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JPRS-UCH-87-007

11 MAY 1987

# USSR Report

CHEMISTRY

19980610 087

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USSR REPORT  
CHEMISTRY

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## ADSORPTION

UDC 541.18.041.182:546.26-162

### STUDY OF AGGREGATIVE STABILITY OF AQUEOUS NATURAL DIAMOND DISPERSIONS IN $AlCl_3$ SOLUTIONS

Moscow KOLLOIDNYY ZHURNAL in Russian Vol 48, No 5, Sep-Oct 86  
(manuscript received 17 Jan 85) pp 1005-1009

[Article by Ye.V. Golikova, O.V. Klachkova, V.I. Kuchuk, and  
Yu.M. Chernoberezhskiy, Leningrad University]

[Abstract] A broad and systematic study was performed of the electric surface properties and stability of aqueous dispersions of natural diamond. It was found that over a broad range of pH (2-12) and concentration ( $10^{-3}$ - $5 \cdot 10^{-2}$  mol/l) of various electrolytes containing singly and doubly charged cations, natural diamond particles carry a negative charge. The surface charge density and  $\zeta$  potential were studied as functions of pH and electrolyte concentration, the position of the isoelectric point was estimated, dissociation and surface complex formation constants were determined and the aggregative stability of the dispersions was studied. This article continues the investigation of the aggregative stability and coagulation of natural diamond dispersions with particle size  $0.5 \mu m$ , specific surface  $20.7 m^2/g$ , concentration of particles in initial dispersion  $2 \cdot 10^7 cm^{-3}$ , by ultramicroscopy in  $AlCl_3$  solutions at  $10^{-6}$ - $10^{-2}$  mol/l, pH 2-5.2. It is found that the energy barrier is absent at  $AlCl_3$  concentrations of as little as  $10^{-6}$  mol/l and attractive forces appear among the particles at all distances. The paradoxical stability of the aggregate state apparently results from the presence of a structural component in the separation pressure, arising due to overlap of boundary layers having structure and thermodynamic parameters other than the volumetric parameters characteristic for the dispersion medium. The system loses its stability at  $AlCl_3$  concentration  $10^{-5}$  mol/l. Increasing the concentration to  $10^{-3}$  mol/l returns the system to the stable state due to heterostabilization of diamond particles by aluminum hydroxide particles formed under these conditions. The results thus indicate that boundary layers play a significant role in the stability of natural diamond dispersions. Figures 4; references 19: 8 Russian, 11 Western.

6508/9835

CSO: 1841/107

EFFECT OF MODIFICATION ON HYDROPHOBICITY OF MINERAL POWDERS OF LAMINAR SILICATES

Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 52, No 12, Dec 86  
(manuscript received 13 Jun 85) pp 1256-1259

[Article by Ye.V. Terlikovskiy, V.V. Simurov and G.M. Veysova, Institute of Colloid Chemistry and Chemistry of Water, UkSSR Academy of Sciences, Kiev]

[Abstract] Owing to their highly developed surface structure, powdered clayey mineral (laminar silicates) are hydrophilic and readily adsorb moisture from air making them unsuitable as polymer fillers unless their surface is modified. This is normally carried out on an industrial scale as a combined step during milling and drying. Since the latter is usually carried out at 423-473 K, the modifier must be heat resistant. In the present work the heat resistance of various cationic, anionic and siliconorganic modifiers was studied. Modifiers GKZh-94 and PMS-700 are capable of imparting maximum hydrophobic effect on polygorskite and are recommended for such use during combined milling/drying operations. Figures 4; references 9 (Russian).

12765/9835  
CSO: 1841/152

AEROSOLS

UDC 541.182.2/.3:536

THERMAL POLARIZATION OF BODIES IN GAS STREAM AND THERMOPHORESIS OF AEROSOLS  
AT LOW KNUDSEN NUMBERS

Moscow KOLLOIDNYY ZHURNAL in Russian Vol 48, No 5, Sep-Oct 86  
(manuscript received 28 Nov 84) pp 851-855

[Article by S.P. Bakanov, V.V. Vysotskiy and A.N. Nekrosov, Department of  
Surface Phenomena, Institute of Physical Chemistry, USSR Academy of Sciences,  
Moscow]

[Abstract] An experimental study is used to determine a coefficient which  
considers the influence of surface curvature on the rate of thermal slippage  
and accommodation factor of momentum and energy for a number of gas-surface  
systems. Consideration of thermal polarization allows more precise analysis  
of the results of studies of thermophoresis of large aerosols than was  
previously possible. An attempt is made to explain the divergence between  
published formulas for thermophoresis rate and experimental data. Figures 2;  
references 14: 9 Russian, 5 Western.

6508/9835  
CSO: 1841/107

UDC 536.423.4:550.462

INFLUENCE OF SPECTRUM OF CONDENSATION NUCLEI ON SPECTRA OF CLOUD DROPLETS  
DURING NATURAL CLOUD FORMATION AND WHEN CETYL ALCOHOL IS PRESENT

Moscow KOLLOIDNYY ZHURNAL in Russian Vol 48, No 5, Sep-Oct 86  
(manuscript received 10 Dec 85) pp 867-879

[Article by B.V. Deryagin and K.M. Merzhanov, Department of Surface  
Phenomena, Institute of Physical Chemistry, USSR Academy of Sciences,  
Moscow]

[Abstract] A study is made of the significance of the distribution of  
condensation nuclei by dimensions in the process of formation of the cloud



droplet spectrum when cetyl alcohol vapor is present as well as in natural cloud formations. This is done by analyzing a number of cycles in model numerical experiments under identical conditions but with different distributions of condensation nucleus dimensions. The process of cloud formation in an ascending flow of a horizontally homogenous vapor-gas mixture is studied. When cetyl alcohol is present it is assumed that the mixture is saturated with its vapor at all altitudes. The cetyl alcohol is found to cause the cloud droplet spectrum to split into two parts or to remain combined when it would split into two parts were the cetyl alcohol not present. The breakup of cloud droplet spectra caused by cetyl alcohol may be effective, producing droplets of over 60  $\mu\text{m}$  diameter and thus leading to precipitation, or ineffective, when droplets do not grow to the necessary dimensions for precipitation. The process is effective only for cetyl alcohol vapor with certain condensation nucleus spectra. Figures 4; references 21: 8 Russian, 13 Western.

6508/9835  
CSO: 1841/107

UDC 541.182.21.3:537

OSCILLATING MOVEMENT OF CHARGED AEROSOL PARTICLES IN STRONG ELECTRIC FIELD

Moscow KOLLOIDNYY ZHURNAL in Russian Vol 48, No 5, Sep-Oct 86  
(manuscript received 14 Dec 84) pp 962-966

[Article by G.I. Surovtsova and V.I. Turubarov, Leningrad Institute of Aviation Instrument Building]

[Abstract] The study of oscillating movements of charged aerosol particles in an electric field has been conducted only for the Stokes flow mode with Reynolds numbers much less than one. This article studies the problem of oscillating movement over a broad range of Reynolds numbers by solution of nonlinear differential equations by a method described in an earlier work. Equations are derived yielding an analytic description of the amplitudes of oscillation and phase shift angles as functions of field voltage and frequency and particle dimension. Figures 3; references 3 (Russian).

6508/9835  
CSO: 1841/107

## DETERMINATION OF MAXIMUM ICE-FORMING ACTIVITY OF METAL OXIDES. INFLUENCE OF METAL OXIDE SURFACE MODIFICATION ON ICE-FORMING PROPERTIES

Moscow KOLLOIDNYY ZHURNAL in Russian Vol 48, No 5, Sep-Oct 86  
(manuscript received 27 Dec 84) pp 1014-1018

[Article by B.Z. Gorbunov, K.P. Kutsenogiy and A.S. Safatov, Institute of Chemical Kinetics and Combustion, Siberian Department, USSR Academy of Sciences, Novosibirsk]

[Abstract] Previous studies had shown that there is an optimal concentration of hydroxyl groups, about 324 per  $\text{nm}^2$ , for which the ice-forming activity of a reagent is maximal. The ice-forming activity of  $\text{SiO}_2$  powder depends on the concentration of hydroxyl on the surface of the particles and is maximal at 3.6 OH groups per  $\text{nm}^2$ . A similar dependence can be expected for other metal oxides. In determining the value of  $N_{\text{max}}$  for a reagent in a fog chamber, one must determine not only the optical aerosol particle diameter, but also the optimal concentration of hydroxyl groups on the surface. This article studies the determination of these concentrations for aerosol particles of  $\text{Al}_2\text{O}_3$  and  $\text{ZnO}$ . Increasing the concentration of hydroxyl groups on the surface of  $\text{ZnO}$  particles increases ice-forming activity by a factor of 60, on  $\text{Al}_2\text{O}_3$  by a factor of 4. This factor must be considered in calculating ice-forming activity of aerosol particles. Figures 2; references 23: 12 Russian, 11 Western.

6508/9835  
CSO: 1841/107

UDC 543.42

## ATOMIC AND MOLECULAR SPECTRA OF SAMPLE COMPOSITION EFFECTS ON ATOMIZATION OF Zn, Cd, Sn, Bi, Pb, and Sb

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 41, No 11, Nov 86  
(manuscript received 24 Apr 85) pp 1965-1973

[Article by I.P. Kharlamov, V.I. Lebedev and V.Yu. Persits, Scientific Production Association for Machine Design and Construction, Moscow]

[Abstract] Analysis of atomic and molecular spectra was used in a study designed to assess sample composition effects on atomization of Zn, Cd, Bi, Sn, Pb, and Sb from steel, using  $\text{HCl}$ ,  $\text{HCl-HNO}_3$  and  $\text{HNO}_3$  solutions. Combination of the spectral data with information on metal oxide evaporation and dissociation kinetics led to delineation of the factors affecting this process. The effects of Fe, Ni and Cr were minimal in the case of Zn and Cd atomization. A somewhat more pronounced effect was seen with atomization of Pb and Bi, and even more so in the case of Sb and Sn. Atomization was found

to be most efficient from  $\text{HNO}_3$  solutions. However, the latter is most applicable to simple and low-alloy steel. The use of  $\text{HCl-HNO}_3$  was found applicable to all high-alloy steel samples following their solubilization in  $\text{HCl}$  and  $\text{HNO}_3$  mixtures. The latter system made it possible to determine  $10^{-3}$  to  $10^{-4}\%$  concentrations of the elements. Figures 5; references 19: 10 Russian, 9 Western.

12172/9835  
CSO: 1841/147

UDC 543.42

#### EVALUATION OF ANALYTICAL APPLICABILITY OF TUNGSTEN COIL ATOMIZER

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 41, No 11, Nov 86  
(manuscript received 15 Jul 85) pp 1974-1983

[Article by A.A. Pupyshev, V.N. Muzgin and V.B. Atnashev, Ural Polytechnic Institute imeni S.M. Kirov, Sverdlovsk]

[Abstract] An evaluation was conducted on a tungsten-coil atomizer to assess its applicability to a wide spectrum of elements. The study was conducted in terms of the experimental relationship between the concentration of the element being analyzed ( $M$ ) and the equilibrium temperature of the reaction ( $T_{eq}$ ).  $T_{eq}$  was calculated from the isobaric-isothermal equivalence potential based on the Van't Hoff equation. Trials with 27 elements demonstrated that  $\log M = f(T_{eq})$  relationships yield a linear plot with a correlation coefficient with a value of ca. 0.85. Thermodynamic calculations demonstrated that improvement of the detection limits may be based on the selection of the appropriate dominant atomizing reaction, rather than by changing the partial pressure of the reaction. Figures 1; tables 2; references 19: 17 Russian, 2 Western.

12172/9835  
CSO: 1841/147

## SYNTHESIS OF REGECOLINE

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 4, Jul-Aug 86  
(manuscript received 6 Feb 86) pp 464-465

[Article by R.V. Alikulov, B. Chommadov, D.M. Pratoeva and M.K. Yusunov,  
Tashkent Order of Labor Red Banner State University im. V.I. Lenin]

[Abstract] Regecoline (I), separated from the above-ground part of the plant *Colchicum kesselringii* Rgl., is the first example of quaternary dehydrohomoproaporphine alkaloids with a spirocyclohexanol ring. Improved synthesis of I from kesselringine (II) was accomplished by two methods with good yields. Photochemical conversion of II in an aqueous methanol solution exposed to sunlight for 36 days produced 77% yield of I. Progress of reaction was controlled by thin layer chromatography. I and unreacted II were extracted with chloroform, evaporated to dryness, and (light orange crystalline) I was isolated from acetone. It was identified by  $R_f$  value, melting point and spectral data. I was also obtained by oxidation of II with iodine in dioxane for four hours. Thin layer chromatography established that the reaction solution contained I ( $R_f$  0.39), II ( $R_f$  0.90) and regelinone ( $R_f$  0.52). I was isolated as the acetyl derivative of I. Acetylregecoline ( $R_f$  0.62) was identified by spectra data. Yield was 86%. Acetylregecoline can be converted into I by hydrolysis with hydrochloric acid into 12-demethylregecoline with subsequent methanolysis. It was established that oxidation of homoproaporphines of II type with iodine leads to the  $C_{6a}$ -dehydroderivative. References 5: 4 Russian, 1 Western.

12886/9835

CSO: 1841/137

## SYNTHETIC ANALOGS OF ALKALOIDS OF PEGANUM. Part 3. PENTAMETHYLENEQUINAZOLONES

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 4, Jul-Aug 86  
(manuscript received 10 Feb 86) pp 465-469

[Article by A.L. Dyakonov, M.V. Telezhenetskaya and S.Yu. Yunusov, Order of Labor Red Banner, Institute of Chemistry of Plant Materials of UzSSR Academy of Sciences, Tashkent]

[Abstract] Pentamethylenequinazolones and pentamethylenequinazolines were synthesized in work already underway to obtain analogs of alkaloids of Peganum L. Monosubstituted 5-, 6- and 8-methoxy-3,4-dihydro-2,3-pentamethylenequinazolones were prepared by condensation of monosubstituted methoxyanthranilic acids with capralactam in toluene in the presence of  $\text{POCl}_3$ . Use of toluene as a solvent in this reaction reduces  $\text{POCl}_3$  amount and lowers heterogeneity of the reaction mixture. For synthesis of 6-methoxy-3,4-dihydro-2,3-pentamethylenequinazolone, 5-methoxyanthranilic acid was replaced with 5-methoxymethylantranilate. Use of the methyl ester instead of the acid doubled the yield. Yield of 81% was reported. For preparing 3-methoxyanthranilic acid, a previously-used synthesis scheme was modified to exclude acylation of the amine group with subsequent saponification of the acyl group. Instead, 2-nitro-3-methoxytoluene was oxidized to the corresponding benzoic acid and reduced to 3-methoxyanthranilic acid, whose yield and its corresponding quinazolone, 8-methoxy-3,4-dihydro-2,3-pentamethylenequinazolone, were doubled. It was shown that the methoxy group in pentamethylenequinazolones is demethylated readily with hydrobromic acid giving the corresponding hydroxy compound. During reduction of 6- and 8-methoxy and 6- and 8-hydroxy-3,4-dihydro-2,3-pentamethylenequinazolones with zinc in hydrochloric acid, the corresponding pentamethylenequinazolines were obtained. This reaction does not proceed smoothly. Yields did not exceed 30-50% because by-products are formed. The corresponding pentamethylenequinazoline derivatives could not be produced from 5-methoxy and 5-hydroxy-3,4-dihydro-2,3-pentamethylenequinazolones. Melting points of the bases and their chlorohydrates are given. Some characteristics of UV, mass and PMR spectra for the prepared compounds are presented. References 11: 6 Russian, 5 Western.

12886/9835  
CSO: 1841/137

APPLICATION OF HETEROPOLY COMPOUNDS TO ANALYSIS OF DRUGS AND BIOLOGICAL  
SAMPLES AND TO BIOMEDICAL RESEARCH

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 41, No 11, Nov 86  
(manuscript received 5 Mar 85) pp 1925-1933

[Article by Ye.N. Semenovskaya, Moscow State University imeni M.V. Lomonosov]

[Abstract] A review is presented of the use of heteropoly acids (HPA) in various areas of biomedical research. In the analysis of drug preparations both direct and indirect methodology is employed, with the HPA serving as precipitants, oxidizing agents, and dyes. For example, in the case of alkaloids P-Mo, P-W or Si-W serve as the reagents of choice for preparing poorly-soluble precipitates. P-W and P-Mo HPAs have found application in analysis of the vitamin B<sub>12</sub> group by changing their absorption spectra. In addition, the HPAs have also found use in developing chromatograms. More general biological applications include the use of these compounds for the analysis of various toxins and other biological materials, the creation of liquid ion-exchange electrodes for phosphate determination, and the isolation in pure form of selected enzymes such as lactase. Biomedical research has seen the use of HPAs as effective sorbents for radionuclides, as synthetic electron acceptors in photosynthetic studies, and as reagents in histochemical and peptide chemistry reactions. To date, however, the scope of application of HPAs in biology has been based on chance rather than on theoretical foundations. The development of kinetic methods of analysis should facilitate further applications of these compounds in biological research. References 83: 1 Hungarian, 40 Russian, 42 Western.

12172/9835

CSO: 1841/147

SPECTROPHOTOMETRIC ANALYSIS OF LANTHANUM, LUTETIUM AND YTTRIUM WITH  
TRIPHENYLMETHANE REAGENTS AND CETYLPYRIDINIUM BROMIDE

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 41, No 11, Nov 86  
(manuscript received 26 Aug 85) pp 2004-2008

[Article by V.N. Azarova and A.I. Kirillov, Irkutsk State University  
imeni A.A. Zhdanov]

[Abstract] A spectrophotometric method was devised for the determination of La, Lu and Y in mixtures by means of complex formation with p-xyleneol-phthalexone-S, o-cresolphthalexone-S, glycine cresol red, and phthalexone-S in conjunction with cetylpyridinium bromide. The resultant complexes were read at wavelengths in the range of 604-650 nm. A computer program written in Fortran was designed for solving the system of equations for these mixed ligand complexes. The lower detectable concentration for La was 0.10  $\mu\text{g/ml}$ , and for Lu and Y 0.20  $\mu\text{g/ml}$ . The working range of ratios for the metals in the mixtures was 1:5. References 18 (Russian).

12172/9835  
CSO: 1841/147

UDC 543.42

PHOTOMETRIC DETERMINATION OF URANIUM IN LOW-GRADE ORES AND CAKES WITH  
ARSENAZO III AND CHLOROARSENAZO III AFTER REMOVAL OF IMPURITIES WITH  
HYDROXYLAMINE

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 41, No 11, Nov 86  
(manuscript received 24 Jun 85) pp 2027-2031

[Article by V.F. Lukyanov, Ye.P. Duderova, Ye.F. Novak, T.Ye. Barabanova and  
N.F. Shcherbakova]

[Abstract] A method has been developed for the removal of impurities (Th, Zr, Ti, rare earth elements) from low-grade ores and cakes with hydroxylamine in order to facilitate photometric determination of uranium. Arsenazo III allowed detection of  $5 \times 10^{-4}\%$  uranium at pH 1.5-2.0, conc. HCl, while with chloroarsenazo III yielded detectable uranium levels of  $10^{-3}\%$ , with standard deviations of  $\leq 0.05$ . Arsenazo III was found to tolerate higher levels of impurities than chloroarsenazo III, thereby demonstrating greater selectivity. Tables 2; references 12: 9 Russian, 3 Western.

12172/9835  
CSO: 1840/147

ANNUAL SESSION OF SIBERIAN DEPARTMENT OF SCIENTIFIC COUNCIL OF USSR ACADEMY  
OF SCIENCES ON ANALYTICAL CHEMISTRY

Moscow ZHURNAL ANALITICHESKOY KHIMII in Russian Vol 41, No 11, Nov 86  
pp 2099-2102

[Article by M.M. Goldshteyn and Yu.S. Shafranskiy]

[Abstract] This annual session was held in Novosibirsk on December 9-13, 1985. The theme of the session was "Analysis of Biological Compounds, Medicinal Preparations and Agroindustrial Products", with the participation of 130 scientists. In addition to topical problems and research reports the session also served as a forum for discussion of administrative matters. Emphasis was placed on the need for more cooperation among the various analytical services, the establishment of more stringent quality control regulations, and the preparation and availability of documented standards.

12172/9835

CSO: 1841/147

UDC 541.6+546.287

QUANTUM CHEMICAL STUDY OF DIPOLE MOMENTS OF 1-SUBSTITUTED SILATRANES IN  
ELECTRON-EXCITED STATES

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 292, No 2, Jan 87  
(manuscript received 19 May 86) pp 384-387

[Article by Corresponding Member USSR Academy of Sciences M.G. Voronkov, D.D. Chuvashyev, G.V. Ratoyskiy and E.I. Brodskaya, Irkutsk Institute of Organic Chemistry, Siberian Department USSR Academy of Sciences]

[Abstract] Dipole moments of molecules in an electron-excited state may be estimated by studying the effects of solvents on the absorption and fluorescence spectra. Quantum chemical calculations for such molecules have been done only for simple compounds. In a previous work, the dipole moments of 1-aryl silatranes in electron-excited state were evaluated and a hypsochromic shift of the long-wave  $\pi \rightarrow \pi^*$  band transition in UV-absorption spectra and a bathochromic shift of this maxima in fluorescence spectra were observed as the polarity of the solvent increased. To establish the nature of these transitions and the structure of 1-substituted silatranes in the excited state, a quantum chemical study was made of 1-methyl- and 1-vinylsilatranes with the CNDO/S method with DBJ2 parametrization was made. The calculations demonstrated that UV-absorption is determined by both forbidden and permitted transitions. Depending on the type of transition, the dipole moment of the 1-vinylsilatrane molecule in the excited state increases or decreases. This was used to explain the reverse shifts in  $\pi$ ,  $\pi^*$  transitions in absorption and fluorescence spectra of 1-arylsilatranes. It is hypothesized that two such transitions take place in the 1-vinylsilatrane



molecule. The first is characterized by a smaller energy input to the silatryl group in the vacant Pi-type molecular orbital in comparison to the occupied. Therefore, the dipole moment of 1-arylsilatrane increases somewhat when going over to this state. This is manifested in the bathochromic shift of the fluorescence spectra with increasing polarity of the solvent. Molecular orbitals which participate in the second transition are characterized by a greater energy input to the silatryl group in the vacant molecular orbitals in comparison to the occupied. On excitation the dipole moment decreases and a hypsochromic shift is observed in the UV-spectra of 1-arylsilatranes. Thus the previously observed contradiction in the direction of dipole moment change in 1-arylsilatranes in the excited state has been eliminated. Tables 2; references 10: 3 Russian, 7 Western.

12765/9835  
CSO: 1841/162

BIOCHEMISTRY

UDC 541.183.26:546.181

ADSORPTION OF WATER VAPOR AND GASES BY BIOPOLYMERS. PART 3. EFFECTS OF  
PRETREATMENT WITH HCl ON HYDRATION OF BIOPOLYMERS

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 60, No 11, Nov 86  
(manuscript received 24 Jul 85) pp 2846-2848

[Article by F.B. Sherman, G.N. Shikhaleyeva and B.M. Kats, Scientific  
Research Institute of Physics, Odessa State University imeni I.I. Mechnikov]

[Abstract] The effects of pretreatment of bovine serum albumin and  $\alpha$ -chymotrypsin with gaseous HCl on subsequent hydration were determined for comparison with hydration obtained under conventional conditions. The 'dry' protein preparations were saturated with gaseous HCl at 298 K under a gas pressure of 60 kPa, with subsequent desorption by evacuation at 1.33 Pa to give proteins with irreversibly-adsorbed HCl. Pretreated proteins evidenced water monolayers and maximum hydration 3- to 4-fold greater than for neutral preparations and acid preparations isolated from aqueous solutions at pH 3-4. These observations demonstrated that pretreatment of dehydrated proteins with gaseous HCl predisposes to a greater degree of hydration that obtained under conventional 'wet' conditions. Further studies shall be required to provide an explanation for this difference. Figures 1; references 8 (Russian).

12172/9835

CSO: 1841/110

## CURRENT TRENDS IN BIOCOORDINATION CHEMISTRY

Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 31, No 11, Nov 86  
(manuscript received 28 Jan 86) pp 2740-2747

[Article by K.B. Yatsimirskiy, Institute of Physical Chemistry  
imeni L.V. Pisarzhevskiy, Ukrainian SSR Academy of Sciences]

[Abstract] Biocoordination chemistry, the branch of bioinorganic chemistry concerned with the behavior of metals in living systems in terms of coordination chemistry, has encountered considerable methodological difficulties in placing the field on a quantitative basis. Part of the problem lies in the extremely small quantities of metal that are present in the biological systems--generally within  $10^{-6}$  to  $10^{-12}$  moles/liter--and in part in the complexity of the binding ligands. To some extent the problem has been approached by highly sensitive physical methods, such as ESR and various forms of mass spectrometry, field desorption, and fast atom bombardment. However, considerable information has been accumulated on the nature of binding to various biological substrates and the kinetic and thermodynamic correlates of such reactions. In addition, many organometal compounds have found application in clinical medicine as diagnostic and therapeutic agents. Figures 3; references 17: 9 Russian, 8 Western.

12172/9835

CSO: 1841/119

CATALYSIS

UDC 541.145

HIGH QUANTUM YIELDS IN PHOTOCATALYTIC FORMATION OF STRONG OXIDANT  $\text{Os}(\text{bipy})_3^{3+}$   
WITHIN LIPOSOMES

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 10,  
Oct 86 (manuscript received 23 Apr 85) pp 2213-2216

[Article by Ye.I. Knerelman and V.Ya. Shafirovich, Chernogolovka Department,  
Institute of Chemical Physics, USSR Academy of Sciences]

[Abstract] In order to obtain an efficient system for the synthesis of  $\text{O}_2$  from water within liposomes, a system was devised for the creation of a strong oxidizing agent within the vesicles. The experimental approach relied on incorporation into the liposomal wall of electron carriers with a high redox potential represented by the  $(\text{bipy})_2\text{M}[\text{bipy}(\text{C}_{17})_2]^{2+}$  complexes, where  $\text{bipy} = 2,2'$ -dipyridyl,  $\text{bipy}(\text{C}_{17})_2 = 4,4$ -diheptadecyl- $2,2'$ -dipyridyl, and  $\text{M} = \text{Ru}$  or  $\text{Os}$ . The liposomes were prepared from dipalmitoyl-DL-alpha-phosphatidylcholine, from which the incorporated oxidizing agents diffused very slowly (less than 10% for  $\text{Os}(\text{bipy})_3^{3+}$  after 20-30 h at ca.  $20^\circ\text{C}$ ). Following illumination at 436 nm, the quantum yield of  $\text{Os}(\text{bipy})_3^{3+}$  within the vesicles corresponded to irreversible oxidation of the photosensitive agent, which, under optimal conditions, approached 30%. Figures 1; references 6 (Western).

12172/9835

CSO; 1841/112

## NOVEL APPROACH TO ACTIVATION OF MOLECULAR OXYGEN

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 10, Oct 86 (manuscript received 3 Sep 85) pp 2329-2330

[Article by A.M. Khenkin, Chernogolovka Department, Institute of Physical Chemistry, USSR Academy of Sciences]

[Abstract] A peroxocomplex between a heme group and  $O_2$  was achieved in a reaction system involving tetra ( $\alpha, \alpha, \alpha, \alpha$ -o-pivaloylphenyl)porphyrin-Fe-Br as the oxygen carrier, trithiylimidazole as the axial ligand, Zn/Hg amalgam as the reducing agent, and methyl viologen as the electron carrier. Exposure of the system to  $O_2$  resulted in the formation of the porphyrin- $Fe^{III}O_2^{2-}$  complex (436 nm, 570 nm,  $g = 4.3$ ), which was stable for several

hours at ca. 20°C. This complex functioned as a catalyst analogous to the cytochrome P-450 system in catalyzing the oxidation of cyclohexane to cyclohexanol with a 200% yield in terms of porphyrin-FeBr. References 5: 2 Russian, 3 Western.

12172/9835  
CSO: 1841/112

UDC 542.91:541.128.34:541.49:546.791

## SYNTHESIS AND CATALYTIC ACTIVITY OF URANIUM (IV) TETRAPHENYLPORPHYRINATE CHLORIDE

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 9, Sep 86 (manuscript received 10 Oct 85) pp 2131-2132

[Article by S.S. Lalayan, A.B. Soloveva and E.A. Fushman, Institute of Chemical Physics, USSR Academy of Sciences, Moscow]

[Abstract] The porphyrinates of some transition metals catalyze nonchain regioselective oxidation of olefins by molecular oxygen in the presence of sodium borohydride. Determination of the significance of the central metal ion in this reaction requires a study of the catalytic properties of the metalloporphyrins with various metals capable of changing valence during the process. This article demonstrates that uranium (IV) tetraphenylporphyrinate chloride, synthesized for the first time, has the corresponding catalytic activity in the oxidation of cholesterol. References 3: 2 Russian, 1 Western.

6508/9835  
CSO: 1841/104

UDC 541.145:542.924:546.212:546.92:539.19:620.187

PLATINUM CATALYST BOUND TO LIPID VESICLE WALL FOR PHOTO-SEPARATION OF HYDROGEN FROM WATER

Moscow KINETIKA I KATALIZ in Russian Vol 27, No 6, Nov-Dec 86  
(manuscript received 28 Jan 86) pp 1378-1383

[Article by V.E. Mayer, L.A. Levchenko and V.Ya. Shafirovich, Department of Institute of Chemical Physics, USSR Academy of Sciences, Chernogolovka]

[Abstract] Fixation of catalysts for separation of hydrogen from water in organized molecular ensembles appears promising as a molecular system for decomposition of water into hydrogen and oxygen with visible light. Results are presented on a study of the structure and mechanism of platinum catalyst added to a previously proposed vesicular photocatalytic system. Electron microscopy showed that the platinum catalyst consists of metallic particles 14 ± 3 Angstroms bound to the walls of the lipid vesicles. Constants for individual stages of electron transfer processes were measured and a mathematical model describing the hydrogen separation process during stationary photolysis is presented. Figures 3; references 17: 4 Russian, 13 Western.

12765/9835  
CSO: 1841/149

UDC 541.128.12:541.124:542.924:546.735

MECHANISM OF OXO-REACTIONS. PART 4. ACTIVATION OF CARBONYLS

Moscow KINETIKA I KATALIZ in Russian Vol 27, No 6, Nov-Dec 86  
(manuscript received 9 Oct 85) pp 1478-1480

[Article by M.S. Borovikov and V.A. Rybakov, Scientific Production Association "Lenneftekhim", Leningrad]

[Abstract] A carbonyl activation reaction mechanism involving changes in the electron multiplet status is proposed for the Oxo synthesis reaction. The basic electron state of Co-unsaturated carbonyl is a triplet as in the case with certain previously reported carbenes, while in the saturated carbonyl it is a singlet. Interconversion with a CO-ligand splitting off is viewed as a carbonyl activation mechanism in the Oxo reaction. References 18: 6 Russian, 12 Western.

12765/9835  
CSO: 1841/149

CHEMICAL INDUSTRY

CHEMICAL INDUSTRY ADVANCES PUBLICIZED AT NEWS CONFERENCE

Moscow TASS in English 2258 GMT 9 Jan 87

[Text] "The Soviet chemical industry ranks first in Europe and second in the world as regards the volume of its output," said Yuriy Besspalov, USSR Minister of the Chemical Industry, addressing a press conference here today.

Highly effective technological procedures are applied in the production of practically all types of chemical products in the USSR with the use of powerful plants, means of automation, and mechanization."

In the current Five-Year Plan period (1986-1990), the minister stressed, "the output of the chemical industry is to grow 32.4 percent. In the next decade it is almost to double as compared with 1990. By the year 2000 the proportion of chemical products, in the aggregate Soviet industrial output, is to reach eight percent as against 6.2 percent in 1986."

"The achievements of the Soviet chemical industry are to be demonstrated at the international specialized exhibition 'Chemistry-87' scheduled to be held in Moscow in September this year. Theoretical and applied research in the field of chemistry and chemical technology, gene engineering and biotechnology, and laser equipment will be mirrored in 13 sections of the Soviet part of the exhibition," Yuriy Besspalov said.

"The Soviet chemical industry," the minister emphasized, "takes an active part in an international division of labor on the basis of cooperation and specialization. Cooperation with colleagues in the socialist countries contributes to the implementation of the comprehensive program for scientific-technical progress of the CEMA member states until the year 2000. The Soviet Union's business ties with firms in the capitalist countries are aimed at resolving questions in such important fields as membrane technology, production of structural plastics, the development of diaphragm electrolyzers for the production of chlorine and caustic soda, manufacture of equipment for the processing of plastics, and manufacture of instruments for scientific research."

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CSO: 1841/124

UDC 667.2:65.011.56.002.5

APPROACHES TO CREATING INFORMATION BASE OF SCIENTIFIC-TECHNICAL, TECHNO-ECONOMIC AND ECOLOGICAL CHARACTERISTICS OF ANILINE DYE PRODUCTS

Moscow KHIMICHESKAYA PROMYSHLENNOST in Russian No 11, Nov 86 pp 697-699

[Article by A.L. Poznyakevich, B.V. Yermolenko and Ye.N. Lyubimova]

[Abstract] Various facets of developing a data base for dye production are summarized. The dyes produced by the Moscow Scientific Production Association of the Scientific Research Institute for Organic Semi-manufactured Products and Dyes include direct dyes for cotton and viscous fabrics; acidic dyes for pure wool and wool blends; dispersion dyes for synthetic fabrics, etc. Parameters include 30-40 related to properties and use effectiveness, more than 50 for technical and economic features, over 20 related to the composition and volume of industrial waste, and data on comparable foreign products and import volumes. Further data are being collected as changes and innovations in the basic product mix occur. Automated data systems for toxic factors, environmental and standardization considerations, and management of hundreds of plants involved in the production of dyes throughout the Soviet Union also form part of the overall project. The various data have been categorized and divided into three groups: group one, general information including colors and formulas, country of manufacture for foreign dyes, use indications and other scientific information; group two includes information on applications and warranty data, economic impact, and patent significance; finally the third group has technical economic information and environmental data. The association regards the comprehensive data base collected so far to be the first step in creating a unified data system for the entire aniline-dye industry in the Soviet Union.

12131/9835

CSO: 1841/142



SUPPORT SOUGHT FOR CREATION OF INTERBRANCH PLASMA TECHNOLOGIES CENTER

Moscow PRAVDA 26 Jan 87 p 3

[Article by Ye. Solomenko, correspondent (Novosibirsk)]

[Abstract] A lengthy article examines problems of the creation of an inter-branch center of plasma and hardening technologies, including electron-beam, laser and other technologies. This center is supposed to be established by the end of 1987 on the basis of the present special design bureau "Energokhimmash". This reportedly was decided by the Siberian Department of the USSR Academy of Sciences and by the design bureau's parent organization, the Ministry of Chemical and Petroleum Machine Building.

It is recalled that "Energokhimmash" was one of a number of industry research institutes and design bureaus that were created in the 1960s and 1970s in Novosibirsk to work on industrial applications of technologies developed at institutes of the academy's Siberian Department. A scientific school of plasma technologies had become well-established at the Institute of Thermophysics, and a large group of this institute's associates went to work at the bureau when it was founded. The bureau was put under the chemical machinery ministry. Throughout the years it has developed plasma generators and other technology in support of its industry. The article recalls the development of one particular unit for plasma treatment of toxic chemical wastes, to turn them into paint solvents.

It is said that now there is a need for developing a wider range of and more powerful and reliable industrial models of plasma generators and units for applying coatings and hardening parts. The new interbranch center is supposed to take existing laboratory models and develop them into industrial machines, and to organize their mass production. The article points out that the reason this was never accomplished in the past is that the design bureau has never had its own experimental production facility, and the ministry seems to be balking even now at providing the support needed for such a facility. The bureau's director, Prof. Anatoliy Petrovich Burdukov, showed the author of the article a recently completed building, in which he said the bureau plans to install units for plasma spray coating, and units for electron-beam, detonation and laser hardening of materials. He explained, however, that the bureau managed to get this building only through some deception, calling it by another name in the construction requisition, and he said it is only a beginning toward the facility that is needed.

In conclusion, the article notes that the new minister of chemical and petroleum machine building, V. Luk'yanenko, has stated intentions to provide support for work on new hardening technologies and for cooperating closely with the Academy of Sciences' Siberian Department. It is also noted that in December 1986 a decision was made to turn the bureau into an affiliate of the ministry's chief institute, the Scientific Research Institute of Chemical Machine Building.

FTD/SNAP

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CSO: 1841/172.

PHARMACEUTICAL INDUSTRY EXPANSION PLANS AND PROBLEMS

Moscow MEDITSINSKAYA GAZETA in Russian 12 Dec 86 p 1

[Article by L.P. Telegin, first deputy minister of the Ministry of Medical and Microbiological Industry]

[Abstract] The author comments on scientific, technical and administrative advances in the medical and microbiological industry, on progress in improving its products, and on the industry's plans for the next few years.

The author relates that capital investment in retooling and reconstruction of plants will amount to 1.3 billion rubles during the current Five-Year Plan period, as compared with 629 million in the 11th Five-Year Plan. Thanks to increased possibilities for broad introduction of the latest achievements of biotechnology, fine chemical engineering and organic synthesis, the introduction of more than 100 new drugs into production is planned during this period. Technology will be developed and introduced for producing more than 20 counterparts of highly effective foreign drugs that have been imported in the past. Development of the pharmaceutical industry's production, scientific-technical and experimental potential is to be substantially accelerated during the next eight years, in line with a large-scale program of the Ministry of the Medical and Microbiological Industry. Plans call for building a number of new plants and experimental shops, expanding and reconstructing existing plants, and creating 22 affiliates of scientific research institutes and design bureaus.

Attention is called to problems with suppliers of equipment and raw materials, which the author says must be resolved if plans are to be met. He complains that the medical and microbiological industry is now receiving less than 35 percent of the equipment it needs to produce medicines in finished forms, and that it is receiving too little machinery of high technical quality. He calls upon all of the country's machine-building industries for help in remedying this situation.

FTD/SNAP

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CSO: 1841/125

## COAL GASIFICATION

### INEXPENSIVE ENERGY, BY-PRODUCT PRODUCTION, CLEAN AIR: ELECTROTECHNICAL MHD-POWER PLANTS

Moscow KHIMIYA I ZHIZN in Russian No 9, Sep 86 pp 15-18

[Article by V.M. Belyaykin, candidate of technical sciences]

[Abstract] Generation of energy from coal produces oxides of nitrogen and sulfur, causing ecological and economic problems. Removing SO<sub>2</sub> from the exhaust gases with scrubbers in steam turbine thermal power plants can increase the capital cost by 20-30%. In magnetic hydrodynamic (MHD) power plants, the MHD generator efficiency reaches 5% and in principle can be doubled. This, combined with the steam turbine generator (about 40%), can give efficiencies in excess of 45% for MHD power plants. A MHD power plant using natural gas with 500 MW capacity will be on stream in 1989 near Ryazan. This will be an environmentally-clean installation with low oxides of nitrogen in the flue gases compared to the conventional thermal power plants burning coal. Using the Ryazan MHD power plant, in which the combustion products are converted into an ionized electro-conducting plasma, as a basis, several operating systems are examined for producing electric power. Fuels (coal) with a high sulfur content and a two-stage combustion are considered with provision for converting the oxides of nitrogen and sulfur into valuable chemical by-products. Because the MHD power plant is more efficient, less fuel is used and less by-product exhaust gas is produced. Four technological systems are examined for the MHD power plant with joint by-product production of sulfur, nitric acid and sulfuric acid, or nitric acid and sulfur (two schemes). These are compared to the conventional thermal power plant. The economics and technology of all four systems were evaluated in the Institute of High Temperatures of the USSR Academy of Sciences and the major steps of the processes were studied experimentally. The costs of all four systems were less than that for the conventional thermal power plant. The best system, with 22% less cost, was the specially developed process with addition of potassium carbonate (potash) to produce sulfur and nitric acid by-products. Also, the four MHD power station schemes are cheaper even when more expensive coal is burned. Cheap Kansk-Achinsk and Ekibastuz coals can be adapted for use in the MHD power plants. Though the first unit of the MHD power plant near Ryazan will burn natural gas, other MHD power plants will burn coal with by-product recovery of chemicals and will have the least damage on the surrounding environment. Figures 2; references 3 (Russian).

12886/9835  
CSO: 1841/108

SPONTANEOUS IGNITION OF MIXTURES OF N-HEPTANE, TOLUENE AND ETHANOL WITH AIR  
UNDER CONDITIONS PRESENT IN INTERNAL COMBUSTION ENGINE

Moscow KHIMICHESKAYA FIZIKA in Russian Vol 5, No 11, Nov 86  
(manuscript received 25 Dec 85) pp 1563-1571

[Article by S.N. Astafyev, S.A. Desnyak and O.D. Ubozhenko, Moscow Physical-  
Technical Institute]

[Abstract] An experimental study is presented of spontaneous combustion of a fuel mixture in advance of the flame front in the process of combustion of a charge in a motor burning a mixture of N-heptane, toluene and ethanol. The kinetics of preignition reactions are analyzed and delay of ignition of peripheral areas in the fuel mixture is calculated. The data generated on the dynamics of combustion with varying content of ethanol in the fuel mixture are used to determine changes in mixture temperature resulting from the addition of alcohol both due to the comparatively high heat of evaporation and due to the influence of ethanol on flame propagation velocity. A systematic deviation between calculated and experimental data is observed, increasing with increasing content of alcohol, indicating that the ethanol has an inhibiting influence on reactions in advance of the flame. Figures 4; references 8: 6 Russian, 2 Western.

6508/9835  
CSO: 1841/89

UDC 541.127:541.124.7:536.46;546.281:456.13:546.171.4

KINETIC FEATURES OF REACTIONS OF SILANE WITH CHLORINE AND NITROGEN  
TRICHLORIDE UNDER RAREFIED FLAME CONDITIONS

Moscow KINETIKA I KATALIZ in Russian Vol 27, No 6, Nov-Dec 86  
(manuscript received 3 Jan 86) pp 1291-1297

[Article by V.V. Azatyan and Ye.A. Markevich, Institute of Chemical Physics,  
USSR Academy of Sciences, Moscow]

[Abstract] Detection and study of chlorination processes taking place under rarefied flame conditions is of great interest to the theory of chemical kinetics because it helps broaden concepts of the mechanisms of complex branched chain reactions. The present work was undertaken to clarify the kinetics of reactions of silane with chlorine and nitrogen trichloride, the latter being a more active donor of chlorine atoms. A new branched chain process was detected in the case of silane and nitrogen trichloride. The reaction rates of silane with chlorine and nitrogen trichloride, the spectral composition and intensity of flame chemiluminescence and the relationship of these values to the initial pressure change spasmodically as the concentration ratios of initial reagents are varied within the autoignition region of a given value. Figures 4; references 17: 15 Russian, 2 Western.

12765/9835  
CSO: 1841/149

UDC 541.127:541.128.3:546.11'16:539.186+621.43.019.2

INFLAMMATION REGION CONFIGURATIONS IN SYSTEMS  $H_2$  WITH  $F_2$

Moscow KINETIKA I KATALIZ in Russian Vol 27, No 6, Nov-Dec 86  
(manuscript received 10 Jan 86) pp 1460-1462

[Article by V.G. Los]

[Abstract] In a previous study three types of configurations were found to be possible in the inflammation region of the simplest linear kinetic scheme having two active sites, and transfer from one type to another is achieved by changing the kinetic parameters of branching and rupturing reactions. In the present work the hydrogen-fluorine reaction is used as an example to demonstrate the relationship between configurations in the inflammation region and the Arrhenius parameters of the elementary stages of the reaction. By varying the Arrhenius parameters a closed inflammation region and a conventional inflammation peninsula were found. Figures 1; tables 1; references: 12 Russian, 3 Western.

12765/9835  
CSO: 1841/149

AUTOMATED LABORATORY STAND FOR STUDYING KINETICS OF ELECTROCHEMICAL REACTIONS

Vilnius TRUDY AKADEMII NAUK LITOVSKOY SSR: SERIYA B in Russian Vol 156, No 5, Sep-Oct 86 (manuscript received 17 May 85) pp 22-25

[Article by P.F. Mechinskas, A.M. Degtyarev, R.D. Milyavichyus and V.Yu. Styapankyavichene, Institute of Chemistry and Chemical Technology, LiSSR Academy of Sciences]

[Abstract] An automated laboratory stand for computer-controlled experiments studying kinetics of metal electroprecipitation is described, adaptable to galvanostatic impulse and galvanodynamic methods, permitting experimental data transfer to graphic display, dual coordinate plotter or an alphanumeric printer. This instrument is based on a microcomputer "Elektronika-60"-KAMAK system which is an interface between a computer and experimental setup; it controls the experiment as well as all measurements. This unit makes it possible to shorten experimental time, record, directly, numerical values of the experiment and thus reduce error. Experiments can be stopped at any stage and initial conditions altered operationally. Figures 1; references 3 (Russian).

7813/9835  
CSO: 1841/130

EXPLOSIVES AND EXPLOSIONS

UDC 541.124.7:541.127:539.19:546.215'171.55:543.422.27

CHAIN REACTION  $N_2F_4 + H_2O_2$

Moscow KINETIKA I KATALIZ in Russian Vol 27, No 6, Nov-Dec 86  
(manuscript received 24 Dec 85) pp 1457-1460

[Article by Yu.R. Bedzhanyan, Yu.M. Gershenzon, S.D. Ilin and V.B. Rozenshteyn,  
Institute of Chemical Physics, USSR Academy of Sciences, Moscow]

[Abstract] An experimental study was made of the title reaction employing  
EPR/IR LMR spectroscopy to measure the concentrations of intermediate active  
sites. A model for a chain reaction is proposed and used to develop kinetic  
relationships for the intermediate active sites. The proposed mechanism  
describes adequately the observed kinetic relationships. It is also  
demonstrated that the above reaction may be used as source for  $HO_2$ .  
Figures 2; references 6: 5 Russian, 1 Western.

12765/9835  
CSO: 1841/149

## FERTILIZERS

UDC 631.893.1,2'3

### PLANS FOR DEVELOPMENT OF FERTILIZER CHEMISTRY AND TECHNOLOGY

Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 5, Sep-Oct 86 pp 7-14

[Article by M. Nabiyev under the "Inorganic and Analytical Chemistry" rubric: "Urgent Problems in the Chemistry and Technology of Fertilizers in the Light of the 27th CPSU Congress"]

[Text] The far-reaching problems posed by our Party's 27th Congress with regard to accelerating socio-economic development can be successfully solved only on the basis of advanced technology and extensive introduction of progressive production processes and flexible production facilities, which will permit rapid restructuring for output of new products which have the greatest economic and social effect.

Fertilizers are being given a significant role in accomplishing the Party's agrarian program. We know that at least half the increase in the yield of agricultural crops usually comes from the use of fertilizers.

Our country is paying exceptional attention to the development of mineral fertilizer production. The resolutions of the 27th CPSU Congress call for increasing output of mineral fertilizers (in nutrients) to 41-43 million tons in 1990 and expanding the assortment and raising its quality.

Plants need compounds which contain many chemical elements, each of which fulfills a certain function and cannot be replaced by another.

Production of complex nitrophosphorus fertilizers is expanding primarily due to sulfuric acid and nitric acid processing of raw phosphate. The phosphorus in raw phosphate is found in the form of compounds which cannot be assimilated by plants (fluorapatite and other minerals). Acutely scarce sulfuric acid, which is used only to break down the raw phosphate, is consumed in increasing quantities in processing natural phosphates. The potassium sulfate (gypsum) byproduct is ballast. About 40 million tons of phosphorus gypsum have accumulated in dumps at the Almalyk, Samarkand, and Novokokand chemical plants alone. Radical ways to use all the discarded phosphorus gypsum must be found.

Ammophos is a complex fertilizer unbalanced in terms of nutrients. According to the agrotechnology now in use in cotton production, the greater part of the phosphorus fertilizer is usually applied at the fall plowing, and ammophos containing 42-50 percent phosphorous anhydride and 10-11 percent nitrogen is used as the phosphorous fertilizer. This amount of



nitrogen is completely lost when it is applied at the fall plowing, which is intolerable.

Heat treatment of phosphates with production of phosphoric acid makes it possible to obtain highly concentrated fertilizers, but is an extremely energy-intensive method.

Production of thermophosphate and cement on the basis of thermoslags in a single technological process is of interest.

In treating phosphates with nitric acid, the acid's active hydrogen ion is used to break down the phosphates, while its anions are the desirable nitrogen component in the finished product. Consequently, the fertilizers retain an overall nitrogen balance, and consumption of sulfuric acid is eliminated [1, 2].

The idea of nitric acid treatment of raw phosphate belongs to Academician D. N. Pryanishnikov [3] and E. V. Britske [4], who pointed out the economy and prospects of this method in 1908. The method for obtaining nitrogen and phosphorus fertilizers in one production process by nitric acid treatment of phosphates is an example of the most complete and comprehensive use of chemical reagents. This permits a sharp increase in phosphorus fertilizer resources and a significant reduction in their net cost -- a major step forward in developing the industry for highly effective inexpensive fertilizers -- and tremendous growth in fertilizer production.

Apatites from the Khibiny Mountains deposit are unique in their content of strontium and rare-earth elements.

The method of separating strontium and rare-earth elements from apatite concentrate by nitric acid treatment is the most developed. Consequently, treating resources from the apatite concentrate of the Khibiny Mountain deposit by nitric acid breakdown is advantageous.

Thus, nitric acid processing of phosphates is an important reserve for successful fulfillment of the 27th CPSU Congress' resolutions regarding development of agricultural production and the country's economy.

Liquid fertilizers are being more and more widely used in agriculture in various countries. This is primarily attributable to economic considerations. Production of liquid fertilizers is less complicated because certain process stages (concentration, crystallization, drying, packaging, etc.) are simplified or eliminated.

Operations with liquid fertilizers can be completely mechanized, beginning with transportation from the plant and ending with application to the soil with comparatively simple machines or attachments, as well as agricultural aircraft. Experience using liquid fertilizers in the USSR and abroad has shown that total labor expenditures required to apply liquid fertilizers (including preparatory operations) are 3-4 times lower than with solid fertilizers. The caking, hygroscopicity, explosion hazard, uneven distribution during application, etc. which are inherent to solid fertilizers are entirely eliminated. Liquid fertilizers are easy to measure and micronutrients, growth agents, and herbicides can be applied to the soil

along with them. Liquid fertilizers can also be used both to spray the soil surface and leaves and to fertilize rows during the growing season. Losses of solid fertilizer in transit from the production plant to the field are high, and the use of nonvolatile forms virtually eliminates losses.

The use of volatile forms of nitrogen fertilizers (ammonia, ammoniates and ammonia water) is not advisable because of high losses during storage, transportation, and application due to elasticity in a hot climate [5]. The most convenient nitrogen fertilizers to use are crude solutions of ammonium and potassium nitrates of urea before they are sent to evaporators. Liquid nitrogen fertilizers with 30 percent nitrogen content and good physico-chemical properties result; the ratio of ammonium nitrate to urea is 1:1 or 1:1.5; crystallization temperature, from 4 to  $-18^{\circ}\text{C}$ ; density, 1.2-1.3  $\text{kg}/\text{cm}^3$ ; viscosity 3.2-3.8; pH, 7 [6].

Complex liquid fertilizers produced abroad (USA) are developed on the basis of thermal or extraction phosphoric acids and single nitrogen fertilizers. The high net cost of phosphoric acid makes these fertilizers expensive. However, they are widely used even under these circumstances.

The USSR has also begun production of complex liquid fertilizers. The UkSSR Academy of Sciences' Institute of Chemistry, together with other organizations, has for several years been developing and testing new SUM-U-zh complex liquid fertilizers based on nitric acid treatment of phosphates. SUM-U-zh is a suspended heavy (density 1.5-1.7  $\text{t}/\text{m}^3$ ), nonvolatile fire- and explosion-proof anhydride. The ratio of nutrients may be varied over a wide preset range. A corresponding amount of additional phosphorus fertilizer per unit of nitrogen is obtained by this method without consumption of sulfuric acid. The net cost of liquid fertilizers (in terms of nutrients) and of capital investment in production facilities is half that for solid fertilizers.

The 11 May 1961 resolution of the USSR Council of Ministers State Committee for Chemistry indicated that "work being done by the UkSSR Academy of Sciences' Institute of Chemistry, together with other organizations, on production and application of complex liquid fertilizers produced by nitric acid break down of phosphates is promising because of the simplicity and low cost of production of these fertilizers, their nonvolatility, and the possibility of combined, completely mechanized application of nitrogen, phosphorus, and other chemicals using overland machinery and aircraft."

The Chirchik PO [Production Association] "Elektrokhimprom" has produced more than 25,000 tons of complex liquid fertilizers. Tests on cotton plants, grain, vegetable, and cucurbit crops, and on vineyards and pasture lands confirmed the positive data from field and production plant tests.

The current state of study of the chemistry, physical chemistry, technology, agrochemistry, and economics of nitric acid treatment of phosphates permits extensive, nearly universal introduction into the country's national economy of production of solid and especially liquid complex fertilizers according to this method. It is now possible to produce a system of single, double, triple, and complex liquid fertilizers containing micronutrients, growth agents, etc.

Speaking of waste-free production of chlorine-free NPK fertilizers, we cannot ignore the fact that application of chlorine-free potassium-containing fertilizers to chlorophobic crops, for example, substantially increases the yield and quality of agricultural output. According to data from NIUIF [Scientific-Research Institute for Fertilizers and Insecto-fungicides imeni Ya. V. Samoylov], in applying chlorine-free potassium fertilizers, the hypothetical net profit per ruble of expenditure depending on soil type is 2.8-2.4 rubles for potatoes, 8.3-9.0 for grapes, and 3.6-7.3 for long-stemmed flax. In applying chlorine-free fertilizers to chlorophobic crops (winter wheat and barley), their yield is 1.7-2.2 centners per hectare higher than when chlorine-containing complex fertilizers are used.

We are developing a waste-free technology for obtaining complex chlorine-free NPK fertilizers and precipitate phosphate fertilizer based on phosphoric and poly-phosphoric acid breakdown of potassium chloride using the resulting hydrochloric acid for acid breakdown of the raw phosphate. In obtaining the precipitate by neutralizing the hydrochloric acid solution of the phosphates with potassium carbonate, a calcium chloride solution forms which may be used in producing cement by the low-temperature saline technology proposed by UkSSR Ministry for the Building Materials Industry's NIISTROMproyektom [Scientific-Research Institute for Building Materials Planning] [7]. According to the ministry's data, the demand for calcium chloride is 200,000 tons of 100 percent  $\text{CaCl}_2$ . Satisfaction of this demand will permit output of about 1.5 million tons of NPK-containing chlorine-free fertilizer with the composition:  $\text{N}:\text{P}_2\text{O}_5:\text{K}_2\text{O}=23:23:11.5$ ,  $\text{Cl}$  1.3-1.5 percent, and about 130,000 tons of precipitate phosphorus fertilizer.

A technology has been developed for obtaining liquid and solid chlorine-free fertilizers [8] by breaking down potassium chloride with polyphosphoric acids, followed by neutralization of the acid products with ammonia or carbamide. These fertilizers contain 50-90 percent of the sum of the nutrients. Liquid polymer fertilizers, unlike well-known solid fertilizers, possess a high concentration of the sum of the nutrients (50-55 percent) and a low crystallization temperature (from  $-25$  to  $-30^\circ\text{C}$ ). If neutral liquid fertilizers are stored for an extended time (6-10 months), their composition and properties do not change.

The technology for each type of fertilizer has been tested at a combined test setup at the Samarkand Chemical Plant with recording of the main technological indicators of the process. Test lots of fertilizers were produced. Agrochemical tests on cotton plants demonstrated the high effectiveness of complex chlorine-free fertilizers as compared with a mixture of standard fertilizers. The average increase in yield is 2-3 centners/hectare.

Simple superphosphate has unsatisfactory physical properties: it cakes, lumps, easily breaks down, and is unsuitable for mechanical application to soil or mixture with other fertilizers unless neutralized beforehand. The physico-chemical properties of simple and double superphosphates must be improved by ammoniation.

During superphosphate ammoniation, the free phosphoric acid from the initial product is completely neutralized, and its moisture content is almost halved. Superphosphate ammoniation causes deep structural changes in the original material, significantly improving its physical properties. Ammoniated superphosphate contains up to 2.0-2.5 percent nitrogen.

If we compare the main indicators in the current GOSTs for granulated (GOST 5956-53) and ammoniated (TU MKhP [Ministry of the Chemical Industry Specification] 4456-55) superphosphate from Karatau phosphorites, the latter is advantageously distinguished by the fact that it is neutral, and contains up to 2.3 percent nitrogen, and 80 percent of it consists of a fraction with granules at least 4 mm in size. We must add that ammoniated superphosphate is not hygroscopic, does not reduce the germinating capacity of seeds, and it is suitable for bulk transport, which makes it possible to cut operating costs.

Switching plants which produce granulated superphosphate to ammoniation will make it possible to release 273,600 tons of lime, which serves as ballast in granulated fertilizer, per year to the national economy.

According to GIPROKhim [State Union Institute for Design of Basic Chemical Industry Plants] data, the factory cost of one ton of the  $P_2O_5$  in ammoniated superphosphate is 12 rubles lower than the net cost of the  $P_2O_5$  in granulated superphosphate due to increased labor productivity and decreased production expenditures for superphosphate ammoniation. If we add that the cost of a ton of nutrients "franko-soil" in the ammoniated superphosphate is, according to the same calculations, 34 rubles 13 kopeks lower than that in granulated superphosphate, the superiority of the first becomes unquestionable.

On the basis of data from SoyuzNIKHI [Union of Chemical Scientific-Research Institutes] and NIUIF, use of one ton of ammoniated superphosphate increases grain yield 2.2 centners/hectare over simple superphosphate; for cotton plants, 2.6; for sugar beets, 296; for potatoes, 15. On the basis of these increases, the hypothetical net profit will be 216 rubles for cotton and 33 rubles for grain per ton of ammoniated superphosphate. The payback period for the additional capital investments related to switching to output of ammoniated superphosphate is less than a year.

Thus, all currently operating simple phosphate plants should neutralize superphosphate by ammoniation with gaseous ammonia or ammoniates instead of neutralization with lime [9].

According to data from the UKSSR Academy of Sciences' Institute for Chemistry, under production conditions at the Kokand Superphosphate Plant, introducing nitric acid or nitrates into the superphosphate production cycle makes it possible to raise the raw phosphate decomposition factor by 6-8 percent.

Considering the scale of superphosphate production, one might hypothesize that introduction of this development will have great national economic effect. Industrial experiments must be performed on use of nitric acid as a constant additive with recording of all technico-economic indicators substantiating the effectiveness of the technique. The results can be used

to solve the problem of widespread industrial introduction of this method.

To improve the physical, agrochemical, and commercial properties of double superphosphates, the UkSSR Academy of Sciences' Institute for Chemistry and NIUIF have developed a technology for ammoniating double superphosphate with gaseous ammonia or ammoniates of ammonium nitrate and urea for continuous and batch production [10]. In ammoniation of double superphosphate with gaseous ammonia, a product containing 46-47 percent  $P_2O_5$  and up to 3 percent nitrogen can be obtained; when it is ammoniated with ammoniates of ammonium nitrate or urea, a complex fertilizer containing 11-12 percent nitrogen and 34-35 percent phosphoric anhydride is the result.

Substitution ammonia or an ammoniating solution for neutralizers improves the technico-economic indicators of superphosphate plants by cutting expenditures related to transporting large masses of lime and fuel to dry the moister product, which is unavoidable in production of granulated superphosphate. Worker sanitation conditions are also significantly improved.

Many years of agrochemical tests have shown that the increase in the yield of raw cotton due to the use of double ammoniated superphosphate is up to 3 centner/hectare as compared with acid.

Our proposal on this problem amounts to switching plants that produce double superphosphate to ammoniation with ammonia or ammoniates (depending on the specific nature of the enterprise).

As a result of theoretical studies of the caking mechanism, we have developed a new method of producing non-caking ammonium nitrate with RFM-RAP additive. This additive is the product of nitric acid decomposition of Karatau phosphorites (RFM) and apatite concentrate (RAP) and is also a fertilizer. Its ingredients, which act as crystallization centers to form crystallohydrates and solid solutions, have a comprehensive positive effect on eliminating caking in ammonium nitrate.

Two of this country's enterprises worked with the use of additive RFM-RAP. Despite the fact that they did not maintain the optimum rates for the additive, the quality of their output systematically exceeded the quality of ammonium nitrated with other additives. In 1964, the Collegium of the USSR Ministry of Agriculture noted the good quality of ammonium nitrate with RAP additive produced by the Severodonetsk PO "Azot." On the basis of the results of a competition in 1975, the Chirchik Production Association was awarded first prize for providing high-quality RAP ammonium nitrate.

The basic standard which describes the quality of ammonium nitrate is its friability and the strength of its granules. According to the results of 1974, at an average annual RAP rate of 0.7 percent  $P_2O_5$  and total friability, the average annual strength of RAP ammonium nitrate granules from the Chirchuk PO "Elektrokhimprom" was 780 g/granule; at a RAP rate of 1.1 percent  $P_2O_5$ , 1,000 g/granule (this is the highest indicator in the sector).

Thus, of the additives used, only RFM-RAP provides complete friability and high granule strength in ammonium nitrate, without requiring an excessive

reduction in the moisture content of the product.

Despite the superiority of the new method for producing non-caking ammonium nitrate, attempts have been made over many years to improve its quality using less-than-optimum or -safe methods. The reason for rejection of RAP has been that its insoluble components form a crust on the surface of concentrate which must be removed during a shutdown by dissolution in nitric acid. With the participation of the Chirchuk PO "Elektrokhimprom" and a branch of the GIAP [State Scientific-Research and Design Institute of the Nitrogen Industry and Organic Synthesis Products], we have improved this method to eliminate crust formation.

The 1975 USSR Supreme Soviet session was devoted to a prudent attitude toward the country's natural resources. Raw phosphate occupies a special place among natural resources. The USSR is a country which possesses large stores of raw phosphate, and it not only supplies it for its own use, but exports it to other countries of the world. However, the time is not far off when the natural phosphate stores may be depleted.

Therefore, development of methods for rational processing of low-grade phosphates, which make it possible to use unconditioned raw phosphate in phosphorus fertilizer production, is very urgent. Current technological processes for processing apatites and phosphorites with a low level of raw stock decomposition must be replaced by progressive methods with complete use of the phosphorus. This includes nitric acid treatment of phosphates, synthesis of more effective fertilizers, development of rational agrochemical methods which increase the effectiveness of fertilizers, especially phosphate fertilizers, and a set of measures to mobilize phosphorus compounds bound in the soil.

The efficiency factor for fertilizers in agriculture is still low. For nitrogen fertilizers, it is no more than 40-50 percent; for phosphorus fertilizers, no more than 15-20 percent.

Differentiated, scientifically sound use of micronutrients, plant growth stimulators, nitrogen nitrification inhibitors and slow-dissolving fertilizers, which promote mobilization of soil phosphorus, and other physiologically active substances is an effective means of raising the efficiency factor for mineral fertilizers and the yield and quality of agricultural products [11].

Members of the UkSSR Academy of Sciences, SoyuzNIKHI [All Union Scientific Research Institute for Cotton Growing], and the SAO VASKhNIL [Central Asian Division of the Lenin Order All-Union Academy of Agricultural Sciences imeni Lenin] have established that microfertilizers and physiologically active substances significantly enhance protein and nucleic acid synthesis, improve the growth and fertility of cotton plants, accelerate ripening of bolls, promote more productive use of water by plants, increase the utilization factor for nitrogen (by 7-10 percent) and phosphorus (by 10-15 percent), reduce the cotton wilt rate by 25-30 percent, and improve the quality of cotton fiber and seeds. According to data from the UkSSR State Agroindustry Administration, microfertilizers are used on an area larger than 1.5 million hectares.

We have developed the chemical basis and technology for producing ammophos, simple and double superphosphates, as well as carbamides containing copper, zinc, cobalt, and molybdenum. The proposed technologies have passed industrial tests. Agrochemical tests have confirmed the high effectiveness of the proposed fertilizers. The corresponding organizational problems must be solved.

Together with the ChF GIAP [not further identified], we have studied the physico-chemical bases and developed a technology for obtaining granulated urea-formaldehyde and complex polymer fertilizers (SPU) [12].

The lots of prolonged-action fertilizers produced have undergone agrochemical tests on the saline soils of Central Asia and have demonstrated high effectiveness.

Increasing fertilizer effectiveness is unquestionably a complex task. Chemists must provide for synthesis of the most effective forms and ratios of nutrients with preset composition and properties with regard for the crop, the nature of the vegetative period, soil and climatic conditions, etc.

Recommendations of agricultural science representatives regarding the composition, properties and nutrient ratios of fertilizers are not always stable and sometimes do not consider all factors as a set. Certain agrochemical recommendations are scientifically unsound from the standpoint of their chemistry. Here is an example. It has been proven that, when water-soluble phosphorous fertilizers are applied to carbonate soils, the phosphorus rapidly converts into forms unassimilable by plants. Moreover, it was recommended that the main amount of phosphorus fertilizers be applied universally at the fall plowing, including to soils to be irrigated. The groundlessness of these recommendations is obvious. From the time phosphate fertilizers are applied to the soil at the fall plowing (October, November) at a depth of 30 cm until the root systems of plants sown in spring develop takes about 6 months. Over this time, most of the fertilizers are converted into forms difficult for the plants to access, which greatly contributes to their low efficiency factor. Studies of the effectiveness of fertilizers often amount only to growing season experiments which evaluate crop yields. Their results are not always reliable, since yield depends on many factors.

There are great reserves for increasing the effectiveness of fertilizer, for example, in correctly combining them with water in irrigated farming. Thus, during irrigation of cotton after fertilization during the growing season, the water is often carried off, and considerable fertilizer washouts are unavoidable. Water loss can be significantly reduced and fertilizer effectiveness increased by alternating furrows to be irrigated with those intended for fertilization.

Let us discuss one example relatively far from our topic, but clearly illustrative of the negative consequences of incorrect application of fertilizer. We have in mind failure to adhere to the schedule for fertilizing and watering cucurbit and vegetable crops.

It is accepted that fertilizing melons, watermelons, and vegetables causes them to lose their taste qualities, to spoil quickly in storage and in transit, and sometimes even to cause intestinal poisoning. But the culprit

is not the fertilizer, but the large amount of it applied directly before harvest, followed by abundant watering to increase weight gain. Abundantly "fattened" with fertilizers, a plant absorbs a large amount of water. The fruit retains the entire amount of "undigested" fertilizer and water, which, instead of increasing sugar content, degrades its taste qualities and leads to intestinal poisoning. The presence of excess water in the fruit causes it to rot during storage.

Crop rotation is a major reserve for increasing bound nitrogen in the soil. In the USSR and abroad, a great deal of attention is being given to growing corn, both as a grain and as silage. Carbamide is usually added to the silage so that animals can assimilate the nitrogen-containing substances found in this crop's composition. People long ago accepted the idea of planting bean crops -- mung beans, cowpeas (lobiya), etc. -- simultaneously with corn. This encourages a sharp increase in the quality of the silage and grain.

As the practice of agricultural experimentation stations shows, legume crops can successfully be grown on irrigated lands. The most productive bean crop in the UkSSR, in both spring and late summer plantings, is cowpeas (lobiya). Mixed plantings of corn and cowpeas are practiced to obtain high-protein silage. They are planted in fields freed after the harvest of peas for grain, early vegetables, and other crops. The cowpea plant mass is used as fodder and green fertilizer. The beans from asparagus cowpeas are used as food. Partial replacement of meat protein by plant proteins in the food allowance is one of the most important conditions for normal human nourishment. One of the best legumes in terms of nutritive qualities is mung beans, which are close to meat in protein composition.

Legumes also have great agrotechnical significance, since they enrich the soil with nitrogen through the Rhizobia which develop on their roots and which can assimilate nitrogen from the air. Thanks to this property, legumes are an excellent forerunner for many crops.

Agricultural scientists, together with chemists, microbiologists, and medical specialists working in sanitation and hygiene, must concentrate their efforts on differentiated and integrated study of the scientific bases and organization of the production of organomineral fertilizers based on mineral fertilizers and manure, sewage wastes, and other organic sources.

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12809

CSO: 1841/140

UDC 66+331.007.2

PROSPECTS FOR DEVELOPMENT OF MINERAL FERTILIZER INDUSTRY AND REQUIREMENTS  
FOR TRAINING OF CHEMICAL TECHNOLOGY ENGINEERS

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA im D.I. MENDELEYEVA  
in Russian Vol 31, No 4, Jul-Aug 86 pp 381-385

[Article by A.A. Kochetkov, First Deputy Minister for Production of  
Mineral Fertilizers]

[Abstract] During the Twelfth Five-Year Plan, mineral fertilizer production will increase by 30-32%, reaching 41-43 million tons of mineral fertilizer by 1990, with 440-480 thousand tons of chemical substances for plant protection to be produced, by the same time. Intensification of production is to be achieved by utilizing the latest achievements of science and technology, sharply increasing the productivity of labor and by economies of raw materials and energy resources. Full and effective utilization of facilities already in operation is an important task. Tasks for the industry include intensive development of the production of liquid fertilizers, development and introduction of technologies for concentrated liquid combined fertilizers from phosphate raw materials. This will require active participation of educational institutions in the training of more and better-qualified engineers. Unfortunately, course and diploma planning is frequently limited to formal copying of existing plans, with generations of students following in each others footsteps. Students must be taught problems of science and technology as they actually exist today, with particular attention given to formation of future team leaders. More flexible education, including more training in the latest specialties, is required. A further problem is the large number of young graduates who refuse to stay where they are assigned to work when they graduate.

6508/9835  
CSO: 1841/99

## COMPLEX LIQUID FERTILIZERS BASED ON PHOSPHORIC ACID EXTRACTION FROM KARATAU DEPOSITS

Moscow KHIMICHESKAYA PROMYSHLENNOST' in Russian No 11, Nov 86 pp 661-662

[Article by L.I. Yevdokimova, A.V. Kononov, M.P. Lobacheva and N.V. Trutneva]

[Abstract] The present article discusses production of complex liquid fertilizers (CLF) and suspended CLF, which are superior to solid chemical fertilizers, using theoretical approaches developed at the Scientific Research Institute for Fertilizers, Insecticides and Fungicides imeni Ya.V. Samoylov. The process aimed at producing a flowing pulp with less than 10% moisture and a composition of  $\text{NH}_3$  :  $\text{H}_3\text{PO}_4$  of less than 0.6-0.7 molar ratio. Regular Karatau deposits used had the following composition:  $\text{P}_2\text{O}_5$ --23.15; F--1.72;  $\text{SO}_3$ --3.05;  $\text{CaO}$ --0.32;  $\text{MgO}$ --2.12;  $\text{R}_2\text{O}_3$ --2.28. Variants were highlighted by neutralization of CLF in ammonia followed by evaporation of the pulp at the same time the orthophosphate is dehydrated to about 65%; the second variant had dehydration by about 30% followed by neutralization of the pulp to pH of 4.5-5 and further increasing dehydration to 60-65%. In the second test, the charge temperature at output rose to 230-280° (compared to an input temperature of 185-195°C). Dehydration increased from 25-30% to 60-65%. In the traditional process for producing CLF, using polyphosphoric acid, output temperatures reach 280-380°C. The fertilizer produced had 19-20%N and  $\text{P}_2\text{O}_5$  with good fluidity, but the product could only be used at temperatures above 20°C, its temperature of crystallization. References 11 (Russian).

12131/9835  
CSO: 1841/142

UDC 631.85:631.454

## USSR FARMING REQUIREMENTS FOR PHOSPHORUS FERTILIZERS AND ALLOCATION OF FUNDS BASED ON PROVIDING SOILS WITH ADEQUATE CONTENT OF PHOSPHORUS

Moscow AGROKHIMIYA in Russian No 11, Nov 86 pp 108-129

[Article by Yu.I. Kasitskiy, L.N. Kartseva, L.S. Kubareva, N.N. Smirnova and L.S. Feoktistova]

[Abstract] This is a review article. Under conditions of ever-increasing reliance of agriculture on chemical fertilizers, it is necessary to provide scientific methods for determination of the needs for various fertilizers and for apportionment of the available funds. In 1985, CC CPSU and the Soviet of USSR Ministers developed a program for chemization of USSR agriculture by year 2,000. Therefore, it became necessary to analyze available methods for prognosticating the needs and allocating the budget

for these activities. There are several methods for this task available: 1) statistical or extrapolation methods; 2) methods based on energy balance of food products; 3) empirical methods based on experimental data on the effectiveness of fertilizers; and 4) balance methods based on chemical analysis of plants and soils. Because the first two are quite relative, capable of determining only general trends, this review concentrated on analyzing the latter two. All of the analytical methods should consider the following points: a) effectiveness of phosphorus fertilizers decreases with increased content of labile phosphorus in the soil; b) the most effective increase in phosphorus efficiency is observed in going from its low to medium content, higher levels being economically less advantageous; c) optimal content of labile phosphorus is reached when introduction of more phosphorus assures an economically optimal harvest. Figures 1; references 61: 58 Russian (1 by Western authors), 3 Western.

7813/9835  
CSO: 1841/138

INORGANIC COMPOUNDS

CONFERENCE ON CRYSTAL CHEMISTRY

Tashkent PRAVDA VOSTOKA in Russian 14 Dec 86 p 2

[Text] An all-Union conference which ended in Bukhara on December 13 was devoted to problems and prospects for the advancement of crystal chemistry. Leading chemists from Moscow, Leningrad, Kiyev, Tashkent, Novosibirsk and other research centers of the country summarized results of basic research that has been done and described new applications for these results.

"One important result of the conference was further coordination of the work of groups at academy institutes and at higher educational institutions which are pursuing research in the field of crystal chemistry," said M.A. Poray-Koshits, corresponding member of the USSR Academy of Sciences, head of a laboratory of the academy's Institute of General and Inorganic Chemistry imeni Kurnakov, and chairman of the conference's organizing committee. "With much interest, participants in the conference familiarized themselves with developments of young scientists of the Bukhara Technologic Institute of the Food Industry and Light Industry who have achieved successes in the field of crystal chemistry. The conference in Bukhara will allow research in this direction to be accelerated."

FTD/SNAP

/9835

CSO: 1841/125

ALUMINUM AS SUPERCONDUCTOR

Leningrad TASS in Russian 22 Dec 86

[Text] Soviet specialists suggest that titanium and its alloys be replaced with aluminum in superconductive systems. At the Volkhov Aluminum Plant near Leningrad they obtained super-pure aluminum with a purity of 99.999 percent. Experiments have shown that in liquid helium at temperatures of minus 272 degrees Centigrade, super-pure aluminum can be superconductive.

/9835

CSO: 1841/124

## FILM-FORMING SOLUTIONS AND DOPING OF SEMICONDUCTORS

Leningrad LENINGRADSKAYA PRAVDA in Russian 9 Jan 87 p 1

[Article by S. Samoylis]

[Excerpt] At the traditional fall Leipzig Fair, the USSR Academy of Sciences' section in the Soviet pavilion is constantly at the center of attention of specialists and visitors. And this is no accident; the best work done by Soviet scientists in recent years is being shown here. At the latest fair, this included a new development by Leningrad scientists which specialists, including foreign ones, called one of the greatest advances in inorganic chemistry.

This innovation was film-forming solutions which were developed and produced at the USSR Academy of Sciences' Institute of Silicate Chemistry imeni Grebenshchikov.

I met with Candidate of Technical Sciences L.F. Chepik in the laboratory of thin-film inorganic coatings, where the innovation originated. Lyudmila Filippovna picked up a small flask from a table. It contained a colorless and transparent liquid that looked like water.

"This is the film-forming solution. And that is where it is used," she said, pointing to an "Elektronika" microcalculator standing on the table.

The semiconductors of which integrated circuits consist must have many properties. This is achieved by introducing certain doping agents into their structure. A gas traditionally has been used as the medium for carrying these doping agents. But this method had quite a few disadvantages: technological complexity, high cost, and most importantly, it did not ensure high enough quality of the electronic components.

"In somewhat simplified terms, the gist of the proposal made by Doctor of Technical Sciences A.I. Borisenko and Candidate of Chemical Sciences N.Ye. Prikhid'ko was this," related Candidate of Technical Sciences S.V. Khashkovskiy, the head of the laboratory. "To use a film-forming solution instead of a gas as the doping-agent carrier. The method of applying it to semiconductor materials is simple: a drop of the solution is spread over the surface of a silicon chip with the aid of a centrifuge and bonded to it by means of rapid heat treatment."

This idea was recognized as an invention, and a certificate of invention was issued for it. It is noteworthy that soon thereafter, the American firm "Emulsiton" also began to advertise a method of producing films from solutions.

"Of course, this advertising was undertaken for the purpose of selling licenses," said Academician M.M. Shul'ts, the institute's director. "We have sent special letters to the USSR State Committee for Science and Technology and to a number of interested ministries, pointing out that this method was developed first in our country and that more extensive research involving it has been conducted here. Moreover, the cost of our materials is 150 times less than the cost of those advertised by the American firm."

Moscow, Leningrad, Novosibirsk, Tallin--these are but a few of the cities where plants have introduced the work of the Leningrad scientists.

Now they are taking on difficult new tasks. "The main problem is to make the film 'thicker'," said L.F. Chepik. "Thus far, it is up to 0.3 micron thick, but a thickness of at least 1 micron is needed. This will make the operation of electronic equipment more reliable. In addition, we will gain a deeper understanding of the physicochemical principles of the process of preparing the solutions, and thus improve their properties."

FTD/SNAP  
/9835  
CSO: 1841/125



UDC 536.421.1

CALCULATION OF THERMODYNAMIC VALUES OF CRYSTALLINE ARGON BY MOLECULAR DYNAMICS METHOD IN ISOBARIC-ISOTHERMAL GIBBS ENSEMBLE

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 60, No 11, Nov 86  
(manuscript received 16 Dec 85) pp 2867-2869

[Article by A.K. Ashurov, Physicotechnical Institute imeni S.U. Umarov, Tajik SSR Academy of Sciences, Dushanbe]

[Abstract] The molecular dynamics method [Ashurov, A.K., and Adkhamov, A.A., Dokl. AN Tadzh. SSR, 28(7): 393, 1985] was employed in determining the energy, isothermic and adiabatic compressibility, sound velocity, volume expansion coefficient, and compressibility factor for a crystalline argon system with  $N = 107$  and  $108$  particles at  $40-90$  K. The thermodynamic factors demonstrated marked deviation from linearity at the experimental temperature range, indicating that linear characteristics of solid argon should be studied at  $T < 40$  K. Sound conductance was similarly affected. The nature of the thermodynamic values in the  $60-65$  K interval did not suggest a change in the structural phase. For more detailed information, such studies need by conducted with  $N > 1000$  systems. Figures 3; references 4 (Russian).

12172/9835  
CSO: 1841/110

UDC 536

REARRANGEMENT OF SEMICONDUCTOR SURFACE DEFECTS STIMULATED BY CHEMICAL REACTIONS ON CRYSTAL SURFACE

Moscow POVERKHNOST in Russian No 11, Nov 86 (manuscript received 23 Jan 86)  
pp 67-72

[Article by A.F. Vyatkin, A.G. Italyantsev, Ch.V. Kopetskiy, V.N. Mordkovich and E.M. Temper, Institute of Problems of Technology of Microelectronics and Highly Pure Materials, USSR Academy of Sciences, Moscow]

[Abstract] A study is made of the possibility in principle of controlling processes of rearrangement of defects by nonthermal effects in addition to

heat treatment. Rearrangement of clusters of point defects stimulated by chemical reactions on the surface of semiconductors is analyzed. Objects differing significantly in their properties, including radiation clusters formed in silicon upon ion implantation, growth defects in gallium arsenide, and surface states in silicon near the Si-SiO<sub>2</sub> boundary, were selected to demonstrate the possibility of rearrangement of defect clusters. It is shown that chemical reactions on the surfaces of semiconductor materials and elements allow control of crystalline lattice characteristics and electro-physical properties of the objects. Chemically-stimulated control of point defect system parameters can be implemented in monoatomic semiconductors, semiconducting compounds and heterosystems as the semiconductor interacts with a chemically-active gas medium and in solid phase reactions at the semiconductor-film interface. Chemical stimulation can accelerate rearrangement of defects or decrease the temperature of processes accompanying structural rearrangement. References 5: 4 Russian, 1 Western.

6508/9835  
CSO: 1841/114

UDC 621.785.3:539.219.1

#### PULSED ION ANNEALING OF ARSENIC-IMPLANTED SILICON

Moscow POVERKHNOST in Russian No 11, Nov 86 (manuscript received 21 Jan 86)  
pp 146-147 (Cat. 15)

[Article by L.S. Ayvazova, M.I. Goncharenko, L.N. Mankova and A.N. Makhlin,  
Kiev Polytechnic Institute]

[Abstract] An experimental study is performed of the effectiveness of annealing of arsenic-implanted silicon by a pulse of protons at 20 keV, 200 μs pulse length, 0.5 and 10 A/cm<sup>2</sup> current density. Studies were performed by measurement of the Hall effect during layer etching of silicon single crystals implanted with arsenic at an energy of 100 keV, dose 1000 μCu/cm<sup>2</sup>. Profiles of the impurity by depth showed sharp peaks of concentration. The utilization factor of the implanted impurity was 0.04 for 0.5 A/cm<sup>2</sup>, 0.62 for 10 A/cm<sup>2</sup>. Figures 1; references 3: 1 Russian, 2 Western.

6508/9835  
CSO: 1841/114

## IODIDE LANTHANIDE COMPOUNDS WITH ALKALI METALS

Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 31, No 11, Nov 86  
(manuscript received 14 Jan 86) pp 2784-2793

[Article by A.K. Molodkin and A.G. Dudareva, People's Friendship University  
imeni Patrice Lumumba]

[Abstract] Conventional physicochemical methodology was employed in an analysis of iodide lanthanide compounds with alkali metals, and the results are summarized in tabular form. This attempt represented the first experimental study of the  $\text{LnI}_3\text{-MeI}$  ( $\text{Ln} = \text{Sm, Gd, Dy, Ho}$ ) and the  $\text{YbI}_2\text{-MeI}$  systems ( $\text{Me} = \text{alkali metal}$ ). Additional IR and fluorescence data are presented for  $\text{SmI}_3$ ,  $\text{DyI}_3$ ,  $\text{HoI}_3$  and  $\text{HoBr}_3$ , as well as  $\text{SmI}_3\text{-MeI}$  compounds. Finally,  $^{127}\text{I}$  NMR spectra were obtained for  $\text{GdI}_3$ ,  $\text{DyI}_3$ ,  $\text{HoI}_3$  and  $\text{RbI-HoI}_3$ . The latter observations indicated that  $\text{DyI}_3$  and  $\text{HoI}_3$  have a crystalline structure close to the ideal octagonal form similar to  $\text{BiI}_3$ .  $\text{RbI-HoI}_3$  also showed two NMR frequencies indicative of the equivalence of all the I atoms. References 24: 20 Russian, 4 Western.

12172/9835  
CSO: 1841/119

## ALCHEMICALLY PURE SILICON

Moscow KHIMIYA I ZHIZN in Russian No 10, Oct 86 pp 28-31

[Article by V.A. Kharchenko, candidate of technical sciences]

[Abstract] A new method for alloying semiconducting silicon, in which contemporary alchemical, that is, nuclear physical transformations of chemical elements are utilized, is reviewed. First, the traditional method for obtaining monocrystalline silicon by the Czochralski procedure is detailed and the alloying (doping) of silicon with additives for preparation of semiconducting devices by the classical methods is considered. The new non-traditional procedure was developed on the principle of nuclear alloying. Silicon is transformed into phosphorus in a nuclear chemical reaction. Alloying is accomplished without the addition of an impurity externally. The concentration of the prescribed additive (impurity) and the uniformity of its distribution depends on the current density of the thermal neutrons and the time of irradiation. Careful studies of irradiation conditions in nuclear reactors of various type were made until optimum conditions were developed to overcome radiation defects in the crystalline lattice which affect the electro-physical properties. Optimum technology for nuclear alloying consists now of two methods of irradiation, and after the irradiation, the silicon ingots are aged for five days for complete decay of the unstable  $\text{Si-31}$  and of other radioactive

isotopes which were adsorbed from the reactor. The nuclear alloying operation is not simple and not cheap. Control, control and again control must be exercised not only after irradiation but also up to it. If all conditions are observed, the electro-physical properties of nuclear alloyed silicon are near ideal. Today, 95-98% of the nuclear alloyed silicon is converted in suitable production for operations under any conditions. In silicon the nuclear alloying effect forms only one necessary element, phosphorus. The possibility of nuclear transformations in other semiconductors for in situ alloying is examined and the prospects are reasonable for some and not for others. Nuclear alloyed silicon will be obtained in increasing amounts in many reactors in many places including in the rejuvenated Chernobyl. Figures 5.

12886/9835  
CSO: 1841/108

UDC 541.127:541.183:546.17+546.21:548.67

ENCAPSULATION OF GASES BY ZEOLITES. PART 1. ENCAPSULATION OF NITROGEN AND OXYGEN AT PRESSURES APPROACHING 100 MPa

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERTIYA KHIMICHESKAYA in Russian No 10, Oct 86 (manuscript received 27 May 85) pp 2178-2182

[Article by I.A. Kalinnikova, N.N. Muchaidze, A.A. Pribylov, V.V. Serpinskiy and G.V. Tsitsishvili, Institute of Physical Chemistry, USSR Academy of Sciences, Moscow]

[Abstract] Experimental data are presented on the encapsulation of O<sub>2</sub> and N<sub>2</sub> by KNaA zeolites (68% K<sup>+</sup>, 32% Na<sup>+</sup>) under temperatures spanning 450-700 K and pressures of 10-100 MPa, with encapsulation times ranging from 1 to 6 h. The resultant measurements demonstrated that kinetic factors dominate the process at 450-500 K, while thermodynamic factors--temperature and pressure--play the dominant role at 550-600 K. Decapsulation studies led to estimates of the energies of activation for desorption for both systems, yielding values of 77±7 kJ/mole for the N<sub>2</sub>-KNaA system and 64±6 kJ/mole for the O<sub>2</sub>-KNaA system. References 8: 3 Russian, 5 Western.

12172/9835  
CSO: 1841/112

## EFFECT OF COMBINED CALCIUM AND MAGNESIUM OXIDES ON PROPERTIES AND QUENCHING OF TITANIUM-CONTAINING ENAMEL COVERS

Tashkent UZBEKSKIY KHIMICHESKIY ZHURNAL in Russian No 5, Sep-Oct 85  
(manuscript received 11 Apr 86) pp 19-21

[Article by A.P. Irkakhodzhayeva and N.A. Sirazhiddinov, Institute of Chemistry UzSSR Academy of Sciences]

[Abstract] Use of a combination of additives improves the properties of ceramic materials much better than the use of individual oxides. A series of initial compositions of enamel frit was studied, changing CaO:MgO ratio from 6 to 0.6. To obtain glossy frit from high Mg content, high temperatures were required (1450-1500°C). In the present study, temperature range of 1000-1150°C was used in which the enamel layer was fully crystallized. Normal shine of these enamels was achieved only with a Ca-Mg ratio of 3 and 4. The strength of Ca-Mg frit increased with increased content of MgO. A conclusion was reached that, to improve crystallization, a 6-7 mole-% of MgO should be used in presence of 6 mole-% of CaO. Figures 1; references 5 (Russian).

7813/9835  
CSO: 1841/139

## EFFECT OF SOME SUBSTRATES ON STRUCTURES OF ELECTROLYTIC MAGNETIC Co-W FILMS

Vilnius TRUDY AKADEMII NAUK LITOVSKOY SSR: SERIYA B in Russian Vol 156,  
No 5, Sep-Oct 86 (manuscript received 17 May 85) pp 14-21

[Article by V.A. Parfenov and V.S. Rachinskas, Institute of Chemistry and Chemical Technology, LiSSR Academy of Sciences]

[Abstract] The goal of this study was to investigate the effect of structure of support materials such as Cu-laminated foil and chemically or electrochemically precipitated non-magnetic Ni-P alloys on formation of the thin Co-W films and their magnetic properties. It was shown that the Co-W film structure was essentially the same whether deposited on Cu support or on electrochemical Ni-P alloy, except that, on the Ni-P alloy, the distribution of Co-W crystallites was more uniform. The Co-W film deposited on chemically precipitated Ni-P layer was different; precipitation rate was different for different segments and the dispersion degree was noncomparable with samples obtained on electrochemically precipitated Ni-P support. Magnetic information carriers made of Co-W alloy electrodeposited on chemical Ni-P support will show anomalies and noise. Figures 3; references 18: 11 Russian, 7 Western.

7813/9835  
CSO: 1841/130

GLASS FORMATION AND ELECTRICAL CONDUCTIVITY IN  $PbO \cdot B_2O_3 - PbHal_2$  SYSTEM

Tbilisi IZVESTIYA AKADEMII NAUK GRUZINSKOY SSR: SERIYA KHIMICHESKAYA  
in Russian Vol 11, No 3, Jul-Sep 86 (manuscript received 30 Nov 83)  
pp 235-238

[Article by B.M. Chabakauri, R.N. Kukharskiy and V.E. Kogan, Institute of Cybernetics, Georgian SSR Academy of Sciences]

[Abstract] The system  $PbO \cdot B_2O_3 - PbHal_2$ , where Hal is F, Cl, Br or I, has been studied to determine the glass formation region and to investigate the temperature-concentration relationship of electric conductivity. Synthesis of glasses was carried out in corundum crucibles with a covering to provide a sharp reduction of  $Al_2O_3$  transfer from the crucibles. Chemical analysis of all glasses contained less than 1% by wt.  $Al_2O_3$ . A high degree of correspondence of the synthetic and analytical compositions was attained for the used synthesis method. Maximum difference of the synthetic and analytical halogen contents of the glasses because of evaporation from the melt was 1.45 at. % F, 0.2 Cl, 0.46 Br and 0.86 I. The regions of glass formation (clear homogeneous glasses) were limited to 78 mol %  $PbF_2$ , 12.5  $PbCl_2$ , 15  $PbBr_2$  and 24.5  $PbI_2$  for the considered pseudobinary systems. The graphical data for electric conductivity at 200°C, its activation energy and its preexponential factor are given. The Cl-containing glasses indicate that the introduction of Cl ions into the glasses was insufficient for securing in them an anion-halogen transfer. For the other halogen glasses at concentration of about 10 mol%  $PbHal_2$ , a transfer is observed from proton conductivity to a conductivity caused both by protons and by halogen ions. For F containing glasses of up to 30 mol%  $PbF_2$ , all F ions are unbridged and take part in the electron transfer. Then at higher  $PbF_2$  concentrations, part of the F ions are bridged in the reaction and take no part in electron transfer. Figures 1; references 10 (Russian).

12886/9835  
CSO: 1841/143

UDC 539.23+537.534

## INTERACTION OF ARGON IONS WITH DEVELOPING FILMS OF RARE EARTH METALS

Moscow POVERKHNOST: FIZIKA, KHIMIYA, MEKHANIKA in Russian No 12, Dec 86  
(manuscript received 28 Nov 85) pp 77-81

[Article by L.F. Lifanova and T.D. Radzhabov, Electronics Institute, UzSSR Academy of Sciences, Tashkent]

[Abstract] The article reports on analysis of thermally-stimulated desorption (TSD) from constantly renewed (CR) films of rare earth metals

deposited during ion irradiation. Spectra of residual gasses and overall air pressure values made it possible to isolate partial argon pressure, and gas activation energy was calculated to determine the predominant gas emission mechanism. Results indicated that argon irradiation enhanced growth of a more regular film structure without supplemental heating of the base; texture values were dependent on the film material being applied and the mass of the bombarding ions. Since prior data were lacking, the authors also calculated coefficients for cathode atomization and ion energy using a Zigmund model. These calculations showed that with a sufficient film thickness, concentration was dependent on current strength and the differences between atomization and deposit. These data are intended for practical applications in producing desired film thicknesses and compositions. References 7:  
5 Russian, 2 Western.

12131/9835

CSO: 1841/148

NITROGEN COMPOUNDS

UDC 541.11:541.57:547.1'128

THERMOCHEMICAL ESTIMATE OF CYCLE TENSION ENERGY JOINTLY WITH Si-N BOND IN SILATRANES

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 9, Sep 86 (manuscript received 15 Jan 85) pp 1976-1981

[Article by M.G. Voronkov, V.A. Klyuchnikov, A.N. Korchagina, T.F. Danilova, G.N. Shvets, V.P. Varyshok and V.M. Dyakov, State Medical Institute, Kemerova; Irkutsk Institute of Organic Chemistry, Siberian Department, USSR Academy of Sciences]

[Abstract] An estimate is presented of the Si-N bond energy jointly with the silatrane cycle tension energy based on the heats of atomization within the framework of the additive bond energy system. Experimental heats of atomization, fragments of the additive system and bond energies in the gaseous substances were calculated by determining the heats of evaporation of tetraalkyl-, tetraalkoxy- and organylalkoxy silanes and the heats of sublimation of several organylalkoxy silanes and silatranes. The possibility is established for organosilicon compounds of using the empirical dependence among energies of additive system fragments, bond energies and bond lengths. The experimental data are used to estimate the energy of the Si-N trans-annular bond jointly with the silatrane cycle tension energies. References 15 (Russian).

6508/9835  
CSQ: 1841/104



SYNTHESIS OF CERTAIN TRITHIENYLPHOSPHINECARBONYL COMPLEXES OF RHODIUM

Moscow IZVESTIYA AKADEMII NAUK SSSR; SERIYA KHIMICHESKAYA in Russian No 9, Sep 86 (manuscript received 15 Mar 85) pp 2105-2109

[Article by Ya.L. Goldfarb, deceased, A.A. Dudinov and V.S. Bugdanov, Institute of Organic Chemistry imeni N.D. Zelinskiy, USSR Academy of Sciences, Moscow]

[Abstract] New carbonyl complexes of rhodium with trithienylphosphine ligands are synthesized, and their catalytic activity is studied. The initial compounds for the synthesis of the complexes were stable chloro-carbonyl complexes of rhodium. The major method of synthesis was based on the use of Li or Mg-organic compounds. References 14; 3 Russian, 11 Western.

6508/9835

CSO: 1841/104

ORGANOMETALLIC COMPOUNDS

UDC 542.91:541.49:547.1'13:547.538.546.76

PREPARATION OF BISARENECHROMIUM  $\pi$ -COMPLEXES FROM PHENYLACETYLENE AND CHROMIUM VAPORS

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 10, Oct 86 (manuscript received 8 Apr 85) pp 2307-2309

[Article by V.A. Sergeev, L.P. Yuryeva, N.N. Zaytseva, A.Yu. Vasilkov, A.S. Kogan and D.N. Kravtsov, Institute of Heteroorganic Compounds imeni A.N. Nesmeyanov, USSR Academy of Sciences, Moscow]

[Abstract] Resistance evaporation of Cr was used to secure atomic Cr for reaction with phenylacetylene to form a mixture of organic and organochromium compounds. Analysis of the products resulted in identification of bis( $\eta^6$ -triphenylbenzene)chromium, a mixture of 1,2,4- and 1,3,5-triphenylbenzenes and their  $\pi$ -complexes with Cr, and organic and organochromium polymers. The bisarene complexes were separated from the other products by oxidation to water-soluble hydroxides and isolated in the iodide form. References 8: 1 Russian, 7 Western.

12172/9835  
CSO: 1841/112

UDC 542.952.1:541.49:546.765:547.1'128

INTER-RING HAPTOTROPIC REARRANGEMENTS IN CHROMIUM TRICARBONYL COMPLEXES WITH 1,1-DIMETHYL-1-SILAACENAPHTHENE

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 10, Oct 86 (manuscript received 23 Dec 85) pp 2324-2326

[Article by Ye.A. Chernyshev, Yu.F. Oprunenko, O.B. Afanasova, V.M. Nosova, Yu.Ye. Zubarev, S.G. Malyugina, A.V. Kisin, V.N. Retunskiy, N.A. Ustynyuk and Yu.A. Ustynyuk, Moscow State University imeni M.V. Lomonosov; Institute of Heteroorganic Compounds imeni A.N. Nesmeyanov, USSR Academy of Sciences, Moscow; All-Union Scientific Research Institute of Biological Methods of Plant Protection, Kishinev]

[Abstract] PMR and x-ray structural analysis studies were conducted on the isomeric products formed by the reaction of chromium hexacarbonyl with

1,1-dimethyl-1-silaacenaphthene. The products differed in the position of the  $\text{Cr}(\text{CO})_3$  group, which showed haptotropic rearrangement between the 6-membered rings when the mixtures were heated (80-115°C) in toluene, benzene, cyclohexane, or decane. Thermodynamic parameters were calculated for the reversible migration of the  $\text{Cr}(\text{CO})_3$  group. References 3: 2 Russian, 1 Western.

12172/9835  
CSO: 1841/112

UDC 539.26+661.865

SYNTHESIS AND STUDY OF RARE EARTH ELEMENT COORDINATION COMPOUNDS OF COMPOSITION  $[\text{LnCl}(\text{TDMFO})_5](\text{BPh}_4)_2$  AND  $[\text{LnCl}_2(\text{TDMFO})_4]\text{BPh}_4$

Kiev UKRAINSKIY KHMICHESKIY ZHURNAL in Russian Vol 52, No 12, Dec 86 (manuscript received 18 Jun 85) pp 1240-1244

[Article by V.M. Amirkhanov, Yu.L. Zub, S.M. Galitskaya and V.V. Skopenko, Kiev University]

[Abstract] The title complex compounds, where TDMF = tris(dimethylamino)-phosphine oxide and Ln = La, Ce-Lu, were synthesized from the corresponding lanthanoid chloride and sodium tetraphenylborate. The resulting complexes were studied using chemical and X-ray analysis, conductometry, cryoscopy, IR- and electron spectra. Conclusions were drawn on the structure of the complexes and their coordination numbers. Figures 3; references 8: 4 Russian, 4 Western.

12765/9835  
CSO: 1841/152

UDC 541.49

MIXED COMPOUNDS OF ZINC AND COBALT WITH SULFANILAMIDES AND HISTIDINE

Tbilisi IZVESTIYA AKADEMII NAUK GRUZINSKOY SSR: SERIYA KHMICHESKAYA in Russian Vol 11, No 3, Jul-Sep 85 (manuscript received 26 Apr 83) pp 172-179

[Article by M.G. Tskitishvili, I.I. Mikadze and M.V. Chrelashvili, Institute of Physical and Organic Chemistry im. P.G. Melikishvili, Georgian SSR Academy of Sciences]

[Abstract] New mixed coordination compounds of double valent Zn and Co (M) with histidine (His) and deprotonated sulfanilamides (A) were synthesized from  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  or  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ , histidine, and A where A is sulfadimesine

(S), or sulfadimethoxine (F) or norsulfazol (L) or sulfapyridazine (R) in molar ratios of 1:1:1. The general formula of the prepared compounds is  $MAHis \cdot nH_2O$  where  $n = 3-9$  and was determined with chemical analysis. The structural model of the carboanhydrase-metal enzymes is important because the active center of the carboanhydrase is combined with an inhibitor for controlling the activity of these biological catalysts. Sulfanilamides are specific inhibitors of carboanhydrase. Thermal stability of  $ZnFHis \cdot 5H_2O$ ,  $CoSHis \cdot 6H_2O$  and  $CoFHis \cdot 3H_2O$  was studied by TGA and DTA and it was indicated that the compounds have practically the same scheme of thermal decomposition with dehydration occurring in two temperature stages at 105-115°C and 180-190°C followed by loss of A at 310-450°C and His at 600-650°C. The end products are oxides of Zn or Co. A potentiometric titration method was used to study the processes of formation of the mixed Zn and Co compounds. The constants of stability ( $lg\beta$ ) and disproportionation ( $log K_d$ ) of the mixed complexes increase with an increase of the dissociation constant ( $pK_a$ ) of the sulfanilamides, but the values  $log K_d/pK_a$  and  $lg\beta/pK_a$  for these mixed compounds are similar. The stability constants of the mixed compounds of Zn and Co with His and A were determined at 25, 35, 45 and 55°C. The values are  $L < F < S < R$  and  $Zn < Co$ . The stability of the mixed compounds is less than that of the metal histidates. Thermodynamic functions  $\Delta G$ ,  $\Delta H$ , and  $\Delta S$  were calculated on the basis of stability constants for the mixed compounds of Zn and Co with His and A and also for Co and Zn with A. The enthalpy change for the formation of the mixed compounds  $MLHis > MFHis > MSHis > MRHis$  is inverse to the order of their stability expressed by the values of free energy changes. In the series of the studied complexes, the difference in enthalpy and entropy changes is the result of the effect of sulfanilamide heterocycle formation. From the experimental and analytical data, the structure of the synthesized compounds is suggested. For example,  $CoSHis \cdot 6H_2O$  has the structure  $[CoSHisH_2O] \cdot 5H_2O$ . Figures 1; references 12: 7 Russian, 5 Western.

12886/9835

CSO: 1841/143

ORGANOPHOSPHORUS COMPOUNDS

UDC 546.65+541.49+547.1'118

RARE EARTH ELEMENT COMPLEXES WITH PHOSPHORYL GROUP-CONTAINING PODANDS  
(ACYCLIC CROWN ETHERS)

Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 31, No 11, Nov 86  
(manuscript received 10 Jan 86) pp 2780-2783

[Article by Z.M. Alibayeva, N.I. Snezhko, N.I. Pecurova, T.Ye. Kron,  
Ye.N. Tsvetkov and L.I. Martynenko, Moscow State University  
imeni M.V. Lomonosov; Institute of Physiologically Active Substances,  
USSR Academy of Sciences, Chernogolovka]

[Abstract] A series of complexes were synthesized between rare earth elements and the podands bis(o-diphenylphosphinylmethylphenyl) ether ethylene glycol and bis(diphenylphosphinylmethyl) ether-3-tert-butyl pyrocatechol. The complexes were formed by the reaction of  $M(NO_3) \cdot 6H_2O$  ( $M = La, Nd, Gd, Ho, Lu$ ) with either ligand in ethanol in a ratio of 1:1, and the products subjected to conventional physicochemical analyses. The complexes were shown to be formed as a result of the interaction of the cations with the terminal phosphoryl groups rather than with the ether oxygen atoms. Furthermore, the resultant complexes evidenced greater thermal stability than did the unreacted ionophores. Figures 1; references 11: 8 Russian, 3 Western.

12172/9835  
CSO: 1841/119

## CHOLINE ANALOGS IN VINYL PHOSPHATE SERIES

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 10, Oct 86 (manuscript received 14 Nov 85) pp 2333-2334

[Article by Yu.G. Gololobov and A.S. Oganessian, Institute of Heteroorganic Compounds imeni A.N. Nesmeyanov, USSR Academy of Sciences, Moscow]

[Abstract] A novel choline analog of vinyl phosphate was synthesized by the reaction of diethyl-3-chloropropen-1-yl-phosphate with trimethylamine. The alkylation yielded trimethyl-N-(O-diethoxyphosphoroyl)allyl ammonium chloride in a 79.5% yield. Dealkylation of the latter by heating for 10 h at 50-70°C led to the betaine trimethyl-N-(O-ethoxyphosphoroyl)allyl ammonium phosphate. References 3: 1 Russian, 2 Western.

12172/9835  
CSO: 1841/112

## COMPLEXING ABILITY OF PHOSPHORYL CONTAINING PODANTS WITH REGARD TO 2,4-DINITROPHENOLATES OF ALKALI METALS

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 11, Nov 86 (manuscript received 14 Jun 85) pp 2451-2456

[Article by T.Ye. Kron, E.I. Sinyavskaya and Ye.N. Tsvetkov, Institute of Physiologically Active Substances, USSR Academy of Sciences, Chernogolovka]

[Abstract] A series of ligands was synthesized. Complex forming properties of these 14 phosphoryl-containing podants, compounds of general formula  $R_mP(O)[CH_2(OA)_nOCH_2P(O)R_2]_{3-m}$  where OA is a link of ethyleneglycol, pyrocatechol or their combination,  $n = 1-6$ ,  $m = 2$  (monopodants),  $m = 0$  (tripodants), were investigated by an electric conductivity method. The complexing ability of the ligands was evaluated with respect to the stability constant of their complexes with ions of alkali metals of the corresponding 2,4-dinitrophenolates in a mixture of tetrahydrofuran-chloroform (4:1). Data for the logarithmic constants of stability ( $\lg\beta$ ) for the complexes of Li, Na, K and Cs as well as their ratios are given. Phosphorus-containing monopodants with short polyether chains between the end phosphoryl groups are effective complex formers with respect to Li cation. Phosphorus containing mono and tripodants of high dentateness form sufficiently stable complexes in the entire series of alkali metals. The stability of the complexes in the case of ligands with flexible glycol chains is higher than with rigid pyrocatechol chains. Figures 1; references 15: 6 Russian, 9 Western.

12886/9835  
CSO: 1841/145

## PESTICIDES

### 27TH CPSU SESSION AND PROBLEMS OF AGROCHEMICAL SCIENCE

Moscow AGROKHIMIYA in Russian No 9, Sep 86 pp 3-5

[Abstract] Fulfillment of the Food Program has been given top priority status at the June Plenum of CPSU Central Committee. The present 6% average annual increment in agricultural production must be increased to 14-16% and grain production increased to 250-255 million tons in 1990. Achievement of such growth rates is realistic since it will be supported by further development of the material and technical base of the agro-industrial complex. Kolkhozes and sovkhoses will be allocated more technology, mineral fertilizers and pesticides, and the area of reclaimed lands will be increased. A 2-3-fold increase in the assortment of pesticides and an improvement in their structure and quality is planned. Output of insecticides, acaricides and preparations having both insecticidal and acaricidal properties will be increased, as well as that of products having highly selective action which break down rapidly and a 100-fold decrease in consumption per hectare. Important problems still remaining are controlling soil fertility to maximize harvests under specific climatic conditions with economical and effective use of fertilizers, determining optimal agrochemical bases for soil fertility by zones, improved application of organic fertilizers and improvements in chemical melioration (particularly liming) using wastes from other industries.

12765/9835

CSO: 1841/156

PETROLEUM PROCESSING INDUSTRY

WORK ON WESTERN SIBERIAN OIL FIELD CONSTRUCTION SLOWS

Moscow EKONOMICHESKAYA GAZETA in Russian No 49, Dec 86, p 4

[Article by V. Voznyak: "Tempos Have Slackened"]

[Text] In October organizations of the Ministry of Construction of Petroleum and Gas Industry Enterprises reduced rates of construction work on oil field projects in western Siberian rayons. Plans for construction and erection work have not been met at many sites. In a month only 100 kilometers of piping in and between fields (out of the 1,400 kilometers left in the quarter's plan) and about 70 kilometers of power transmission lines (of the 430 planned for the fourth quarter) were laid. Virtually no land-based oil field projects were started up this month.

As before, construction of gas refineries in western Siberia is unsatisfactory. The lag in these construction projects, permitted since the beginning of the year, was not made up even by October. What's worse, plans for construction and erection work on structures at the Krasnoleninsk, Noyabrsk, and Gubkinsk gas refineries last month were seriously underfulfilled, and the Lokosovsk Refinery was not started up.

Construction organizations blame these deficiencies in work mostly on poor weather conditions. But it has long been known that October is one of the most complex periods, and subcontracting organizations should have taken this into account in construction plans. Then why are the prolonged impassibility of roads, lack of good roads, and related problems of delivering workers to remote sites and supplying materials and equipment to them not taken into account during planning, organization, and performance of construction and erection work?

12809/9835  
CSO: 1841/140



## DISCOVERY ABOUT OIL FORMATION AID TO SYNTHETIC FUEL PRODUCTION

Baku BAKINSKIY RABOCHIY in Russian 28 Dec 86 p 3

[Article by R. Akhmetov, correspondent]

[Excerpt] On December 25, a scientific discovery by Academicians A.A. Trofimuk and N.V. Cherskiy, Doctor of Geological and Mineralogical Sciences V.P. Tsarev, and Candidate of Chemical Sciences T.I. Soroka was recorded in the USSR State Committee on Inventions and Discoveries. This discovery broadens theoretical concepts of the transformation of organic substances into hydrocarbons.

It was thought that oil and gas formed from organic substances buried millions of years ago at a depth of more than 2 kilometers in rocks of the sedimentary sheath, and that the process of formation took place at certain pressures and at temperatures above 70-80 degrees Celsius. However, geologists occasionally found pools of liquid fuel at lesser depths and at lower temperatures. Proponents of this theory explained the occurrence of such deposits as the result of extrusion of petroleum from the Earth's mantle.

"Not all scientists agreed with this hypothesis, of course," said N.V. Cherskiy, who for 50 years has been doing research in the field of prospecting, surveying and extracting of hydrocarbon fuel materials. "We noted that the majority of oil and gas deposits are found at the edges of mountain ranges, where earthquakes often occur. As is known, earth tremors propagate longitudinal and transverse seismic waves that bear great energy. According to one hypothesis, their mechanical energy is transformed into chemical energy in the course of reactions in which thermal energy plays no part. Consequently, oil can form at lower temperatures than those 'prescribed' by theory."

To test this hypothesis, experimental investigations were performed at the Institute of Physical-Technical Problems of the North, which belongs to the Yakutsk affiliate of the USSR Academy of Sciences' Siberian Department. Effects produced by seismotectonic processes on the transformation of organic minerals into hydrocarbons were studied. The specialists constructed a model of an underground stratum consisting of sand, clay, coal and scattered organic matter. All of this material was placed inside a vessel, and the

air was pumped out of it. It was then constantly subjected to the action of elastic seismic waves for a prolonged period of time--from several months to a year. In other words, the laboratory's associates simulated, at a very rapid pace, the natural process of oil creation, which takes millions of years. When the vessel was opened, elements of petroleum and combustible gases were found in it.

The Siberian scientists thus demonstrated that oil can form in the sedimentary sheath of the Earth's crust even at a temperature of 20 degrees, and at lower pressures than had been thought.

Results of this scientific study make it possible to prospect hydrocarbon fuel materials more purposefully. Tectonic and seismic activity of Earth's interior is becoming a new criterion for evaluating the prospects of finding oil and gas in regions.

The authors of the discovery think that it will become possible in the future to build plants for producing oil and natural gas from lignites, peat and other organic substances. Such a method of obtaining petroleum products may prove to be more profitable than making synthetic liquid fuel from bituminous coal.

FTD/SNAP

/9835

CSO: 1841/125

## WAVE TECHNOLOGY TO ASSIST IN OIL AND GAS EXTRACTION

Moscow TASS in Russian 24 Dec 86

[Text] Researchers of the Machine Science Institute under the USSR Academy of Sciences have developed technology based on vibration processes which helps increase the output of oil and gas bearing wells five-fold.

"To speed up the lifting of oil and gas it is sufficient to place a small generator of wave vibrations at the bottom of a well," said Professor Rivner Ganiyev, demonstrating a small steel cylinder with several holes. "Traveling through these holes, oil and gas are mixed to produce self-induced vibrations," he went on. "Further lifting occurs thanks to mechanical forces of the wave-generating process without additional consumption of energy."

"The general theory of wave-generating process mechanics being devices at the institute makes it possible to increase gas and oil pipeline output with the help of vibrations. Besides, vibration is used to effectively separate oil from gas and hard particles and to obtain more top-quality gasoline and other light fractions during oil processing.

"Vibration processes do not need any additional power supply for they occur primarily due to self-induced mechanical vibrations. The introduction of new vibration technologies will, therefore, help drastically to reduce power consumption during oil extraction, transportation, and processing."

The first installations for high-speed oil and gas extraction will soon be shipped to West Siberian deposits.

/9835  
CSO: 1841/124

UDC 665.61[47+57]:665.61.07

IMPROVED PETROLEUM RESEARCH PROGRAMS

Moscow KHIMIYA I TEKHNOLOGIYA TOPLIV I MASEL in Russian No 12, Dec 86 pp 4-6

[Article by E.F. Kaminskiy, K.A. Demidenko and V.A. Dorogochinskaya]

[Abstract] In order to devise a program for more efficient utilization of available petroleum resources, two unified programs were recommended by the 5th All-Union Conference on Expansion and Improvements in Petroleum Research Programs. Program No 1 represents fundamental approaches to replacing old technology with new, establishing new state standards, and restructuring the entire oil exploration and refinery processes. Program No 2, was designed to provide physicochemical data on oil, hydrocarbon levels and composition in oils derived from different deposits, and oil products. These programs have been designed to replace the previous three-program plant to assure greater cost effectiveness in the petroleum industry. References 6 (Russian).

12172/9835  
CSO: 1841/132

UDC 621.892

RADIOISOTOPE METHOD FOR TESTING ANTIPITTING PROPERTIES OF ENGINE OILS AND THEIR ADDITIVES

Moscow KHIMIYA I TEKHNOLOGIYA TOPLIV I MASEL in Russian No 12, Dec 86 pp 29-30

[Article by S.P. Avdeyenko, Yu.S. Zaslavskiy, I.O. Konstantinov, G.P. Belyanchikov and A.I. Leonov, All-Union Scientific Research Institute of Oil Refining]

[Abstract] A radioisotope method has been devised to provide more rapid and sensitive method for testing engine oils and their additives for their antipitting qualities. The method is based on measuring the wear on a

radioactive tappet in terms of the increase in radioactivity of the oil and additives being tested. The tappet is rendered radioactive by being irradiated to a depth of 15-20  $\mu\text{m}$  with accelerated 11 MeV protons. The irradiation leads to the formation of Co-56 with a half-life of 77.3 days, yielding 511, 845 and 1247 keV gamma quanta. The method was found to be in excellent agreement with conventional pounding tappet techniques, with the advantage that results were available in 1 h. In addition, of the additives tested additive "A" clearly tested as a superior product, with absolutely no pitting. Figures 1; references 20; 8 Russian, 12 Western.

12172/9835  
CSO: 1840/132

UDC [665.767;621.9.079]:519.87

DATA BANK FOR PREDICTING PROPERTIES OF ADDITIVES AND QUALITIES OF COOLANT LUBRICANTS

Moscow KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL in Russian No 12, Dec 86  
pp 31-34

[Article by A.I. Chulok and V.V. Kafarov, All-Union Scientific Research Institute of Instruments; Moscow Institute of Chemical Engineering imeni D.I. Mendeleev]

[Abstract] An outline is presented of the principles of computer-based evaluation of the qualities of coolant lubricants and properties of additives, concentrating on the creation of an appropriate data bank. The information gathering, collation, and analysis is then used for the formulation of structure-activity relationships in the form of a readily accessible data bank. Various descriptors have been devised to relate chemical and physical characteristics to bactericidal, antioxidative and anticorrosive properties, with the descriptors grouped and ranked as to significance and predictive reliability. Figures 2; references 8 (Russian).

12172/9835  
CSO: 1841/132

## PHARMACOLOGY AND TOXICOLOGY

### POSSIBLE AND IMPOSSIBLE IN VITRO TOXICITY ASSAYS

Moscow KHIMIYA I ZHIZN in Russian No 10, Oct 86 pp 66-71

[Article by Yu.S. Rotenberg, doctor of medical sciences]

[Abstract] Millions of chemical compounds are known. The degree of their toxicity is expressed in a lethal dosage terminology LD<sub>50</sub>. The value of LD<sub>50</sub> for different compounds varies over a wide range from µg/kg to g/kg. In the USSR, chemical compounds are grouped into four classes from extremely dangerous to low hazardous. In the West, more than 10 million/year laboratory animals are used to determine LD<sub>50</sub> toxicity dose at a great expense. Five years ago, an experiment at 100 laboratories in Western Europe and in laboratories in USSR, in which LD<sub>50</sub> for five well-known compounds was determined, showed that the LD<sub>50</sub> varied by a factor of 2.4 to 8.4. Because of the great expense and low accuracy of animal testing (in vivo), a campaign was initiated for alternate non-animal (in vitro) methods. There were pro and con proponents and arguments for the in vitro methods. Today there are thousands of tasks devoted to biological activity of chemical compounds on different models in vitro, but this is inadequate for basic conclusions because the required conditions for testing a large number of compounds under identical conditions in a quantitative ratio for in vitro and in vivo relating the chemical structure and biological activity are lacking. The whole body tends to be viewed as a photograph rather than as a biological hologram. The biological hologram differs from the physical photograph because all its fragments do not carry equal information. Simple models based on in vitro tests cannot give the answers for the body. It is impossible to extrapolate model experiments. Reported data from toxicity studies of chemicals using fish (guppies) in home aquariums, expressed as EC<sub>50</sub>, is compared with LD<sub>50</sub> for mice. Using logarithmic coordinates, the results are linear and quite unexpected. A plot of toxicity expressed as lg 1/DL<sub>50</sub> and lg 1/EC<sub>50</sub> gave the equation  $\lg 1/LD_{50} = 0.1 + 0.51 \lg 1/EC_{50}$ . LD<sub>50</sub> values for mammals versus effective, in vitro, concentrations for various models are presented by adapting reported literature data. They are:  $\lg 1/LD_{50} = 1.49 + 0.42 \lg 1/EC_{50}$  for ovary cells of Chinese hamsters,  $\lg 1/DC_{50} = 1.20 + 0.52 \lg 1/EC_{50}$  for cells of mice brain tumor, and  $\lg 1/LD_{50} = 1.30 + 0.55 \lg 1/EC_{50}$  for mitochondria of rat liver. These equations gave sufficiently accurate reproductions of the toxicity. From the linear plots, it is concluded that in vitro methods cannot be substituted completely for studies on the body. The biological and pharmacological

effects of the compounds on quantitative and qualitative analysis of the whole body is too complex. Alternate simple methods are not possible. More than one experimental model is needed including clinical observations. Each method is good in its place and time and their coexistence thrives in the hierarchy of models. Figures 1.

12886/9835  
CSO: 1841/108

UDC 547.783 + 547.854.5

#### NEW BARBITURIC ACIDS

Yerevan ARMYANSKIY KHMICHESKIY ZHURNAL in Russian Vol 39, No 10, Oct 86  
(manuscript received 1 Jul 85) pp 613-615

[Article by E.G. Mesporyan, E.V. Martirosyan and G.B. Ambartsumyan,  
Yerevan State University]

[Abstract] Because hydantoin derivatives possess interesting biological properties, a series of novel hydantoin barbiturates was synthesized. Sodium 5,5-dimethylhydantoin reacted with ethylenechlorohydrin, followed by thionyl chloride reaction gave 3(2'-chloroethyl)-5,5-dimethylhydantoin. The latter, upon reaction with sodium derivatives of diethylalkylmalonates, in presence of sodium alkoxide, yielded diethyl esters of (5,5-dimethylhydantoino-3)ethylalkyl malonic acid which, condensed with urea, produced the desired 5-alkyl-5-[2-(5'',5''-dimethylhydantoino-3'')-ethyl]barbiturates, crystalline products soluble in alcohol and dimethylformamide, insoluble in ether, hexane and benzene. No biological data are reported. References 5: 2 Russian, 3 Western.

7813/9835  
CSO: 1841/144

## POLYMERS AND POLYMERIZATION

### LIQUID-CRYSTAL METHOD FOR DETECTING SURFACE FLAWS IN MATERIALS

Moscow SOTSIALISTICHESKAYA INDUSTRIYA in Russian 15 Jan 87 p 4

[Article by A. Assovskaya]

[Excerpt] Scientists of the USSR Academy of Sciences' Institute of Macromolecular Compounds and the State Optics Institute have developed a method of inspecting the surfaces of materials that is new in principle.

Candidate of Technical Sciences M. Tomilin dipped a small paint brush into a vial containing a cloudy liquid, then spread it over a crystal. Seen through a microscope, the appearance of the crystal changed suddenly. Brightly colored cracks and craters with uneven edges appeared in place of blurred and shadowy spots and patches of light.

As is known, molecules of liquid crystals rearrange themselves from the effect of even a weak electric field or a slight temperature differential. Turning in relation to the observer, they begin to refract light differently and polarize it. It is as if these optical effects enable us to see both the electric field and the temperature.

But won't the microscopic relief of a surface also change the orientation of molecules and produce a kind of kaleidoscope of colors in liquid crystals? In asking this question, the scientists assumed that molecules must not simply scatter over a plane but must fill up all of its invisible pores and cavities, lining up along flaws like ranks of soldiers. The liquid crystals would therefore provide pictures of cracks, microscopic roughness and various inclusions, and color them in various hues, if a sufficiently thin layer were applied.

Such was the idea for the new nondestructive testing method. Some were skeptical about it at first. After all, to see flaws was not enough; protuberances and depressions had to be distinguished from each other and their real sizes had to be measurable. Cracks sometimes appeared to be 10 times as large as they actually were.

Doctor of Physical-Mathematical Sciences E. Aero formulated a theory which resolved these problems. It explained and predicted the reactions of liquid



crystals to different kinds of flaws. M. Tomilin confirmed these conclusions experimentally and interpreted the pictures of all of these microscopic flaws. As a result, the researchers backed up their qualitative information with precise quantitative data.

The list of flaws which liquid crystals can make visible is growing longer. The Leningrad scientists already can identify flaws in the structure of lavesan film, marks left by machining on metal, faults in semiconductors, and inclusions of foreign materials, for example.

This original method has great prospects in machine building as well as in the optical and electronics industries. Liquid crystals reveal defects in glass and steel equally well. The method is simple, inexpensive and graphic.

Development of a whole system with broad capabilities is now being considered by the Leningrad scientists. Instead of a human checker, a special electronic device will 'examine' multicolored images and relay them to display tubes. A computer will then be able to gather and analyze this information and impartially compare real pictures with reference standards, making objective inspections automatically.

FTD/SNAP

/9835

CSO: 1841/172

UDC 541.147

KINETICS OF ATTENUATION OF SINGLET OXYGEN LUMINESCENCE IN POLYMERS.  
INFLUENCE OF POLYMER MATRIX ON EXTINCTION OF TRIPLET STATE OF SENSITIZER  
BY MOLECULAR OXYGEN

Moscow KHIMICHESKAYA FIZIKA in Russian Vol 5, No 11, Nov 86  
(manuscript received 25 Dec 85) pp 1488-1495

[Article by A.P. Darmanyany and M.Yu. Matveyev, Institute of Chemical  
Physics, USSR Academy of Sciences, Moscow]

[Abstract] The kinetics of attenuation of luminescence of  $^1O_2$  were used to determine the lifetime of  $^1O_2$  in an amorphous polymer with saturated bonds and in polymers with unsaturated bonds. The rate constants of extinction of luminescence by the polymers in methylene chloride, and of the unsaturated bond polymers in the polymer matrix, were determined. The quantum yield of generation of  $^1O_2$  and rate constants of extinction of the triplet state of anthracene by molecular oxygen in the polymers were determined. As the oxygen pressure increased, the rate constant of extinction of the triplet state increased in proportion to the oxygen concentration in the polymer, while the lifetime of luminescence decreased to a limiting value which is apparently the true lifetime of singlet oxygen in the polymers. The quantum yield of oxidation products in the polymer films with unsaturated bonds is close to the quantum yield of generation of  $^1O_2$  by the sensitizer used. Previous studies, which obtained lower values of quantum yield, may not have considered the effects of shielding of sensitizer molecules in microscopic pores or the degree of crystallinity of the specimens. Figures 2; references 33: 12 Russian, 21 Western.

6508/9835  
CSO: 1841/89

## PHOTOCHEMICAL CROSS-LINKING OF POLYETHYLENE, INITIATED WITH MONO- AND BINUCLEAR QUINONES

Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 52, No 12, Dec 86  
(manuscript received 12 Mar 85) pp 1309-1312

[Article by P.V. Zamotayev and A.A. Kachan, Department of Petrochemistry, Institute of Physical Organic Chemistry and Coal Chemistry, UkSSR Academy of Sciences, Kiev]

[Abstract] Polyethylene can be modified by cross-linking to give a product with altered properties. Cross-linking can be photoinitiated with certain aromatic ketones and quinones. A study was made of polyethylene cross-linking with ultraviolet light in the presence of benzoquinone, 1,4-naphthoquinone and some of their derivatives. Changes in absorption and luminescence spectra during irradiation were used to determine quantum yields of photoconversion and maximum yield of cross-linking per molecule of photoinitiator. Photoinitiating capability of quinones and their derivatives increases in the series: benzoquinone, 1,4-naphthoquinone and 9,10-anthraquinone. Figures 2; references 9: 5 Russian, 4 Western.

12765/9835

CSO: 1841/152

UDC 539.194

## THEORETICAL STUDY OF ELECTRON STRUCTURE OF POLYACETYLENE, DOPED WITH LITHIUM

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 292, No 2, Jan 87  
(manuscript received 11 Feb 86) pp 391-394

[Article by G.L. Gutsev, A.I. Boldyrev and Corresponding Member USSR Academy of Sciences A.A. Ovchinnikov, Institute of Chemical Physics, USSR Academy of Sciences, Moscow]

[Abstract] Interest in studying the electron structure of conjugated polymers has grown markedly in recent years because these compounds may be used as a base to synthesize organic materials having metallic conductivity. Such materials are prepared by doping the polymers with either donors or acceptors. However, the mechanism of the dopant's action on the electron structure of the conjugated polymer is still open. In the present work the electron structure of lithium-doped polyacetylene cluster was calculated using a discrete-variational method. Preliminary study indicates that polyene 1,3,5,7,9-trans-C<sub>10</sub>H<sub>12</sub> is entirely satisfactory as a model for an infinite trans-PA chain. The single electron energies of the two upper occupied molecular orbitals, the three lower vacant molecular orbitals, the compositions of these MO and the charges on the C and Li atoms are listed

in a table. In all cases there is a total transfer of valent lithium electrons to the lower  $\text{Pi}^* = \text{MO}$ . Therefore, the levels formed chiefly by the Li 2s-states are valent. In comparison to undoped PA, the upper occupied levels ( $\text{Pi}$  and  $\text{Pi}^*$ ) in doped PA are shifted to the side of least energy, although their relative distribution and composition are not changed. Figures 1; references 11 (Western).

12765/9835  
CSO: 1841/162

## RADIATION CHEMISTRY

### DISCOVERIES ABOUT SYMMETRY AND RADIOACTIVE MATERIALS' BEHAVIOR

Moscow VECHERNYAYA MOSKVA in Russian 19 Dec 86 p 2

[Text] Yesterday, two major scientific discoveries were recorded at the same time in the USSR State Register of Discoveries. Moscow scientists are credited with both of them.

The phenomenon of radioactivity has been known since 1896. In a comparatively brief period of time, scientists have found a considerable number of uses for energy of the atom. Radioactive substances are broadly utilized in the diagnosing and treatment of illnesses, for example. These substances are used to remove electrostatic charges in the textile industry, and nuclear batteries which are unique generators of electric current are operating successfully in beacons.

Processes involving solid radioactive substances with high electrostatic resistance had not received much study until recently. Among these substances are glass, ceramics and composite materials into which radioactive isotopes have been introduced by one method or another.

Research by Academician V. Spitsyn and Doctor of Chemical Sciences V. Gromov at the USSR Academy of Sciences' Institute of Physical Chemistry has provided answers to many questions. In particular, their discovery of the existence of a stable electrical charge allows new interpretations to be made of features of the behavior of materials during catalysis, dissolution, etc., which is of both scientific and great practical significance.

The authors of the other discovery are scientists of the Institute of Theoretical and Experimental Physics: L. Okun', corresponding member of the USSR Academy of Sciences, and doctors of physical-mathematical sciences B. Ioffe and A. Rudik.

One of the central concepts of physics is that of symmetry. The generally known laws of the conservation of energy and momentum are derived from this concept. The three symmetries which are called discrete--bilateral, three-dimensional and charge symmetry--play a particularly important role in contemporary science. Charge symmetry exists between particles and

antiparticles. Analyzing their properties, the researchers concluded that violation of bilateral symmetry must necessarily be accompanied by violation of one of the other two discrete symmetries.

The law that was discovered plays an important role in the understanding of the microscopic world and in the evolution of the universe.

FTD/SNAP  
/9835  
CSO: 1841/125

## DIELECTRICS DOPED WITH RADIOACTIVE ISOTOPES

Moscow TASS in English 19 Dec 86

[Text] Soviet scientists have discovered conditions under which electric charges accumulate on the surface of dielectrics--non-conductors of direct electric current.

They have established that such charges originate when radioactive isotopes are inserted into the dielectric.

The results of the research carried out by a group of staff members of the Institute of Physical Chemistry of the USSR Academy of Sciences were entered in the State Register of Discoveries on Thursday.

A TASS correspondent has been told, at the USSR State Committee for Inventions and Discoveries, that this research by scientists is of great practical importance, since radioactive compounds are widely used in branches of the Soviet economy.

The discovered phenomenon will be applied in research, in work with radioactive catalysts, at nuclear power stations, and when diagnosing some diseases.

A discovery in the field of elementary particles was also registered in Moscow on Thursday. The discovery is of great scientific interest to physicists-theoreticians and astrophysicists.

/9835

CSO: 1841/124

## SOLID PHASE RECRYSTALLIZATION OF SILICON LAYERS ON AMORPHOUS DIELECTRIC SUBSTRATES BY SCANNING LASER RADIATION

Moscow POVERKHNOST in Russian No 11, Nov 86 (manuscript received 27 Mar 86)  
pp 86-89

[Article by A.V. Demchuk, A.M. Pristrem, N.I. Danilovich and A.M. Kravchenko, Minsk Radiotechnical Institute]

[Abstract] Results are presented from studies of solid phase recrystallization of silicon layers on amorphous dielectric substrates under the influence of continuous scanning CO<sub>2</sub> laser radiation at 10.6 μm wavelength, and a mechanism is suggested to explain the increase in grain size due to thermoelastic stresses arising in the structure upon laser treatment. The experimental substrates were silicon single crystals with a layer of oxide 0.5 μm thick produced by heating to 1423 K. Chemical vapor phase precipitation was used to apply a layer of polycrystalline silicon 0.5 μm thick doped with phosphorus 10<sup>19</sup> cm<sup>-3</sup>. The specimens were exposed to laser radiation with maximum power density 10<sup>4</sup> W/cm<sup>2</sup>, scanning speed 2.5 cm/s, laser spot diameter 0.65 mm, scanning line overlap 85%, heating the substrate to 673-823 K. The change in surface layer structure after laser treatment was studied by electron microscopy and x-ray diffraction analysis. Thermoelastic structural stresses were found to have a significant influence on the process of solid phase recrystallization of the surface. Formation of a more defect-free structure in the surface layer during laser recrystallization was accompanied by activated movement of grain boundaries in the nonhomogeneous field of thermoelastic stresses with subsequent annihilation upon merging of grains. Figures 3; references 7: 2 Russian, 5 Western.

6508/9835  
CSO: 1841/114



STUDY OF RADIATION DEFECTS IN FILMS OF CHROMIUM BOMBARDED WITH  $\text{He}^+$  AND  $\text{H}^+$  IONS

Moscow POVERKHNOST in Russian No 11, Nov 86 (manuscript received 2 Jul 85)  
pp 115-118

[Article by L.P. Tichchenko, T.I. Peregon, A.G. Koval and G.I. Galutskikh,  
Kharkov State University]

[Abstract] Continuing their study of thin metal, film-implanted hydrogen or helium systems, the authors used the methods of measuring resistivity, thermal desorption mass spectrometry and electron microscopy to study processes of accumulation, interaction and annealing of intrinsic radiation defects and implanted gases in chromium films. Epitaxial chromium films about 1000 Å thick formed in a very high vacuum, were bombarded at room temperature with  $\text{He}^+$  or  $\text{H}^+$  ions at 10-40 keV,  $5 \cdot 10^{17}$  -  $5 \cdot 10^{20}$  ions per square meter. Accumulation of radiation defects in the films was studied by measuring the change in resistivity during bombardment. Annealing of the defects formed was studied by the spectra of rates of restoration of resistivity in the 290-800°C temperature interval. The films were then heated to 2200°C to study the liberation of helium and deuterium from the specimens in a vacuum and the structural changes were studied. The hydrogen and helium were found to be located with crystalline lattice radiation-induced defects. Hydrogen was liberated when the specimens were heated to the annealing temperature, while helium remained within the films, forming gas bubbles which did not leave the specimens until they were heated almost to the melting point. Figures 3; references 9 (Russian).

6508/9835  
CSO: 1841/114

DISSOCIATION OF  $^{13}\text{CF}_2\text{Cl}_2$  MOLECULES IN TWO-FREQUENCY  $\text{CO}_2$  LASER PULSE FIELD

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 60, No 11, Nov 86  
(manuscript received 16 Dec 85) pp 2863-2865

[Article by V.Yu. Baranov, A.P. Dyadkin, S.A. Kazakov, V.A. Kuzmenko and  
S.V. Pigulskiy]

[Abstract] The phenomenon of multiphoton selective dissociation of molecules in a  $\text{CO}_2$  laser field appears promising for use in isotope separation, leading to studies on the dissociation of  $^{13}\text{CF}_2\text{Cl}_2$  molecules as a result of two-frequency excitation. Graphed data relating selectivity and degree of separation of the two C isotopes to laser intensity, gas pressure and lag time between pulses demonstrated that with the two-frequency

approach the dissociation yield remains constant while selectivity increased two-fold. Concomitantly, the energy of CO<sub>2</sub> laser emission required for the dissociation decreases two-fold, and the optimal working pressure of freon diminished from 12 to 2 mm Hg. Optimum results were obtained with a lag time of 10 msec or less, while higher lag time transformed the process into, essentially, a single frequency mode. Figures 3; references 12: 7 Russian, 5 Western.

12172/9835  
CSO: 1841/110

UDC 541.14

DYNAMICS OF COLLISION-INDUCED DISSOCIATION IN CROSSED CsBr+Xe MOLECULAR BEAMS. EXPERIMENT, PULSE MODEL

Moscow KHIMICHESKAYA FIZIKA in Russian Vol 5, No 11, Nov 86  
(manuscript received 11 Jul 85) pp 1514-1520

[Article by V.M. Akimov, A.I. Mayergoiz and L.Yu. Rusin, Institute of Chemical Physics, USSR Academy of Sciences, Moscow]

[Abstract] A study is made of collision-induced dissociation  $\text{CsBr} + \text{Xe} \rightarrow \text{Cs}^+ + \text{Br}^- + \text{Xe}$ , and the dynamics of this reaction are studied based on a pulse model. The effects of strong variation of scattering characteristics near the reaction threshold as a function of energy of internal degrees of freedom of molecules before the collision are particularly emphasized. The variation in full cross section as a function of collision energy and internal salt molecule energy is determined, as are the differential cross sections. The phenomena are well described by the modified pulse interaction model. Figures 5; references 16: 5 Russian, 11 Western.

6508/9835  
CSO: 1841/89

## GAIN OF HF-LASER WITH TWO-QUANTUM TRANSITIONS AND RESONANT OPTICAL PUMPING

Moscow KHIMICHESKAYA FIZIKA in Russian Vol 5, No 11, Nov 86  
(manuscript received 14 Jan 86) pp 1577-1578

[Article by A.D. Margolin, A.V. Mishenko and V.M. Shmelev, Institute of Chemical Physics, USSR Academy of Sciences, Moscow]

[Abstract] When powerful resonant oscillation acts on a system of non-harmonic oscillators, the distribution of molecules among oscillating levels differs sharply from the Boltzman distribution. Calculations have shown that full population inversion to upper oscillating levels can occur in 100-150 ns with laser power 30 MW/cm<sup>2</sup>. The gain of the medium based on a single-quantum conversions to upper levels is great and depends little on level number. Generation of induced radiation at upper oscillating levels with resonant optical pumping can occur when a selective resonator is used or a nonselective resonator is switched at the proper moment. This article notes one curious situation occurring in such systems with resonant optical pumping. In contrast to chemical pumping, strong oscillating nonuniformity is achieved with optical pumping in the area of the upper oscillating levels, where the Einstein factors for two-quantum transitions are significantly higher than those of one-quantum transitions. This should cause a great increase in gain of the medium for two-quantum transitions in the area of high oscillating numbers. This indicates the possibility of converting the radiation of chemical-gas dynamic HF lasers into another spectral range with an increase in frequency of output radiation by about 30%. Figures 2; references 4: 1 Russian, 3 Western.

6508/9835  
CSO: 1841/89

UDC 546.791.175:669.882

## REACTIONS OF URANIUM WITH NITRATE MELTS

Leningrad RADIOKHIMIYA in Russian Vol 28, No 6, Nov-Dec 86  
(manuscript received 22 Apr 85) pp 722-725

[Article by V.P. Denisov, I.V. Korobeynikov, K.N. Kuttyrev, V.I. Pyatkov and S.P. Raspopin]

[Abstract] A study was made of the reaction of metallic uranium with a eutectic mixture of molten sodium and potassium nitrates at 234-510 degrees C in an inert atmosphere. A uranium electrode and a silver reference electrode were immersed into the melt, the uranium potential fixed and gas evolution observed visually. Results indicated that the degree of uranium oxidation is a function of the melt temperature. At 236-367 degrees C

uranium dioxide is formed, which is subsequently oxidized to diuranate at higher temperatures. As the reaction proceeds, alkali metal nitrides are accumulated in the nitrate melt and nitrogen dioxide is given off. Figures 4; references 5: 4 Russian, 1 Western.

12765/9835  
CSO: 1841/161

UDC 539.1.074.27

RADIOMETRY OF FISSION FRAGMENTS AND ALPHA-PARTICLES USING PLASTIC FILMS AND AIST SPARK TRACK COUNTER

Leningrad RADIOKHIMIYA in Russian Vol 28, No 6, Nov-Dec 86  
(manuscript received 1 Dec 83) pp 816-820

[Article by A.V. Yevdokimov, V.Ye. Kopchenov, A.S. Krivokhatskiy, V.A. Nikolayev and A.I. Shipunov]

[Abstract] Preparations containing transplutonium elements have a high specific alpha-activity as well as neutrons and fission fragments. Radiometry of these types of radiation is readily carried out with a track detector employing a plastic film. In the present work a simple device was designed. Tracks were captured on nitrocellulose films (alpha-particles) and polycarbonate films (fission fragments) and recorded with an automated AIST or ISTRa spark track counter. Track density can be determined in 3-5 min at 5% accuracy at 8000 tr/sq cm. Figures 5; references 10: 3 Russian, 7 Western.

12765/9835  
CSO: 1841/161

UDC 622.765

DIELECTRIC PERMEABILITY AND STRUCTURAL CHANGES DURING THERMODYNAMICALLY IRREVERSIBLE WATER-ICE PHASE CONVERSION

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 60, No 12, Dec 86  
(manuscript received 25 Feb 85) pp 2932-2935

[Article by L.G. Karchurin and Mussa Tandia]

[Abstract] In a previous work anomalies were detected in the complex dielectric permeability of thermodynamically irreversible crystallizing water. In the present work a laser optical-electronic technique was employed to study the kinetics of water-ice phase transformation and structure of the phase boundary. Holographic photography of the crystallization front showed that at 15-20 V crystallization potential, a

marked increase in dielectric loss takes place in the UHF range. It was also confirmed that at a high degree of thermodynamically irreversible crystallization, an effect similar to the so-called Zavoyskiy effect takes place. In both cases an anomalously high resonance absorption of RF energy takes place. In one case the cause is the external magnetic field, and in the other it is due to the passing of the crystallization front. Figures 4; references 7 (Russian).

12765/9835  
CSO: 1841/157

UDC 535.21

KINETICS OF MONOMOLECULAR PHOTOCHEMICAL REACTION DURING LASER EXCITATION OF REAGENT

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 60, No 12, Dec 86  
(manuscript received 6 Mar 85) pp 3079-3084

[Article by V.V. Gusev, V.A. Dubrovskiy and B.A. Medvedev, Saratov State University imeni N.G. Chernyshevskiy]

[Abstract] Knowledge of monomolecular reaction kinetics is needed to control photochemical processes and photodissociation kinetics in particular is important in optimizing photodissociation parameters for lasers. A study was made of the effects of continuous and pulsed laser radiation in the visible and UV ranges on the reaction rate constant and product yield in a theoretical monomolecular irreversible photochemical reaction. The feasibility of determining the excited state of a reagent leading to transition into an activated complex (divergence of reaction channels) is demonstrated for both "slow" and "fast" reactions. Figures 4; references 5: 3 Russian, 2 Western.

12765/9835  
CSO: 1841/157

CHANGES IN ION EXCHANGE PROPERTIES OF AMPHOLYTE VPK DURING IRRADIATION IN  
COMPLEX METAL FORM. PART 2. ION EXCHANGE PROPERTIES OF VPK IRRADIATED  
IN STRONTIUM COMPLEX FORM

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 60, No 12, Dec 86  
(manuscript received 4 Mar 85) pp 3101-3103

[Article by S.V. Tabakova and Ye.D. Kiseleva, Institute of Physical  
Chemistry, USSR Academy of Sciences, Moscow]

[Abstract] In a previous study of the effect of ionizing radiation on Ampholyte VPK partially filled with strontium ions it was demonstrated that carboxyl groups, forming stable coordination bonds with strontium ions, do not break down on irradiation, but the breakdown rate of the carboxylic acid groups not tied to the complex, increased and exceeded that of carboxylic acid groups when irradiated in the hydrogen form. In the present work a study was made of the changes in physical chemical and ion exchange properties of Ampholyte VPK irradiated in the strontium form at maximum filling (4.6 mg-eq/g) and  $2-10 \times 10^6$  Hz. It is demonstrated that the basic processes taking place are oxidation of the matrix and breakdown of the sorbent bonds. Breakdown of the strontium complex with sorbent ion exchange groups during irradiation was not observed. Figures 1; tables 1; references 5 (Russian).

12765/9835  
CSO: 1841/157

STUDY OF CONFORMATIONAL STRUCTURE AND ORIENTATIONAL CRYSTALLIZATION OF  
STEREOREGULAR *cis*-1,4-POLYISOPRENES

Moscow KAUCHUK I REZINA in Russian No 12, Dec 86 pp 4-7

[Article by A.P. Berezkina, K.V. Nelson and S.K. Kurlyand]

[Abstract] Synthetic rubber obtained by polymerization of isoprene over a titanium salt catalyst (SKI-3) appears to be a close analog of natural rubber in polymer chain microstructure, but differs markedly in physical properties. To clarify this discrepancy, a study was made of the molecular orientation of natural and synthetic polyisoprenes during deformation over a wide temperature range. Sample strips were stretched at 50 mm/min to near the limit in a thermal chamber or cryostat which was placed in a H-100 "Hilger" IR-spectrophotometer. Temperatures were varied from -35 to 120 degrees C. Analysis of the data shows that orientational crystallization occurs in sequential stages with crystallites forming in folded chains in the first stage. A feature of the crystallization common to both natural rubber and certain polyisoprenes (composition SKI-3 with *cis*-1,4-oligoisoprene) is the presence of a deformation zone in which the degree of crystallization remains constant while the sample is being stretched. This zone evidently reflects the restructuring of sub-molecular structure related to crystallite breakdown from the folded chains and the formation of crystallites primarily in unfolded chains. Data on the correlation of conformational structure to orientational crystallization of *cis*-1,4-polyisoprene makes it possible to use a physical approach in evaluating the properties of synthetic rubbers. Figures 6; references 10 (Russian).

12765/9835  
CSO: 1841/153

WATER TREATMENT

INTRODUCTION OF SCIENTIFIC DEVELOPMENTS OF ALL UNION SCIENTIFIC RESEARCH  
INSTITUTE VODGEO

Moscow VODOSNABZHENIYE I SANITARNAYA TEKHNIKA in Russian No 12, Dec 86  
pp 25-26

[Article by S.V. Yakovlev, O.V. Demidov, All Union Scientific Research  
Institute of VODGEO]

[Abstract] A recount of achievements of the title Institute is presented:  
production of disc rotatory locks, treatment of circulating water in air  
conditioning systems, development of equipment for water purification,  
automation of pump stations, development of anticorrosion covers for  
sewer pipelines, etc. In addition, research projects were carried out in  
such areas as treatment of sewage sediments from galvanization plants,  
biochemical treatment of sewage, use of open hydrocyclones for separation  
of sewage particulates, removal of nitrogen from effluent, flotation  
purification methods and other appropriate areas.

7813/9835  
CSO: 1841/131



HYDROLYSIS OF WOOD PULP BY FREEZING IN DILUTE SULFURIC ACID

Moscow GIDROLIZNAYA I LESOKHIMICHESKAYA PROMYSHLENNOST in Russian No 7,  
Oct-Nov 86 pp 11-12

[Article by A.T. Porubova and S.A. Sapotnitskiy, Wood Technology  
Academy imeni S.M. Kirov]

[Abstract] Optimal conditions were determined for the hydrolysis of sawdust without excessive loss of monosaccharides by freezing in dilute sulfuric acid. The optimum degree of hydrolysis of glycosidic bonds, sufficient to ensure solubilization of 90% of the polysaccharides, was attained at  $-60^{\circ}\text{C}$  with 6 h of digestion in the frozen state by 2.5%  $\text{H}_2\text{SO}_4$ . Below  $-60^{\circ}\text{C}$ , decomposition of the monosaccharides was accelerated, and above  $-40^{\circ}\text{C}$ , the process was ineffective. Growth of *Candida scottii* on hydrolysate diluted to contain 1.2% reducing substances yielded a biomass containing 55% protein in a 60% yield in terms of the reducing sugars. References 2 (Russian).

12172/9835  
CSO: 1841/117

## POTENTIAL USE OF TALL OIL IN ELECTROTECHNICAL INDUSTRY

Moscow GIDROLIZNAYA I LESOKHIMICHESKAYA PROMYSHLENNOST in Russian No 7,  
Oct-Nov 86 pp 17-18

[Article by R.G. Shlyashinskiy, senior scientist, A.Yu. Klyuyev, senior engineer and S.S. Puyat, senior laboratory technician, Institute of Physicoorganic Chemistry, Belorussian SSR Academy of Sciences; B.D. Bogomolov, doctor of technical sciences, Arkhangelsk Institute of Wood Technology]

[Abstract] Studies on the dielectric characteristics of tall oil prepared from different sources revealed marked differences attributable to the relative concentrations of abietic acid and fatty acids. Among the various samples tested, those produced at the Bratsk plant were particularly interesting for application to the electrotechnical industry, because of their high  $\rho_v^{110}$  and low  $t_g^{110}$  constants due to high abietic acid levels and low fatty acid concentrations. Incorporation of the Bratsk tall oil into the formulation of PM-3 cable saturant resulted in a product exceeding the OST 160.686.052-73 dielectric standard requirements for this application. Power cables AAB and AASH<sub>v</sub> with the modified MP-3 cable saturant have undergone successful tests in actual use. References 8 (Russian).

12172/9835  
CSO: 1841/117

UDC 630\*86.006:658.562

## TRENDS IN STANDARDIZATION IN WOOD CHEMISTRY INDUSTRY

Moscow GIDROLIZNAYA I LESOKHIMICHESKAYA PROMYSHLENNOST in Russian No 7,  
Oct-Nov 86 pp 23-24

[Article by O.V. Skvortsova, head, Department of Standardization, candidate of technical sciences, and V.K. Lipovetskaya, group leader, Central Scientific Forestry Research Institute]

[Abstract] A review is presented of some of the more recent developments in setting quality standards affecting the wood chemistry industry. The standards encompass both the products and the means of production, but allow for modification to meet local needs. Although attempts have been made over the years to cover all aspects of the industry, further work remains to be done to cover such factors as control systems, certification programs and unification.

12172/9835  
CSO: 1841/117

NEW TECHNICAL PREREQUISITES FOR TRUCKING DANGEROUS CARGO

Moscow GIDROLIZNAYA I LESOKHIMICHESKAYA PROMYSHLENNOST in Russian No 7,  
Oct-Nov 86 pp 25-26

[Article by L.V. Obidina, senior scientist and T.Ye. Kuznetsova, junior  
scientist, Central Scientific Forestry Research Institute]

[Abstract] Analysis of existing regulations covering the automotive transportation of wood chemistry products has revealed the need for further refinement. The intent is to insure greater safety under normal operating conditions, as well as to minimize any damage to personnel and the environment in case of spills, accidents and collisions. Specific regulations have been developed for the transportation of such products as butyl acetate, 80% acetic acid, turpentine, lacquers, and so forth. The promulgation of new regulations and their implementation will go a long way in filling current gaps and in providing a solid foundation for improving the transportation sector of the wood chemistry industry.

12172/9835  
CSO: 1841/117

MISCELLANEOUS

USSR ACADEMY OF SCIENCES CHEMICAL INSTITUTE AT GORKIY

Moscow KHIMIYA I ZHIZN in Russian No 9, Sep 86, No 10, Oct 86

[Article by V. Polishchuk, KHIMIYA I ZHIZN special correspondent, "Arrive at Shchberbinka"]

[No 9, Sep 86 pp 7-14]

[Excerpt] When I began to write about the Chemistry Institute of the USSR Academy of Sciences, which is located in the city of Gorkiy, I became firmly convinced on the third day there that everything which they are showing, telling and explaining to me could perhaps fit into a two-volume novel. Knowing another thing not less certainly--our journal does not print and will not print such a genre, I condensed my tome extremely, as the result of which the minichapters presented below have appeared. Many of them could completely become the theme for an independent ode, epic, or dissertation.

Part I. Glass and Metal

1. Exhortation

A white, five-story box built 13 years ago, is decorated with a long glassed-in addition like a cottage veranda, in which a not very spacious administration is located, and there is a dining room in the semi-basement. In these brief years, the box has become crowded--the veranda has been converted into a passage connecting the "old" structure with the newer staggered sand-colored structure erected based on some kind of latest architectural trend. The two departments into which the institute is subdivided now almost do not intermingle--each is in its own housing. And it is not difficult to notice between their associates a certain good-natured rivalry. This is like campaigners from neighboring regiments who take part in the total battle within the formation of a single division.

A comparison with divisions, by the way, is rather conventional: even when the plentiful production services which are unusual for an academic institution are taken into account, barely six hundred workers are employed here. And indeed its chief is not at all unlike a stern general.

"When can I speak with the director?" "Any time, it is not necessary to register."

Academician Grigoriy Alekseyevich Razuvayev, when you enter the office, rises and sits down at the lower end of a long desk cross-wise to his own--he does not like to cut himself off from a conversationalist. Then, when you leave, he again rises and unfailingly accompanies you to the door.

He inquires about what the guest has had time to look at and suggests, "Have you seen planar optics? You put down the sheets you have written on--the whole surface is magnified without curvatures and it is not a magnifying glass. And photographic recording without grain? You look with your eye--a thin dash, and you magnify two hundred times and have a legible line of text. And coatings? Chromium carbide is applied on ceramics so that if you try to peel it off, it tears along the ceramic."

I ask, "What will you recommend of pure science? It appears that it is somewhat slighted--and in your opinion, why is this? For each of such simple everyday comprehensible things there are basic research and theory." And he explains:

"From theory it is necessary to find results. Precisely, yesterday at our seminar one talented Moscow colleague came forward; he is obtaining amazing compounds. Our colleagues ask, 'And where will they be used?' He answers, 'I am not concerned with applied problems.' But who then will be concerned with them? To discover what a substance may be used for can be done only by the one who worked with it personally with his hands. Imagination is necessary here also; it is useful, if you will, to study scientific fantasy. It is not obligatory to oneself, of course, to bring the matter to the working plant, you know, but it is necessary to make recommendations, to join with interested enterprises, and to pay attention to engineers and technologists. We were already accustomed to act in this way. And indeed how was it among scientists? They begin to fight each other and invent apparatus amateurishly. It is obtained nastily--they give up and for no particular reason publish in a journal. And there you see, the Germans and Japanese pick it up and construct a plant."

Shop sciences in a literal sense are masterly: glass blowing, mechanics, carpentering, instrument building, electrical shops... A diverse service, which ordinarily is hidden in a basement basically (to reach it, tunnels are necessary in which a casual person without fail loses his way) is actually a foundation. Without it, you do not achieve either small or great discoveries.

Both a hydrogen plant (the flow of this gas is so large that you do not save up to carry balloons) and cryogenic installations producing liquid nitrogen and even helium are in operation at the Gorkiy institute beyond other ordinary shops (do not count on well-wishers; many of the newest instruments have electromagnets--with superconducting winding, and without liquid helium they are useless). They are responsible for this technical foundation here as at a good plant and require no less from it. The results are available. To order from the mechanics any, even the most intricate apparatus made of difficultly workable stainless steel, is not a problem (just try to get such a thing at

another institute); semicommercial all-soldered fractionating systems made of quartz which are not one story high also are not a problem--more will be said about them.

As for organometallic compounds, they are nearly the most popular subjects of research here--however, they have caused little trouble. A paper describing almost all of them (Footnote \*) (V. Mey. "Tochka, tochka, zapyataya" (Period, Period, Comma)) has already been published in KHIMIYA I ZHIZN concerning research in this field which was distinguished by a State Prize last year. And the enigmatic "flexible crystal" which responds to light in such a way--both visible and infrared--has also been written about, both in the Doklady's of the USSR Academy of Sciences and in ZNANIYE--SILA.

Hopes for a tranquil life went up in smoke, just as I stepped on the threshold of room No 211, where new-fledged laureates Gleb Arsentyevich Abakumov (he is deputy director of the institute) and Vladimir Kuzmich Cherkasov are situated. From the time that these publications appeared, here, it turns out that they have succeeded in discovering no less than a new form of isomerism--redox isomerism.

It hardly is worth explaining what isomers are: even a student knows that these are compounds which are identical in molecular composition but differ in the arrangement of some of their parts--atoms or groups of atoms. Here, if one views formally, in all only an electron is shifted: the nature of these free-radical complexes is such that it can be located both on the central metal atom and on the ligand-quinone bound to it. And, moreover, in other cases it migrates reversibly: isomers dissolved in the appropriate medium are in equilibrium, quietly migrating back and forth (such transitions since time immemorial have been called tautomerism).

When Abakumov and Cherkasov first told their colleagues about electronic tautomerism, they had to hear many acrid and even malicious words: indeed, they said you do not know that any electron shifts are instantaneous and to observe in principle is impossible. Then, however, everything fell into its place. The migration of the electron, as it was explained, is accompanied by a shift, a restructuring of the system of ligands surrounding the central metal atom. Sometimes a new ligand (solvent molecule) is joined to it, and sometimes only the "architecture" of the old is changed. They gave me the freshest, just recorded spectra illustrating the especially sharp, beautiful case of the redox-isomerism of one of the copper complexes. The hosts of the room, however, were glad not only because they were studying how to construct one more curious compound (an ordinary case) but also the rich analogies with natural enzymes, which also contain copper. Such enzymes play a role of no small importance in cell respiration, and who knows whether such a redox-isomerism controls their finely regulated work--indeed it could be implemented as the result of an abrupt intermittent rearrangement of the protein tangle enveloping the metal atom.

The science of building all possible organometallic compounds is interwoven here with art, even with history. They are debugging, for example, a semicommercial method for obtaining diethyl zinc, a compound with a 130 year biography, the first organometallic compound in the world. Now this insidious

liquid, which ignites in air--all these years it has remained a laboratory curiosity--was needed for matters especially of the earth and as an intermediate product of different syntheses. And compounds of an extremely "modern" form--complexes of transition metals with aromatic hydrocarbons--are being produced simultaneously for even more prosaic needs.

It was not so long ago, I remember, that chemists only disputed about the enigmatic nature of these novelties, and now Doctor of Chemical Sciences Georgiy Alekseyevich Domrachev economically explains to me that it was as if the metal atoms creep into the space between the planenesses of the molecules of the liquid, and a liquid complex is obtained which is almost indistinguishable in volume, but, of course, much heavier. Indeed, however, the organometallic compound technology laboratory (Domrachev is the director) works not with a liquid in a small flask, but with "snow" frozen on a wall of a steel apparatus cooled with liquid nitrogen and in which a high vacuum is maintained. In order for the organic ingredient to evaporate, without special trouble, the metal "volatilizes" in the form of separate atoms after heating by an electric furnace or by an electron beam.

In such a state, it is strongly active. The synthesis does not require any additional reagents or conditions on the part of the experimenter. The atoms themselves volatilize into all the intermolecular spaces, provided even the smallest defect is found in the crystal structure of the "snow." The advantages of such a technology are that the substance needed is obtained at once, in one step; it is possible not to be hindered either in the selection of ligands (side groups attached to the aromatic ring almost do not interfere in the matter) or by the low stability of other complexes (they also do not break up in the cold). Well, finally, such a method of synthesis is not only practical but elegant. And is this really of little importance?

They showed me samples of liquids obtained on an ethylbenzene base. The chromium complex is brown, the molybdenum complex is green, the vanadium complex is red, and the titanium complex is darker, similar to potassium permanganate. The ampoule of it is withdrawn from the condenser for only a minute (it is unstable at room temperature, so that the coloring, perhaps, is scrutinized not completely precisely. Of course, it is impossible to prepare such a complex by another method.

#### 4. Again, Glass, or More Precisely, Glasses

Comparatively recently, before this institute was built, a laboratory for stabilization of polymers existed. It grew up around the laboratory inherently--and maintained fidelity to the problem. The experience accumulated here is focused, in particular, on using PVC, polyvinyl chloride, which is produced on a very large scale, cheap, but alas, not the most durable of polymers. It was studied to be converted into a rigid, transparent material, in appearance differing little from traditional organic glass manufactured from expensive acrylates. It would seem not to be a great innovation. But what it actually presages, Doctor of Chemical Sciences Borisovich Troitskiy, deputy director of the transparent polymer materials laboratory, explained to me:

"If a shop, ordinary among plant shops, is built with a roof not made of ordinary silicate but of such a glass, for only one metal structure, an economy of many thousand [rubles] is obtained, and it is indeed somewhat easier. And in addition it is not hammered, and it conducts heat weakly. Together with the Moscow Central All-Union Industrial Building Research Institute, we determined that the demand for such a material reaches a million square meters per year. The economic effect, however, per every thousand square meters is of the order of a million rubles. Until we succeed, however, we are continuing tests. Lights with such a glass have already lasted for a period equivalent to 5 years of use. We are hoping to reach 10 also..."

"Perhaps this is the material for roofs of the future. It is possible to make gigantic light-weight ceilings for stadiums and circuses out of four millimeter sheets with plastic reinforcement. In order always to see the sky..."

And this is just one glass.

I saw nothing unusual in a completely transparent, colorless specimen. Really from the end view for some reason or other it changes to red.

"That's it, red...It also is a glass made of polyvinyl chloride, but with a luminescent additive. We developed it jointly with the Moscow Institute of General and Inorganic Chemistry and the Kaprolactam Production Association, which is in Dzerzhinsk. The additive is very small, but not less than half of the ultraviolet falling on the glass changes it to a red color. What is the result? Plant vegetation is accelerated in a greenhouse glass enclosed with such a material; the additional light almost exactly strikes the absorption of chlorophyll molecules at the maximum. Tomatoes ripen several days earlier, and cucumbers ripen a whole week earlier. There are no limits to this yet."

From glass with a red opalescence, a kaleidoscope of institute impressions transfer my memory to another, from which a slide was made. At first glance it is rather mediocre, black and white, with a picture of some book-plate. Abakumov, shunting me into a crowded room, where a projector was placed among other equipment, asked me to aim the apparatus directly at the curtain. Then something was rotated and regulated in the projector--and an ordinary picture was regenerated into the negative.

The host demanded a hypothesis--why? I failed to devise anything intelligible, and with cheerful triumph he explained to me that the slide is not ordinary--it is a relief and therefore "regenerated" under light. It is not made on a prepared film but it is as though decanted from a liquid. The monomer, more precisely, a low molecular weight oligomer with a polymerization photoinitiator additive, is poured in a thin layer on a soaked (very shallow) bar lit by a lamp--and the relief is decanted precisely. The liquid composition is extremely sensitive...

## 5. Radical Solutions

You shouldn't fall into such general optimism. Indeed, how does this happen? The correspondent comes quickly, checks the list of achievements dictated by



the local commanding officer and creates a picture engraved as if with mountain tops.

The difficulties of this young (the average age of the associates is less than 30) collective are not less than the achievements. The institute is located on the outskirts, and occasionally it is not simple to arrive there on time during the morning peak. And there is housing for associates and a kindergarten... Or, if you return to working problems, these include reagents and instruments... The institute is unique in many ways, in particular in that it does not have a single nuclear magnetic resonance spectrometer. There is a unique transit time mass spectrometer with a laser activation (they built it themselves), but there is no NMR, and you cannot make it in this way. Contract work here meanwhile annually is performed for a million rubles and more, exceeding the plan task by a factor of 1.5. It would be possible, they themselves acknowledged, to do several times more, and they would find customers instantaneously. The time has passed when in the eyes of industrial people, academic science in usefulness was not far ahead of theology: the institute has been able to gain a strong practical reputation. But the antiquated situation stifled it, in accordance with which neither the staff timetable nor the compensation of associates depends on the contract sums...

Gleb Arsentyevich Abakumov, who has just fervently talked about the new glasses and the metamorphoses of radicals, while going from the laboratory to his deputy director's office, becomes gloomy:

"We cannot pay for the work for the contracts, and holding more than one job is forbidden. There is, however, hope that a great deal will be changed soon..."

It is here that I first heard these words: a temporary collective. The essence is briefly that a project is developed to set up for three years an interdepartmental laboratory with a specific task--the development of new optical materials. The head organization--the Leningrad State Optics Institute--obtains equipment for the problem and several million [rubles] of funds for wages, which will be shared with "subcontractors" working in different cities, including Gorkiy in particular. Most significant is the fact that the collective will be free of trifling cares. By showing a business-like basis, he himself will be able to decide how many workers and what skill to select within the limits of the funds released. If necessary, multiple positions are connected whether from other organizations or from their own organization, with additional payment to them of a set percentage of their salary.

Until this is finally authorized, but after the 27th CPSU Congress and after the decisions made at the annual sessions of the Academy of Sciences, there is hardly any doubt that it will be approved.

And there are problems anew. Someday it will be decided, and now, this very day, at the threshold there is a curtailment, not retention, which is inevitable during conversion to the new system of payment for labor, which especially stimulates labor. The system is correct, I do not dispute, but how is it to be obtained? Today you lay off trained, experienced people, and

tomorrow, when the "subcontracted" rates arrive, you will contract for unskilled novices.

This is how the management revolves...

There are other collisions. The PVC with the luminescent additive invented here, as they say, might be diverted from our hands on the world market: who indeed does not understand how advantageous the accelerated maturing of any hothouse crops is. But a flexible film and not a rigid film is suitable for hothouses. Effective plasticizers are required for PVC film. They are known, but we still are not producing them in a sufficient quantity..."

A good pesticide has been created in the polymer stabilization laboratory--it is a tin compound, which is more effective by a factor of five than the foreign preparation Plektran, which is also an organotin compound. They circulated the proposal to begin production of the new material, but they heard in reply that it is absolutely impossible, as there is a shortage of tin.

Perhaps some radical solutions will be found for these problems also?

#### 6. Breaking Apart the Science of Organometallic Compounds.

Even among those who work professionally on these same organometallic compounds, many are certain that the most important is some kind of method for building them. And they still lounging about without outside help. This is still one of the prejudices which you get rid of instantaneously here. To break apart, in spite of the proverb, seems to be not at all simpler than building. If, of course, breaking apart is in vain.

The multicolored complexes which Domrachev showed me, and also many other volatile organometallic compounds, are made for a single purpose: "to understand" metal atoms in the gaseous phase by means of them, and then to break apart the molecular structure at the place needed by the previously stipulated form. This is carried out with such virtuosity, that unfortunately, it is not worth mourning about it, the construction. Even the simplest variant--the metal remains and the organic part volatilizes completely--also gives metal coatings which are regular in thickness and composition, and their strength is not always achievable by means of electroplating. Indeed, the metal is not at all mediocre, but occasionally is extraordinarily active, for example, in the role of a catalyst.

Another variant which is sought more--a ligand also is partially broken on the surface of the article. Not only metal, but also its carbide, is obtained. Or any one carbide is obtained which has strongly defined properties and composition.

Some outwardly similar apparatus exists in addition to the cryogenic synthesis apparatus in the organometallic compound technology laboratory. Ordinary ceramic tubes are loaded into it, and resistors with a very small variance in resistance--of a smaller order than usual--are removed. You do not see what takes place inside the apparatus, alas, but they explained that the tubes at

first automatically are put on a wire "shampooer," proceed through a hot zone and then another cold zone which, however, is saturated with chromium ethylbenzene complex vapors. It is converted to carbide on the hot surface--it also is a resistive layer. The productivity of the automatic device, which is small, the size of a kitchen kettle, is many thousands of articles per hour. Such kettles already exist at the plant...

This same chromium carbide, applied under other conditions to a cutting instrument prolongs its service life by a factor of several times (Still more! In hardness it exceeds only Almaz and Borazon).

Plastic products do not adhere to their coated molds, and the molds themselves, it appears, last forever. At least, those made several years ago are still not worn out.

Tubes made of ordinary steel, if chromium carbide is applied on the inside, are found to have such corrosion resistance that they "hold" boiling phosphoric acid, in which steel itself dissolves like sugar.

Ethylbenzene after decomposition of the complex, by the way, is recirculated and is recovered almost completely--not more than 10 percent of it is consumed in the formation of carbide. The ratio in the complex is sixteen atoms of hydrocarbons per atom of chromium.

And in addition, they are able to make here a carbide coating which is not homogeneous but stratified, a composite.

And in addition, titanium carbide is on the threshold (it is obtained from the same almost nonviable complex). It is even more promising for a cutting instrument.

They also are on the threshold of ceramics obtained by the same method--nitride, boride, silicide...

## 7. Culture

G.A. Abakumov:

"By the way, about complexes...KHIMIYA I ZHIZN has already written about how ortho-quinones can directly dissolve metals. In truth, this was first observed not in Moscow but here in our institute. But I won't talk about that... Quinone also dissolves copper at 70-80 degrees. And at 150-200 degrees it separates out again. I do not know that any more will come from it, but for a beginning we greased with such a copper complex a bearing in a fan which ventilates electronics in our spectrometer. Trouble had been constant with it, and every month or so, we had to reset it. Now it has already been working for three years, on some days without stopping.

"If it is taken apart, it must be this--where there is scarcely a defect, a crack--a local superheating is beginning, the complex is decomposing, it draws out its copper, volatilizes..."

Shortly after this monologue, I heard a dialogue in which Doctor of Chemical Sciences Mikhail Nikolayevich Bochkarev, deputy director of the polynuclear organometallic compounds laboratory, participated. Reproaching us, he says, for one remark in our journal concerning misgivings about whether such organometallic compounds are useful (and meanwhile they discovered very suitable catalysts among them which are active under mild conditions), he began to talk about a certain completely new polymer, the molecules of which probably resemble a round head of cheese with plenty of holes. And there was not yet complete certainty about their having such an arrangement--and Bochkarev has already argued with Abakumov (and the correspondent was involved in this) about this: for what useful purpose is it possible to arrange this very roundness and holey shape.

The correspondent listened, became involved, and himself mentally folded his hands. The Food Program--one, the decision about the connection between basic science with actual practice; two, about the speeding up of the development of machine building; three, acceleration... The human factor... In all positions these people could have, as they say, reported long before how special attention was attracted to so-called "hot" problems. What is to be said about this to the squabblers? They are not surprised and shrug their shoulders--we, they say, are headless, are we not?

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[Excerpt] Clean Zone

It is the practice for workers in a structure built two years ago to change clothes for a "shift"; it is stricter than for any other excellent worker. If you forget a briefcase behind the door with the plate "clean zone", the kind host who has volunteered to deliver it does not forget first to put on slippers, robe, and cap. It is incomprehensible if you are not accustomed constantly to "count your cards", which is almost inherent for all here at the Chemical Institute of the USSR Academy of Sciences in Gorkiy.

"And now we shall see how they analyze them," invited Aleksandr Nikolayevich Moiseyev, Party organizer, who kindly volunteered to show me around all the "clean zones".

Previously I was only able to read about much of what I was brought to see in several laboratories working with analysis and developing technology (Aleksandr Nikolayevich, by the way, is in charge of one of them). Auger spectroscopy, classical flame spectrometry, but with a preliminary treatment of the sample which permits the impurities to be "broken down" in an amount of  $10^{-9}$ , even  $10^{-10}$  mole percent, gas chromatography for research on contaminants in volatile substances...

Two methods were particularly striking: laser spectroscopy and photoelectric spectroscopy, which I in ignorance would have assumed by hearsay to be the long-known photoelectronics.

The laser was implemented in a unit built together with the Moscow Spectroscopy Institute of the USSR Academy of Sciences: a powerful (homemade)

nitrogen laser supplies two others--with rearrangeable frequencies. The frequencies are selected so that the atoms of the unknown impurity are excited resonantly (in two steps). Both beams are focused on the small window of a solid vacuum unit in which the substance is vaporized (atomized). The sensitivity is up to  $10^{-10}$  atom percent. For the first time I saw a workable instrument with two quantum excitement serving the needs of chemists.

As for photoelectric spectroscopy, however pressed you are, you do not cram it in this essay. It is a separate subject. An incredibly sensitive (theoretically up to  $10^{-15}$  atom percent, it is better still to talk simply: it can find all of 10-100 impurity atoms in a cubic millimeter of very pure semiconductor) method invented by the Soviet physicists T.M. Lifshits and F. Ya. Nad and now used abroad under the name FTIS, in Russian FTI--photothermal ionization. The Gorkians were the first in the country to outfit themselves with it--no wonder that the correspondent had not even heard about the innovation.

The original variant of FTI required contacts to be soldered to the sample. But indeed this is inevitable contamination! A no contact unit was developed here. Now it is possible to analyze not only monolithic cuts of a substance but also different powders and films.

"The method is especially valuable in that it gives information directly about those impurities which are especially undesired because they raise the electrical conductivity. We ourselves work with semiconductors, and for them this is a target characteristic," explained Senior Scientific Associate Boris Aleksandrovich Andreyev. "Here, see on the screen: distinct narrow peaks, as on an infrared spectrum (this, by the way, also is a rebuilt infrared spectrophotometer). Aluminum, gallium, boron. We now observe the first two reliably at a content of  $10^{10}$  atoms per cubic centimeter ( $10^{-10}$  atom percent), and boron--even  $10^8$  ( $10^{-12}$  atom percent). What is remarkable is that the target, engineering characteristic appears simultaneously also to be the best analytical feature. In work with ultrapure substances, this principle, it was explained, is universal: if you want to raise purity, you track the target characteristic.

"It is an astonishing enterprise; almost everyone in this place is employed in a specific task like a trade, and one philosophical truth after another is discovered..."

### 3. How Much Does a Particle Weigh?

"It is difficult to determine precisely the purity of the germanium which we obtain," noted Anatoliy Vladimirovich Gusev, scientific secretary of the institute and deputy director of the laboratory at which the substance is obtained, which today reaches ultrapurity. "The content of the most undesirable so-called electrically active impurities responsible for the concentration of the carriers of the charge is not more than  $10^{10}$  atoms/cm<sup>3</sup> ( $10^{-10}$  atom percent). There are highly sensitive methods of analysis for these impurities, which enable them to be determined at such a low level of concentrations. Estimation, however, of the other impurities is circumscribed by the limitation of the sensitivity of the methods which are used for their

determination. For some impurities it comprises  $10^{-5}$  atom percent. Therefore, we also say conservatively that the impurity content is no higher than  $10^{-5}$  atom percent. However, actually, it probably is considerably lower.

"The most promising method for obtaining germanium of such purity seemed to be the hydride method in conjunction with crystallization--zone fusion and directed crystallization from the melt.

"At such a boundary of purity, the connivances of alkalest appear even in germanium. Material for the combustion boat along which the coil of the heater for the melting zone passes unhurriedly, and even the air in the environment in which the weighed portion is prepared also become a problem."

There is one more ultrapure zone in this laboratory--a hermetic dust-free room with a sluice in which the entering stream of purified air is blown.

"What is one particle of dust? Let us estimate," proposes Anatoliy Vladimirovich. "If it is half a micron in size (such cannot be eliminated completely even in our "ultrapure"), the mass is of the order of  $10^{-12}$  g. Several dozens of such little grains can spoil slabs of germanium having a mass of 100 g."

"Is the result that you approach the limit of terrestrial potentialities?"

"Something like that, not far from it. Indeed, you cannot avoid constructional materials in the melt under terrestrial conditions. Consequently, it is not possible to exclude the contaminating action completely. The effect of impurities in a gaseous medium, the residual gases of a vacuum and a number of "terrestrial" factors also show up. Up to this time, the record of purity has been raised by one order on the average of every 5-6 years. It is not excluded that a subsequent jump will have to be completed under nonterrestrial conditions and without the presence of man, because he (man) raises dust."

Not without reverence, I looked at the plump piece of shining material covered with thick glass which was carved by the no contact method from a very pure, central zone of a slab. Dozens of particles... Even a fairy tale princess who suffered insomnia because of a pea would not notice such a trifle. The material also in reality is devilishly sensitive. Rectifiers manufactured from it in collaboration with associates of Academician G.N. Flerov, neither in susceptibility to negligible doses of ionizing radiation or in resolving power are inferior to the best world specimens. Complete satisfaction is in store for the physicists for whom these products are intended. In contrast to those previously used, it is not obligatory to store such rectifiers at the temperature of liquid nitrogen--they do not lose sensitivity even at room temperature.

It is naive, one would think, to recall this patriarchal legend in a century of cybernetics. But it is necessary for anyone who takes up the development of engineering of the new generation to begin, as lovers of Latin say, "ab ovo"--from the egg, in our day also.

From what, do you think, does the production of ultrapure silicon, germanium, and boron halides begin? From the manufacture of the highest fractionating towers made of molybdenum or "superdry" quartz glass.

They have to be surveyed on three levels. On the bottom level "cubes" are arranged in which high-boiling impurities are accumulated. The middle level, three meters high, is the basic cubes where the initial raw material product is fed according to a particular system. Somewhere, under the ceiling is that part of the structure which "drives off" and accumulates the especially volatile fraction. The final, absolutely transparent product (even boron bromide when highly purified loses its tendency to redden and decomposes under light) is collected in a receiving vessel with two stopcocks, which has been preliminarily washed with a liberal portion of the same absolutely transparent product. When approximately half of the volume is collected, the stopcocks are shut off.

How then, however, does one detach this vessel to remove it? This problem seemed insolvable.

"Only with a burner," explained Nagim Khalilovich Agliulov, deputy director of the laboratory of the technology of ultrapure substances, "We shut off the stopcocks, evacuate the tubes leading to them, and unsolder. The liquid remains like this--in the sealed ampoule with stopcocks without contact with air."

"Do not approach your technology with a wrench..."

"That is true. The apparatus is delicate. And the product remains rather expensive. We are even contemplating replacing the quartz with niobium or tantalum. These metals do not contaminate the production--and actually do not differ so very much in price from our quartz. Meanwhile, units made of them can be assembled by ordinary methods.

"Liquids recoverable with such infinite labor--in all are only the starting materials for the manufacture of ultrapure materials. The institute supplies them to many organizations. Silicon chloride, moreover, is partially required on site. 'Ultradry' quartz is made from it."

##### 5. A Fishing Rod with a Telecamera

The scale of tactlessness, which I blurted out at the exhibition by calling the bar for the light guide a "fillet", I succeeded in appraising only at the place where these bars were made. Here nonhydroxylquartz is also required--water or its radicals absorb infrared light, which leads to losses. However, this is still not all: homogeneous quartz has an index of refraction which naturally is identical in all directions, and the beam just the same will be partially "dispersed" in lateral directions. It is necessary to return it from these directions. Perhaps material is required which is not completely homogeneous, with a reflecting "thin crust" around the central core. And at the same time it is not brittle and is flexible--light guides frequently wind around your finger...

I saw a machine tool like a lathe, but with two identical synchronously rotatable heads. A quartz tube was clamped between them which was illuminated by a burner flaming from the side. The structure was placed in a glassed-in box like an exhaust hood--as they explained to me, for ventilation and removal of dust from the air. In general, by the way, I passed through all the "clean zones" without knowing how the substances they were working with there smelled--and some of them have a reputation for being extremely malodorous.

The tube installed between the heads, they explained to me further, is the only specimen, ordinarily, of commercial quartz which is accepted here. It is used only as a reactor, an external shell. Genuine quartz, however, is being grown within. A mixture of ultrapure silicon chloride with ultrapure oxygen is blown through the tube. When heated by the burner, it is converted into the dioxide and carried away by a stream of chlorine gas. The burner by sliding, and if necessary, by running along the tube, regulates the rate of the reaction.

Another regulator is the tempo of the intake of the starting materials. The program arrangement controls all these tempos, and also at the same time the inflow of gas into the burner. Moreover, at definite moments it includes the input of germanium chloride in addition to silicon chloride--in the "sandwiched pastry" installed within the tube is a glass packing with a high index of refraction which is the reflecting layer. They make two such layers alternating with pure quartz; but there are three--a minimum of losses is achieved at such a price during light transfer...

When the delivery of everything being used is completed, the program arrangement (which is sheltered beside the box of the display with the keyboard) sharply adds gas into the burner, the tube softens and collapses--and is converted into an intermediate product, and it barely congeals and is soldered into a sterile film.

It further journeys to the wire-drawing apparatus. An old-fashioned word, perhaps, also rather crude in relation to a molded electronic structure: somewhere under the ceiling of a two-story room a heater is radiating which brings the intermediate product to white incandescence, the glass gradually becomes clarified, it is stretched downwards--it is measured, annealed, and calibrated along the way... Then it is wound to the ground floor on a bobbin; it is very much like an ordinary fishline.

I say to my hosts that now, most likely, when fishing you track the take of fish directly under the water? You take such a villainous fishing line, a telecamera, to it. At least you are sorry for the fish... They smile politely: here at the confluence of the Oka with the Volga, fishing actually is held in esteem, but up to now we have not reached such refinement. But the fishing line is still not the final product. And then (also at an extremely intricate "rolling mill") a bright plastic sheath is put on. Red, blue... But now a light guide, the diameter of which the mill controls with a precision of hundredth of a millimeter, is considered to be ready.

This, however, pertains to quartz light guides, which have already become, one might say, assembly line--they are consigned according to the orders of



different organizations not one hundred versts away. And in the laboratory of Doctor of Chemical Sciences Mikhail Fedorovich Churbanov, they showed me "fishing lines" of the most different colors and shades: orange, gray as an old woman's hair, even black. The color belonged not to the sheaths but to the glasses themselves, which are manufactured from arsenic sulfide or selenide and germanium compounds. Each material has its own advantageous features. Some impinge upon the far infrared region in which quartz is not transparent, and this enables not only high, but also plain ordinary temperatures to be measured remotely; to transmit along the fiber the images for "heat sights". Others not only impinge but also promise a still lower level of losses than quartz. For example, fluoride glasses containing sodium, barium, aluminum, and rare-earth elements. Theoretically, their losses can become even lower than that of quartz by a factor of two.

"Work with these glasses requires infinite patience," Senior Science Associate Igor Vladimirovich Skripachev told me. "Each step--the synthesis of the material, its purification, and drawing--is separate, often laborious research. Hundreds of man-hours are spent for each specimen of glass suitable for drawing. And, moreover, far from every drawing is successful, indeed any experiment is a step to the new; experimental equipment, partially homemade..."

## 6. Plans

This department is well known in our country and abroad as a center for the integrated study of the problems of ultrapure substances. However, not only is scientific research being conducted here, but also the turning out of the pilot scale batches of ultrapure products.

The demand for the products of technological laboratories is especially strong, in particular for volatile halides. A consignment of germanium chloride at a price of 150,000 rubles, for example, is now ready for shipment to the German Democratic Republic. It is demonstrably complimentary, if you will: a country of highly-developed chemistry, but the substance is purchased in Gorkiy... A pilot plant is vitally necessary. There is a decision in principle to construct it, and even the means have been appropriated. But the institute simply is not putting up the plant. A third structure is being built soon here in Shcherbinka. And who does not know that such business is not done in only one such structure. The structure in which we visited has already been finished for a long time, but only now have some of the wounds finished being licked. A third building, however, is also very much needed. Technological subdivisions and the shops are accommodated in it more freely. For example, glass blowing can be carried out in more powerful hydrogen burners...

Light-weight black ceramics is like anthracite but when polished its cut is observed to be unexpectedly laminated, as if it were the structure of wood. Shaking a core on his palm, Georgiy Alekseyevich Domrochev explained:

"Silicon-carbide. It withstands 2000 degrees, and, moreover, it is not very friable. What do we make it from? From any organosilicon compound, even from waste. The fineness is not in the raw material but in the method... The

Japanese, by the way, built their famous ceramic engine from something similar. Up to now it is the only prototype they have. We have richer experience, very likely, in connection with the manufacture of materials made from organoelementary compounds.

"Perhaps we shall also try out an engine."

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CSO: 1841/0106

## CURRENT PROGRESS IN CHEMISTRY

Moscow ZHURNAL NEORGANICHESKOY KHIMII in Russian Vol 31, No 11, Nov 86  
(manuscript received 21 Apr 86) pp 2732-2739

[Article by V.A. Legasov]

[Abstract] M.V. Lomonosov was the first to anticipate the tremendous influence that physics and mathematics would exert on chemistry, and much of the progress in chemistry has confirmed his prescience. Currently, some of the most active areas of chemistry are concerned with the synthesis and production of new materials. Developments in polymer science continue at an unabated pace, but equally significant progress has been made in metal chemistry. At the present time, steel alloys are available that meet all technical requirements when alloyed with less than 10% tungsten and about 5% molybdenum. Considerable progress is being made in surface science, yet the underrepresentation of chemists in this field limits the full potential of the scientific research and practical applications of surface phenomena. Semiconductor-based sensors with sensitivities on the order of ppm, and in the case of some gases on the order of ppb, open up new vistas in analytical chemistry. Finally, the dream of alchemists is coming true in that fast neutrons may be used to transform one element into another. The full exploitation of the practical side of this development shall rest on the close cooperation of radiochemists, nuclear physicists, and engineers. Yet another area of rapid advances is represented by various forms of membrane technology, that has already found wide application in chemical engineering, biotechnology, and medicine. Figures 1; references 3 (Russian).

12172/9835  
CSO: 1841/119

NEW ORGANIC METAL-BIS(ETHYLENEDITHIO)TETRATHIAFULVALENE TETRAFLUOROBORATE:  
 (BEDT-TTF) $_2$ BF $_4$ ·CH $_3$ CN

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 11,  
 Nov 86 (manuscript received 12 Jul 85) pp 2581-2583

[Article by Ye.I. Zhilyayeva, O.N. Kroschka (deceased), R.N. Lyubovskaya,  
 R.B. Lyubovskiy, L.O. Atovmyan and M.L. Khidekel, Chernogolovka Department  
 of Institute of Chemical Physics, USSR Academy of Sciences]

[Abstract] Bis(ethylenedithio)tetrathiafulvalene was oxidized with  
 Cu(BF $_4$ ) $_2$ ·6H $_2$ O in a ratio of 1:2 in a solvent mixture of MeCN and trichloro-  
 ethane to obtain a new cation-radical salt of composition (BEDT-TTF) $_2$ BF $_4$ ·  
 MeCN (I) with a tetrahedron anion. The composition and structure were  
 established by X-ray diffraction. Crystallographic data for I are  
 a = 20.006(7) Å, b = 13.340(4), c = 7.756(4),  $\alpha$  = 70.55(3) $^\circ$ ,  $\beta$  = 112.46(3),  
 $\gamma$  = 79.12(3). The spatial group P $\bar{1}$ , V = 1681(1) Å $^3$ , M = 897.2.  $D_{calc}$  =  
 1.783 g/cm $^3$ , Z = 2, F(000) = 910. I belongs to the triclinic system.  
 A projection of the crystalline structure of I in the ab plane is given.  
 The electric conductivity of I at room temperature is ~30 (ohm cm) $^{-1}$ .  
 A relationship of relative resistance and temperature showed I to have  
 a metallic nature of conductivity to 4 $^\circ$ K. By comparison, (BEDT-TTF) $_2$ ClO $_4$   
 0.5C $_2$ H $_3$ Cl $_2$  displayed this to ~16 $^\circ$ K. By decreasing the size of the tetra-  
 hedron anion BF $_4^-$  (in comparison to ClO $_4^-$ ) and the size of the solvent  
 molecule, the metallic composition in I was stabilized to more lower  
 temperatures. Figures 2; references 11: 4 Russian, 7 Western.

12886/9835  
 CSO: 1841/145

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