differences in the make-up and properties of the liquid products formed as a result of heat destruction of salt-bearing coals from the Novomoskovskiy Deposit that had been pretreated with

solutions of acids and alkalis. It was found that processing salt-bearing coals with alkaline solutions increased their yield of liquid products. The tars obtained from the starting coals and from those processed with alkalis or acids differed from the standpoint of their make-ups and properties. Both the unprocessed and processed tars did, however, turn out to have nearly identical amounts of aromatic protons. As the temperature at which the fractions were boiled increased, the amount of aromatic proteins (as determined by PMR spectra) decreased. Differences discovered in the IR and PMR spectra of the fractions of the tars investigated indicated that their make-up depends not only on the distinctive features of the coals in question but also on the conditions under which they are processed. Figures 5, tables 2; references 20: 16 Russian, 14 Western.

UDC 541.123:681.3:502.55.625.5

#### Thermodynamic Study of Behavior of Selenium and Arsenic in Processes of Oxidation and Reduction Heat Destruction of Coals

907M0307D Moscow KHIMIYA TVERDOGO  
TOPLIVA in Russian No 4, Jul-Aug 90 (manuscript received 24 Nov 88) pp 50-54

[Article by N. V. Malykh and I. Z. Pertsikov, Irkutsk Polytechnic Institute]

[Abstract] Selenium and arsenic are present in coals in microquantities. Investigating the prevalence of elements in light of the increasing scales on which coal is being processed is particularly important since coals with a high content of arsenic and selenium are sources of environmental pollution. The goal of the study reported here was to determine the forms of selenium and arsenic compounds that will be present in the products of the burning, coking, and gasification of coals. The study computations were made by using the program ASTRA on a YeS-1050 computer. Coals from the Irsha-Borodinskiy deposit were selected for the burning and gasification, and coals from the Karagandinskiy deposit were selected for the coking. The burning of coal was examined in the temperature range from 400 to 1,400°C at a pressure of 0.1 MPa, coking-heating was examined at temperatures from 400 to 1,200°C at a pressure of 0.1 MPa without access to air, and the artificially derived model of coal gasification by a mixture of air and steam was calculated for a pressure of 1.1 MPa and a temperature between 400 and 1,400°C. A total of 213 potential products were sought in the samples (168 gaseous-phase and 45 condensed-phase compounds). The computations showed that  $\text{SeO}_2$  was the most likely selenium product formed when coal is burned. It was discovered that when coal is burned (an oxidative process)  $\text{SeO}_2$ ,  $\text{As}_2\text{O}_3$ ,  $\text{As}_2\text{O}_4$ , and  $\text{As}_2\text{O}_5$  are formed, whereas during coking and gasification (reductive processes)  $\text{H}_2\text{Se}$ ,  $\text{SeH}$ ,  $\text{Se}$ ,  $\text{As}_4$ , and  $\text{As}_2$  are formed. These selenium and arsenic compounds pose an increased ecological threat. Figures 4, table 1; references 11: 5 Russian, 6 Western.

UDC 662.612.13

#### Effect of Hydrogen Peroxide on Process of Absorption of Dissolved Oxygen by Solid Combustible Minerals

907M0307E Moscow KHIMIYA TVERDOGO  
TOPLIVA in Russian No 4, Jul-Aug 90 (manuscript received 21 Dec 89) pp 55-59

[Article by I. V. Aleksandrov, I. I. Kossov, and I. N. Alfimov, Moscow Chemical Technological Institute imeni D. I. Mendeleev]

[Abstract] A study examined the initial stage in the oxidation of solid combustible minerals by dissolved oxygen and the intermediate products of its reduction. The principal objects of study were shales from the Maarduskiy phosphorite deposits in the Estonian SSR ( $\text{W}^a$ , 0.8%;  $\text{A}^d$ , 82.3%;  $\text{C}^{\text{daf}}$ , 67.65%,  $\text{H}^{\text{daf}}$ , 7.58;  $\text{N}^{\text{daf}}$ , 3.63%,  $\text{S}_t^{\text{daf}}$ , 2.61; and  $\text{O}_d^{\text{daf}}$ , 18.53%) and from the rocky interlayer between the Nos 2 and 3 coal seams in the Talbulag strip in Mongolia ( $\text{W}^a$ , 2.0%;  $\text{A}^d$ , 82.2%) and activated carbon. It was concluded that two main factors are necessary for oxidation of solid combustible minerals to occur. The first is the capability of the organic mass of solid combustible minerals to reduce  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  and  $\text{O}_2$  to  $\text{H}_2\text{O}_2$ ,  $\text{HO}_2^-$ , and other products of the reduction of oxygen at a rate sufficient for the existence of a reversible cycle with respect to ionic forms of iron. The second factor is the presence in solid combustible minerals of a reduction capacity to establish and maintain the  $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$  ratio within specified limits determining the direction of the process of the decomposition of hydrogen peroxide and, consequently, the mechanism of the oxidation of solid combustible minerals overall. The presence in solid combustible minerals of water-soluble organomineral compounds with the participation of metals of variable valence or the possibility of their forming during the oxidation process must be taken into account when studying the mechanisms of the oxidation of carbonaceous rocks and shales and must also be used when developing methods of preventing endogenic fires. Figures 4; references 12 (Russian).

UDC 662.74:552

#### Processing Brown Coal Into Liquid Products at ST-5 Pilot Plant

907M0307F Moscow KHIMIYA TVERDOGO  
TOPLIVA in Russian No 4, Jul-Aug 90 (manuscript received 29 Nov 89) pp 84-90

[Article by A. A. Garkusha, A. A. Krichko, A. S. Maloletnev, B. P. Sizykh, and M. K. Yulin, Combustible Minerals Institute]

[Abstract] The purpose of the ST-5 Pilot Plant is to develop a production regimen to hydrogenate coal and to develop a single production cycle that would include those processes starting from the preparation of coal and ending with the production of motor fuels (gasoline with

different octane numbers, diesel fuel, etc.). The plant includes facilities for separating coal and paste, liquid-phase hydrogenation of coal paste, processing of slime with regeneration of the molybdenum catalyst, and distillation of the hydrogenation product. At the plant, hydrogen is produced by the water electrolysis method, and a unit for adsorption concentration of water-containing gas is provided to make full use of the hydrogen. Nonoxidized and low-metamorphosis coals with a mineral portion of no more than 10%, a C:H ratio not exceeding 16, a yield of volatile matter of at least 35%, and at least 80% petrographic components of the vitrinite and liptinite groups were used for the hydrogenation. Brown coal from the Borodinskiy deposit of the Kansk-Achinsk Basin was subjected to hydrogenation under pilot operating conditions at the plant. The gasoline and diesel fuel produced from distillate fractions of products of the liquefaction of coal were analogous to petroleum products from the standpoint of their properties. It was determined that under conditions at the pilot plant the specific thermal effect of the coal hydrogenation process amounted to 760 kJ/kg raw material. The degree of transformation of the organic mass of coal reached 87 percent, and the coefficient of regeneration of the molybdenum catalyst was 97.2%. Figure 1, tables 5; references 4: 2 Russian, 2 Western by Russian authors.

UDC 662.75:542.941

#### Liquefaction of Brown Coal Under Conditions of Ion Hydration

907M0307G Moscow KHIMIYA TVERDOGO  
TOPLIVA in Russian No 4, Jul-Aug 90 (manuscript  
received 16 Feb 88) pp 91-94

[Article by V. G. Lipovich, V. V. Zemskov, and V. P. Medvedeva, Institute of High Temperatures, USSR Academy of Sciences]

[Abstract] The methods for destructive hydrogenation of coal that have been developed to date have comparatively low technical and economic indicators since liquefaction of the coal matter at low space velocities requires the use of high temperatures and pressures, expensive equipment, and consumption of a large amount of hydrogen. Consequently, increasing attention is being paid to developing unconventional methods of processing solid combustible minerals that would produce synthetic liquid fuel and raw materials for the chemical industry under softer conditions and with less energy consumption. In the study reported herein, the ion hydration method was used to liquify the organic mass of brown coal at a temperature between 250 and 350°C at a pressure of less than 10 MPa. The method had been used previously at the same temperatures but with a lower pressure (up to 5 MPa). This time, however, formic acid was selected as the acid component. Coal

from the Irsha-Borodinskiy deposit was used. Its particles ranged in size from 0.125 to 0.250 mm, and it was characterized by indicators of  $A^d = 5.2\%$  and  $W^a = 0.3\%$ . The specified fraction was dried for 5 hours at 105°C. The experiments were conducted in a rotating autoclave (capacity, 1 l) in the temperature range from 250 to 500°C. The contact time amounted to 0.5 hours. The starting mixture consisted of coal, tetrahydronaphthalene [Tetralin], and formic acid (in a 1:1.3:0.7 ratio). The resultant products were found to contain an insignificant quantity of asphaltenes and preasphaltenes and to consist primarily of low-molecular weight oils with a high hydrogen content. Figures 2, tables 2; references 2 (Russian).

UDC 669.004.82.097.3:665.7.032.54

#### Using Nonferrous Metallurgy Slimes as Catalysts for Liquefaction of Kansk-Achinsk Brown Coal

907M0307H Moscow KHIMIYA TVERDOGO  
TOPLIVA in Russian No 4, Jul-Aug 90 (manuscript  
received 19 Sep 89) pp 95-98

[Article by T. V. Borodkina, K. V. Yermilov, N. V. Koroleva, and V. G. Lipovich, Moscow Chemical Technological Institute imeni D. I. Mendeleev]

[Abstract] A study examined the catalytic activity of polymetallic slime from nonferrous metallurgy when it was used in the process of hydroliquefaction of Irsha-Borodinskiy brown coal. During the experiment, a 0.5-l laboratory autoclave was used to hydrogenate Kansk-Achinsk coal. Tetrahydronaphthalene (Tetralin) (75 g per 25 g coal) was used as the solvent. The process temperature ranged from 375 to 425°C, and the working pressure in the device was 10 MPa. The element make-up of the coal was as follows (%):  $C^{daf}$ , 68.03;  $H^{daf}$ , 4.82;  $N^{daf}$ , 0.76; and  $S_t^{daf}$ , 0.16. Technical analysis data were as follows (%):  $W^a$ , 8.57;  $A^d$ , 8.64; and  $V^{daf}$ , 57.00. The catalytic activity of the averaged nonferrous metallurgy slime was examined at different process temperatures and catalyst concentrations. Introducing the catalyst at 425°C had little effect on the degree of coal transformation; only at a concentration of 4% did the degree of conversion increase by 2%. The yield of liquid products varied greatly. At 375°C, adding 4% catalyst increased the depth of transformation from 57 to 77%; however, the yield of target liquid products was only 3%. IR spectroscopy data revealed that the catalyst probably causes deep destruction of the aliphatic and naphthene products since few were present in the hydrogenation product of the catalytic liquefaction. It was demonstrated that, on account of the lack of compensation for the cracking and hydrating functions of the catalyst, using averaged nonferrous metallurgy slime during the process of hydrogenation liquefaction of brown Kansk-Achinsk coal does not result in any significant yield of liquid products. Figures 4, tables 2; references 5: 4 Russian, 1 Western.

UDC 541.14

**Diffusion and Recombination of Methyl Radicals With Atomic Hydrogen in Xenon at 77 K***907M0308A Moscow KHIMIYA VYSOKIKH ENERGIY in Russian Vol 24 No 4, Jul-Aug 90 (manuscript received 3 Aug 88) pp 297-301*

[Article by Ye. I. Grigoryev, D. O. Zhukov, and L. I. Trakhtenberg, Physical Chemical Scientific Research Institute imeni L. Ya. Karpova]

[Abstract] This study examines the diffusion and recombination of methyl radicals with atomic hydrogen in methane-xenon matrices and the recombination of methyl radicals with thermal hydrogen atoms generated in the gaseous phase upon dissociation of hydrogen. Xenon-methane matrices were prepared in thin-walled quartz ampules (internal diameter, 3 mm) at 77 K by precipitation of a xenon-methane gas mixture as the molar methane content in the mixture was varied from 1.7 to 2.7%. The pressure of the gas mixture fell at a rate of 670 Pa/min, and after preparation of the matrix the methane residues were evacuated to a residual pressure of  $10^{-3}$  Pa. Analysis of the thawed matrices showed the following: the molar methane content in the solid phase was 1.5, 2.0, and 2.5%, respectively, for starting gas mixtures with methane contents of 1.7, 2.2, and 2.7 percent. Methyl radicals were produced by using  $\gamma$ -radiation at a dose strength of 10.8 kGy/h in a dose of 21.6 kGy. Hydrogen atoms were generated at a hydrogen pressure in the gaseous phase amounting to  $10^{-2}$  Pa on a platinum filament 0.1 mm in diameter. The error in measuring the concentration of radicals was between 10 and 15%. The diffusion coefficient of the methyl radical was determined as being  $3.5 \cdot 10^{-18}$  cm<sup>2</sup>·s<sup>-1</sup>. The error in determining this coefficient on the basis of kinetic data regarding their destruction when the specimens were stored in liquid nitrogen (calculated in accordance with the error additivity law) did not exceed 20%. It was demonstrated that the constant of the rate of recombination of the hydrogen radicals in a xenon matrix is significantly higher than that of the recombination of hydrogen atoms with methyl radicals ( $2 \cdot 10^{-11}$  cm<sup>3</sup>·s<sup>-1</sup> in the case of the latter). The authors acknowledge that this estimate is calculated with a precision up to that of Henry's constant and is thus elevated in view of the fact that it does not consider the adsorption characteristics of hydrogen on xenon. Figures 3; references 15: 11 Russian, 4 Western.

UDC 541.15

**Interaction of Hydrogen Atom With Sulfonyl Group During Radiolysis of Sulfolane in Aqueous Solution***907M0308B Moscow KHIMIYA VYSOKIKH ENERGIY in Russian Vol 24 No 4, Jul-Aug 90 (manuscript received 16 Nov 88) pp 309-313*

[Article by N. A. Vysotskiaya, N. A. Ogurtsov, and A. A. Revina, Physical Chemistry Institute imeni L. V. Piszarzhhevskiy, UkSSR Academy of Sciences]

[Abstract] To date, the mechanism of sulfones has only been studied in two works, where it was found that

hydrated electrons complex with the sulfonyl group, thereby leading to the formation of sulfonyl anion-radicals. The present study examines the details of the mechanisms of the interaction of radical products of the radiolysis of water with sulfones. Sulfolane (thiolane-1,1-dioxide) (one of the simplest representatives of this class) was selected as the study compound. Sulfolane purified by twice distilling it at 140°C under a pressure of  $(1.1 \text{ to } 1.6) \cdot 10^3$  Pa was used. The resultant product had a melting point of 24-25°C. Solutions prepared on the basis of tridistilled water were deaerated or saturated with N<sub>2</sub>O and sealed into glass ampules. They were irradiated with  $\gamma$ -rays of <sup>60</sup>Co on a UK-250000 unit, and the sulfolane concentration before and after irradiation was determined by the gas-liquid chromatography method on a Chrom-42 chromatograph, with 3-butoxysulfolane used as an internal standard. The radiation-chemical yield [G(-C)] of the consumption of sulfolane was determined by graphic differentiation of the sulfolane-dose concentration curves at the initial point. The pulsed radiolysis was conducted as described elsewhere. G(-C) was found to equal  $1.6 \pm 0.3$  (He),  $3.0 \pm 0.2$  (N<sub>2</sub>O), and  $1.7 \pm 0.2$  (He, pH 1.3) molecules/100 eV for sulfolane concentrations ranging from 0.006 to 0.03 mol/dm<sup>3</sup>. It was concluded that the reaction of the complexing of hydrogen atoms to the -SO<sub>2</sub> group and reactions of the regeneration of sulfolane from short-lived intermediate products are more efficient than are recombination reactions. The pulsed radiolysis method revealed an adduct of the hydrogen atom and -SO<sub>2</sub> group, i.e., a hydrosulfolane-1-yl radical ( $\lambda_{\text{max}} = 330$  nm). Figures 2; references 12: 6 Russian, 6 Western.

UDC 541.15:541.64

**Kinetics of Radiation Graft Polymerization of Styrene on Polyethyleneterephthalate Nuclear Membranes***907M0308C Moscow KHIMIYA VYSOKIKH ENERGIY in Russian Vol 24 No 4, Jul-Aug 90 (manuscript received 6 Feb 89) pp 314-319*

[Article by N. I. Zhitaryuk, P. A. Zagorets, and V. I. Kuznetsov]

[Abstract] Polyethyleneterephthalate (PETF) film is the most suitable material for producing nuclear membranes. The nuclear membranes manufactured by using PETF have pores with very low conicity. A number of works have shown the possibility of improving the performance parameters of polymer membranes by modifying their surface properties, but to date there are no systematic data regarding changing the properties of nuclear membranes by radiation graft polymerization. The study reported here examined the kinetics of the radiation graft polymerization of styrene on lavsan nuclear membranes. The nuclear membranes were produced on the basis of biaxially oriented PETF film (lavsan) 10  $\mu$ m thick. The films and membranes for the



grafting were used without additional washing. The radiation graft polymerization was conducted by using two methods: preliminary irradiation in air and preliminary irradiation in a vacuum. The authors proposed a kinetic equation for processing the curves of the accumulation and dependence of the relative content of graft polymer on the time for which the PETF was held after irradiation had been completed. Ratios of the constants of the rate of growth and breaking of the chain were derived for membranes with different parameters. It was concluded that, in the case of preliminary irradiation of PETF in air, in the initial stage at 70°C grafting is initiated primarily by the captured radicals. Since, when PETF is irradiated in air, the radicals located in the amorphous phase oxidize rapidly, the only source of active centers initiating the grafting can be crystallites. The radicals localized in the volume of the crystallites either diffuse to their surface (because of the difference in concentrations of the paramagnetic centers in the amorphous and crystalline areas of the polymer), where they initiate the growth of graft chains, or else the graft chains located in the amorphous phase exert pressure on the crystallites, thus causing their partial destruction. This in turn reduces the crystallinity of the base and results in the appearance of new radical centers together with the existing ones. Figures 4, table 1; references 13: 1 Russian, 9 Western.

UDC 541.64:547.321

#### Nature of Active Centers Occurring During Radiolysis of Ammonium Oxide

907M0308D Moscow KHIMIYA VYSOKIKH ENERGIY in Russian Vol 24 No 4, Jul-Aug 90 (manuscript received 18 Jan 89) pp 326-328

[Article by A. A. Davranov, S. I. Kuzina, M. R. Muydinov, and I. M. Barkalov, Chemical Physics Institute, USSR Academy of Sciences]

[Abstract] When ammonium oxide is subjected to radiolysis, active centers form in it that are capable of initiating the polymerization of olefins and fluoroolefins. Thanks to their high heat stability and long life, such centers are effective initiators of the polymerization of gaseous tetrafluoroethylene (TFE) at room temperature. The study reported herein used the electron paramagnetic resonance (EPR) method to study the kinetics of the formation and transformation of paramagnetic centers occurring during radiolysis of ammonium oxide. It was discovered that radiolysis of  $Al_2O_3$  entails the formation of paramagnetic centers, the EPR spectra of which are independent of recording temperature (77 to 300 K) and represent an asymmetrical singlet with  $\Delta H = 4.3$  mT calculated for  $>O^{\cdot-}$  ion centers. The radiation yield, determined on the basis of the initial segments of the curves of the accumulation of paramagnetic centers in the dose range to 1 kGy, turned out to be little dependent on the irradiation temperature and amounted to about 10 particles per 100 eV. Upon ultraviolet illumination of the irradiated  $Al_2O_3$  specimens, the

intensity of the EPR spectrum diminished while the concentration of paramagnetic centers decreased by about 80%. The rate of polymerization of TFE on the irradiated  $Al_2O_3$  specimens dropped sharply. The authors were unable to record the polymerization of TFE on the starting ammonium oxide subjected to photolysis. Figures 2; references 7: 6 Russian, 1 Western.

UDC 541.15:546.46-36

#### Radiolytic Transformations of Strontium and Barium Hydroxides and Their Crystal Hydrates

907M0308E Moscow KHIMIYA VYSOKIKH ENERGIY in Russian Vol 24 No 4, Jul-Aug 90 (manuscript received 9 Nov 88) pp 329-334

[Article by L. I. Barsova, T. K. Yurik, S. L. Orlov, and M. B. Zubareva, Physical Chemistry Institute, USSR Academy of Sciences]

[Abstract] This article reports a study of the processes for the formation and stabilization of paramagnetic centers and the molecular radiolysis products ( $H_2$  and peroxide compounds) in polycrystalline specimens of strontium and barium hydroxides as a function of the content of crystallization water. Specimens of  $Sr(OH)_2 \cdot xH_2O$  and  $Ba(OH)_2 \cdot xH_2O$  (x being between 0 and 7.4) and their respective deuterated strontium and barium hydroxides were synthesized from chlorides in accordance with the previously described method and were dried by the lyophilic drying method. After being held in a desiccator over granulated KOH for half a year, the octahydrates transformed into monohydrates. Another series of barium hydroxide octahydrates was obtained by the method of decomposition of especially pure barium hydroxide in a vacuum at 973 K followed by hydration of the resultant water or deuterium oxide. Crystal hydrates with the lowest crystallization water content were obtained by calcining the specimens at the respective temperatures. This led to the formation of  $Sr(OH)_2 \cdot H_2O$  and  $Ba(OH)_2 \cdot 1.7H_2O$ . Anhydrous  $Sr(OH)_2$  was obtained when the specimens were evacuated to  $1.33 \cdot 10^{-3}$  Pa at 403 K, and anhydrous  $Ba(OH)_2$  was obtained at 473 K. The primary radiolysis products of all of the hydroxides were  $O^{\cdot-}$  ion radicals and H atoms. Their magnetic resonance characteristics and yields were dependent on x. Electron  $F_A$ -centers appear when specimens with a low water content were subjected to  $\gamma$ -irradiation. Their yields increased as the specimens were dehydrated further. No correlation between the yields of molecular products and the content of crystallization water was discovered. On the basis of the experimental data obtained during the study, the authors proposed a 15-step mechanism of the radiolytic transformations of strontium and barium hydroxides and their crystal hydrates. Figures 2, table 1; references 21: 11 Russian, 8 Western, 2 Western by Russian authors.

UDC 541.15:662.41

**Formation and Accumulation of Gaseous Products in Crystalline Lattice During Radiolysis of Lead Styphnate***907M0308F Moscow KHIMIYA VYSOKIKH ENERGIY in Russian Vol 24 No 4, Jul-Aug 90 (manuscript received 10 Jan 89) pp 335-339*

[Article by S. M. Ryabykh, N. V. Martynova, and O. A. Lavrenyuk, Kemerovo State University]

[Abstract] This article examines the laws governing the accumulation of gaseous radiolysis products of lead styphnate  $C_6H(NO)_{23}O_2Pb \cdot H_2O$ . This compound, a typical initiating explosive, is capable of withstanding not only explosive but also slow chemical decomposition under the constant effect of an external energy factor such as elevated temperature or radiation. Lead styphnate was obtained by the "stream-into-stream" (streams of sodium styphnate and lead nitrate) method at 20 and 90°C. The lead styphnate precipitated was filtered, washed with water and alcohol, and dried. The result was a yellow powder with individual crystals on the order of 50  $\mu m$  in size; its purity was determined as being 98.6%. The powder was subjected to  $^{60}Co$   $\gamma$ -irradiation at a dose rate of 5.0 Gy/s at a temperature of 60°C. From 0.01 to 0.05 g irradiated lead styphnate was placed in a dish filled with the solvent dimethylformamide. The gas liberated during the dissolution process, i.e., the volume of gas retained by the crystalline lattice, was calculated. It was discovered that when lead styphnate crystallites are irradiated, gaseous radiolysis products are held by the crystalline lattice all the way up to a dose of 4 MGy. The complex nature of the kinetic curves of the accumulation of gaseous radiolysis products of lead styphnate in the dose range up to 20 MGy was established. The authors' interpretation of these data considers the processes of the formation, growth, and destruction of cavities filled with gaseous radiolysis products within the volume of the crystals. Figures 2; references 12: 11 Russian, 1 Western.

UDC 621.373.8.038.82

**Pulsed Chemical HF- and DF-CO<sub>2</sub> Lasers Based on Photon Branching Chain Reactions Initiated by Thermal Decomposition of Finely Dispersed NaN<sub>3</sub> Particles***907M0308G Moscow KHIMIYA VYSOKIKH ENERGIY in Russian Vol 24 No 4, Jul-Aug 90 (manuscript received 23 Nov 88) pp 372-377*

[Article by V. I. Igoshin, V. A. Katulin, and S. Yu. Pichugin, Kuybyshev Department, Physics Institute imeni P. N. Lebedev, USSR Academy of Sciences]

[Abstract] This article reports a numerical analysis of the operation of  $D_2F_2$ -CO<sub>2</sub>- and  $H_2$ -F<sub>2</sub>-lasers based on a photon branching chain reaction that is initiated by the thermal decomposition of NaN<sub>3</sub> particles. During the course of their investigation the authors establish the possibility of creating a purely chemical intensifier of laser infrared radiation based on a mixture of  $D_2F_2$ -CO<sub>2</sub>(H<sub>2</sub>-F<sub>2</sub>) and finely dispersed NaN<sub>3</sub> particles. Their computations were based on detailed kinetic laser models. For example, their investigation of the characteristics of a chemical H<sub>2</sub>F<sub>2</sub>-laser entailed the use of an equivalent two-level model of a hydrogen fluoride laser that considered the rotational relaxation rate and anharmonism of the HF molecules and numerical solution of an equation system that included equations for the following: the chemical kinetics in an H<sub>2</sub>-F<sub>2</sub>O<sub>2</sub>-He mixture, the mean number of oscillatory quanta of H<sub>2</sub> molecules, the temperature of the laser medium, the populations of the upper and lower levels in the equivalent two-level diagram of the laser, and the temperature and radius of spherical NaN<sub>3</sub> particles in a field of infrared radiation. According to the authors' calculations, the radiation generated by  $D_2F_2$ -CO<sub>2</sub>- and  $H_2$ -F<sub>2</sub>-lasers with a mixture of dispersed NaN<sub>3</sub> particles (about 0.1  $\mu m$  in size) under a pressure of 0.1 MPa may exceed the energy an infrared laser radiation consumes to initiate a chain reaction by a factor of 20 to 60. Tables 3; references 8: 7 Russian, 1 Western.

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