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EXAMINING THE EFFECT OF NANOSILVER ON THE ANTIBACTERIAL FIRE-RETARDANT COATINGS FOR PHARMACEUTICAL ENTERPRISES (p. 4-9)

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We examined the effect of nanosilver – ionic silver, intercalated into interlaminar spaces of montmorillonite, as a biocidal additive to antibacterial fire-protection coatings for pharmaceutical enterprises.

We determined stability of intumescent coatings composed of ammonium polyphosphate/pentaerythritol/melamine/EVA/titanium oxide with additives of montmorillonite, modified with guanidine and quaternary ammonium cations as well as ions of silver in relation to mold and wood-staining fungi. It was shown that the application of a mixture of biocides – montmorillonites, modified with ions of silver and polyhexamethyleneguanidine cation, improves the class of biocidal effectiveness of coating from “not effective” to “effective”. It was established that the mixture of Ag-montmorillonite and PHMG-montmorillonite demonstrated the synergistic effect against mold and wood-staining fungi and provided the “highly effective” class of biocidal effectiveness. According to data of microbiological studies, the paint, which contains in its composition the mixture of Ag and PGMG cations, exerts a disinfectant effect in relation to gram-positive and gram-negative bacteria (including tuberculosis), as well as mold fungi.

Field fire studies of intumescent paints for wood with the additives of Na-MMT, TSTA-MMT, PHMG-MMT and Ag-MMT were conducted in line with GOST 16363. It was shown that the admixtures of nanoclays into water-based intumescent paints decrease the temperature of flue gases and transfer wood into group I of fire-retardant effectiveness.

Results of the study allow us to recommend the introduction of the mixture (PHMG-MMT+Ag-MMT) into formulations of

intumescent paints as an effective antibacterial additive. Its properties are predetermined by the suppression of proliferation of gram-positive and gram-negative bacteria, mold and wood-staining fungi.

Keywords: nanosilver, polyhexamethyleneguanidine, fire protection, montmorillonite, antibacterial coatings, intumescent compositions.

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DETERMINING A DEPENDENCE OF
THE EFFECT OF INERT ELECTROLYTE ON
A DIFFICULTLY SOLUBLE SALT
UNDER DIFFERENT CONDITIONS (p. 10-16)

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We examined the impact of various factors on the salt effect, which enhances the solubility of difficultly soluble salt, exerted by the presence of inert electrolyte that has neither common cation nor anion. It was conducted experimentally, by examining the ratios of solubility products of different salts in different solvents, as well as at different ionic strength. The goal was to select such ionic strength where the activity coefficient is minimal, that is, the enhancing effect is maximal.

It was established that such factors as dielectric permittivity of the solvent, the anion charge affect enhancing coefficients but do not affect the value of ionic strength at which the salt effect is maximal.

It was found that dielectric permittivity of the solvent has a direct impact on the multiplying factor of the “salt effect”; we also established dependence of the anion charge and the magnitude of the “salt effect”. In addition, it was influenced by the degree of bond ionicity between the cation and the anion, in other words, the difference in electronegativities according to Pauling (EN).

The obtained data are of high theoretical interest for physical chemistry, as well as for the design of new adsorbents and in other situations where it is required to improve the solubility of a difficultly soluble salt.

Keywords: activity coefficient, dissociation, generalized momentum, difficultly soluble salt, inert electrolyte, salt effect.

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STUDY OF THE INFLUENCE OF THE TEMPLATE
CONCENTRATION UNDER HOMOGENEOUS
PRECIPITATION ON THE PROPERTIES OF
Ni(OH)₂ FOR SUPERCAPACITORS (p. 17-22)

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Nickel hydroxide is widely used as an active material for hybrid supercapacitors. The most electrochemically active is α -Ni(OH)₂.

synthesized using template homogeneous precipitation. In order to achieve maximum characteristics, it was necessary to study the influence of the template concentration on structural, surface and electrochemical properties of Ni(OH)₂ samples. For this purpose, Ni(OH)₂ samples were prepared using template homogeneous precipitation, with Culminal C8564 (template) concentrations of 0 %, 0.5 %, 1 %, 2 %, 3 % and 4 %. Structural properties of the samples were studied by means of X-ray diffraction analysis, size and particle morphology – by means of Scanning Electron Microscopy, the electrochemical characteristic – galvanostatic charge-discharge cycling in the supercapacitor regime. It has been demonstrated that an increase of the template concentration to 0.2 % leads to a decrease of crystallinity and particle size. However, a further decrease of concentration leads to increase of crystallinity and aggregation of nickel hydroxide particles. The influence of the template concentration on the electrochemical properties is different for different concentration ranges. At low template concentrations (below 0.2 %), the specific capacity of the samples is almost independent of cycling current density. The optimal concentration for this range is 0.1 %, with the maximum specific capacity of 499 F/g. Nickel hydroxide prepared with 0.1 % of Culminal C8564, is recommended for use at low and medium current densities (below 80 mA/cm²). At high template concentrations (0.3–0.5 %), the specific capacity increases significantly with an increase of current density. The optimal concentration for the ranges was 0.4 %, with the maximum specific capacity of 525 F/g. Nickel hydroxide samples prepared with 0.4 % of Culminal C8564, is recommended for use in high-speed supercapacitors with high discharge current densities (120 mA/cm² and above).

Keywords: nickel hydroxide, template synthesis, homogeneous precipitation, specific capacity, supercapacitor.

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THE RHEOLOGICAL ANOMALY IN WATER-SILICATE SYSTEMS: A POSSIBLE THERMODYNAMIC EXPLANATION (p.23-28)

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A rheological anomaly, consisting in the reversible increase in solution viscosity with increasing temperature, is a typical property of aqueous solutions of aminosilicates (polysilicates of aliphatic amines, amino alcohols and other amino compounds). To explain this anomaly, a simple mathematical model of interrelated acid-base and polycondensation equilibria in such solutions is proposed. The proposed calculation model assumes a direct dependence of the solution viscosity on the polymerization degree of silicate anions, as well as the indepen-

dence of the dissociation constant of silanols and the polycondensation equilibrium constant on the degree of anions polymerization.

Based on the assumptions made, a system of eight linear and nonlinear equations was constructed and solved. The results of calculations performed for concentrated solutions of aminosilicates (methylamine and piperidine silicates), as well as sodium and tetramethylammonium silicates, confirm the presence of a positive temperature dependence of the polymerization degree of silicate anions in the aminosilicate solutions, in contrast to the solutions of silicates of the strong bases. Thus, the proposed mathematical model of polymerization-hydrolysis equilibria in aqueous silicate solutions qualitatively explains the existence of the rheological anomaly in aqueous solutions of aminosilicates and its absence in solutions of alkali silicates and silicates of quaternary ammonium bases. In addition, this model correctly reproduces the displacements of the molecular mass distribution of silicate anions with changes in chemical composition and concentration of solutions.

The proposed approach makes it possible to clarify the mechanism of the rheological anomaly, to understand the roles of various thermodynamic factors in its occurrence, and, as a consequence, to conduct a more meaningful search for new silicate and non-silicate systems with the same anomaly.

Keywords: soluble silicates, silicates of amines, aqueous solutions, anomalous rheology, thermogelation, polycondensation.

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RESEARCH INTO METHANE OXIDATION ON OXIDE CATALYST OF THE APPLIED TYPE (p. 29-34)

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Technical characteristics and activity of oxide catalyst, applied on fibers ALSIFLEX-KT1600, were studied. As a catalytic contact, we used spinel (% by weight): Al_2O_3 – 10; MgO – 3; $(\text{Cr}_2\text{O}_3+\text{NiO})$ – 0.4.

As a result of conducted studies, the structure of the carrier and the catalyst were studied, anisotropy of properties was established, and technical characteristics were determined: density of the catalyst, which made up 0.3 g/m^3 , 90.4 % porosity, hydrodynamic resistance of the catalyst's layer at different voluminous loads, and specific surface area. Catalyst activity was studied at complete methane oxidation. Activation energy E_a made up 86.241 kJ/mol, while temperature of complete methane conversion amounted to 800 °C and that of 50 % conversion made up 550 °C. Macrokinetic equation of the rate of complete methane oxidation for this catalyst was obtained. Research results proved high activity of the catalyst, resistant to exposure to high temperatures (1000–1200 °C) and volumetric loading ($\tau=0.03$ –0.05 s).

The obtained results indicate relevance of the use of the developed catalyst for catalytically stabilized combustion of hydrocarbon fuels with improved performance, technological and environmental characteristics.

Keywords: catalyst, metal oxides, mineral fiber, methane oxidation, specific surface area.

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ANALYSIS OF PLASTICIZER EFFECTIVENESS DURING ALKALINE CEMENT STRUCTURE FORMATION (p. 35-41)

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The problem of plasticization of alkaline cements was analyzed and the ways of its solution were offered. The problem is related to the structural instability of a number of chemical admixtures that are effective in plasticisation of clinker cements in the highly alkaline media of hardening cement. Superplasticizers based on polyesters lose their steric effect due to the hydrolysis reaction. On the other hand, selectivity of action of chemical admixtures is associated with the changes in a wide range of compositions of alkaline cements. In addition, the degree of changes in the structure of admixtures depends not only on the medium pH but also on the nature of the alkaline component, the production process and use of such cements. Generalization of the problems made it possible to proceed with the expansion of the range of substances from the class of surface active substances (SAS), their experimental verification and the application proposal for plasticization of alkaline cements. As plasticizing SAS characterized by stability of molecular structure in alkaline media, low- and high-molecular compounds from the class of acyclic (aliphatic) compounds or fatty compounds were considered. The polyester-based superplasticizers traditionally applied in plasticization of calcium cement systems were used for comparison. Variation of the nature and ratio of components in the composition of alkaline cements as well as the chemical admixture nature were taken as the main factors in the study of features of cement plasticization. Comparative evaluation of effectiveness of these admixtures indicates selectivity of use taking into account composition of alkaline cements. As a result of this research, systematization of classes of chemical compounds according to their effectiveness as plasticizers for alkaline cements was proposed. Such a systematization can be used in development of commercial products in a form of plasticizing additives for concretes and mortars.

Keywords: alkaline cement, chemical admixture, surfactant, granulated blast furnace slag, cement paste, plastic strength.

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EXAMINING THE EFFECT OF ELECTROSYNTHESIS CONDITIONS ON THE Ni-P ALLOY COMPOSITION
(p. 41-46)

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The Ni–P alloys are widely used as catalysts, magnetic and wear resistant materials. Properties of the nickel-phosphorous alloys are defined by the composition. A highly regulated technique to obtain the alloys with specified composition is the electrosynthesis. It is a relevant task to establish dependences of the alloy composition on the process conditions. In the present work we examined the influence of electrolysis parameters on the Ni–P alloy composition, obtained from the methanesulfonate and sulfate electrolytes. It is shown that an increase in the concentration of sodium hypophosphite, acidity and temperature of the electrolyte increases phosphorus content in the alloy. It was established that when carrying out the electrosynthesis under galvanostatic mode, a change in the alloy composition is predetermined by the rate of phosphorus formation. Atomic phosphorus is formed as a result of the course of two reactions. There occurs the electroreduction and disproportionation of hypophosphite-anion involving hydrogen ions. An increase in the concentration of hydrogen ions in the near-electrode layer contributes to an increase in the rate of phosphorus formation and growing phosphorus content in the alloy. That is why the alloys with a higher content of phosphorus are formed at lower pH indices of the electrolyte and at higher temperature. It was established that weak buffer properties of the methanesulfonate electrolyte are responsible for the lowered phosphorus content in the synthesized alloy. High pH index in the near-electrode layer reduces the rate of phosphorus formation. Established regularities might prove very useful when designing new technologies of the Ni–P alloy electrosynthesis of specified composition from the methanesulfonate electrolyte.

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Keywords: electrosynthesis, Ni–P alloy, methanesulfonate electrolyte, buffer properties, phosphorus formation.

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EFFECT OF CALCIUM AND MAGNESIUM OXIDES ON THE PROPERTIES OF EXPANDING CEMENTS AND PLUGGING MORTARS (p. 47-52)

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Plugging expanding cements ensure a better quality of insulation of productive oil and gas-containing layers from aquifers. We examined the effect of additives in the oxide form of expansion on

the physical-mechanical properties of cements and plugging mortars. It was established that the introduction of calcium oxide and magnesium oxide additives in the amount of 20 % by weight leads to an increase, respectively, by 20–40 % and 12–36 % in cement water consumption, and reduces by 20–32 % and 52–64 % strength of the cements with additives in comparison with additive-free cement. It should be noted that the introduction of a magnesium oxide additive results in a more significant reduction of cement strength (by 40–47 %) and plugging mortars strength (by 29–44 %) in comparison with the samples with a calcium oxide additive.

Cements and plugging mortars with a calcium oxide additive yield a much greater increase (by almost three times) in the dimensions of samples than a magnesium oxide additive. The negative impact of magnesium oxide on the strength of cements and plugging mortars can be explained by the features of hydration products of this additive. Magnesium hydroxide is formed in the form of fibers and flakes and it does not consequently participate in the formation of crystalline structure of cement stone. At the same time, calcium hydroxide can, in the process of hydration, form calcium hydrosilicates and portlandite, which somewhat reduces the negative effect of this additive on the strength of cements and plugging mortars.

In addition, with an increase in temperature, based on data from electron microscopic analysis, there occurs the formation of a larger mass of magnesium hydroxide due to the formation of smaller fibers instead of the large lamellar ones. The total weight of new formations increases – the expansion of the hardening mass of the plugging mortar also grows. However, these new formations of magnesium hydroxide do not possess strength and, in general, cement stone essentially loses strength compared to the cement stone with a calcium oxide additive. This confirms inappropriateness of using magnesium oxide as the additive in the production of expanding plugging cements.

Keywords: oxide expansion, cement, expanding plugging mortar, physical-mechanical properties, microstructure.

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POLYELECTROLYTE EFFECT ON SPECTROPHOTOMETRIC DETERMINATION AND INTERACTION OF SCANDIUM (III) WITH ERIOCHROMCYANINE (p. 53-58)

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The influence of cationic water-soluble polyelectrolyte PSPMG on the interaction of scandium (III) with organic reagent eriochromcyanine is studied. Because the study of the possibility of obtaining new, more effective, modified reagents with a complex of better analytical characteristics is an actual analytical task.

The optimal conditions of complex formation were experimentally determined: the pH range (5.5–6.5), the order of the adding of the components (1 – scandium, 2 – ECR, 3 – PSPMG, 4 – buffer solutions), the composition of the Sc-ECR-PSPMG complex (1:4:1) were experimentally determined and the molar absorption coefficient – $1.8 \cdot 10^5$ was calculated. A sensitive spectrophotometric method for scandium determination in solutions at the level of 10^{-7} mol/L was developed.

The optimal scandium sorption parameters in the form of three-component systems Sc-OR-modifier on solid-state carriers were established, scandium sorption isotherms were constructed, sorption parameters of A_{gran} and K_{ads} were calculated. The test systems for the identification of scandium as ternary compounds in polyurethane foam and cotton were proposed, calibration curves in the concentration range from $1 \cdot 10^{-6}$ – $1 \cdot 10^{-5}$ mol/L were built and the colorimetric method of identification of scandium in solutions that accelerate analysis was proposed.

It is shown that the PSPMG application is a promising direction for improvement of chemical-analytical characteristics of organic reagents (eriochromcyanine and chromazurol S) because its usage increases the sensitivity and selectivity of the spectrophotometric determination of scandium in the form of a complex Sc-OR-PSPMG.

Keywords: scandium, eriochromcyanine, polyelectrolyte, test method, surfactant, spectrophotometric technique.

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STUDY INTO THE INFLUENCE OF CONCENTRATION OF IONS OF CHLORINE AND TEMPERATURE OF CIRCULATING WATER ON THE CORROSION STABILITY OF CARBON STEEL AND CAST IRON (p. 59-64)

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The impact of the chloride ions concentration and the temperature of the circulating water on the process of corrosion destruction of carbon steel and cast iron has been investigated. It has been shown that an increase in the concentration of chloride ions causes a shift in the values of the stationary potentials of steel and cast iron to the region of negative values and reduces the passive state of these alloys. This leads to an increase in the corrosion rate of St. 3 steel and CI 18-36 cast iron. The results of electrochemical studies have shown that the more reliable protective films are formed on steel than on cast iron. The limiting concentration of NaCl, at which reliable operation of equipment made from these alloys is possible, depends on the pH of the solution. At pH=7, it is about 1.2 g l⁻¹, which is about an order of magnitude less than at pH=12. When the circulating water temperature rises, the corrosion rate of steel and cast iron increases. The stationary potentials of steel and cast iron are shifted to the negative range, and the polarization of the anode process decreases. Corrosion process is limited by the rate of oxygen supply to the cathode areas

Keywords: circulating water, corrosion process, chloride ions, passivity, polarization dependence, pitting, oxide-hydroxide films.

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