ABSTRACT AND REFERENCES

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DEVELOPMENT OF CHEMICAL METHODS FOR INDIVIDUAL DECONTAMINATION OF ORGANOPHOSPHORUS COMPOUNDS (p. 6–14)

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The methods of individual decontamination of organophosphorus esters of paralytic action were studied using the decontamination of paraoxon (O, O-diethyl-O-4-nitrophenylphosphate) and methyl parathion (O, O-dimethyl-O-4-nitrophenylthiophosphate) from solid surfaces (metal, fabric, plastic) as an example. The mixtures of urea hydrogen peroxide, boric acid, cetylpyridinium chloride and montmorillonite nanoclay as decontamination systems were studied. The study showed that application of the micellar system together with nanoclays significantly increases a degree of adsorption of substrates from an infected surface. At the same time, the presence of an activator (boric acid) in systems with urea hydrogen peroxide contributes to an increase in the reaction rate in micellar medium by almost 20 times comparing with systems without activation.

It was established that the studied micellar systems preserved the supernucleophilicity of HOO^--anion in relation to electrophilic substrates – paraoxon and methyl parathion. It was concluded that the presence of montmorillonite (sodium- and organomodified ones) increased the magnitude of α effect, both in systems with urea hydrogen peroxide only and in systems with boric acid activator.

The effect of the acceleration of decomposition of organophosphorus substrates in micellar medium by montmorillonite derivatives was established. This fact could be used for the design of «green» decontamination systems of fast action.

An analysis of data on the rate of deactivation of paraoxon and methylparathion on solid surfaces in the studied micellar decontamination systems made it possible to choose the system based on urea hydrogen peroxide, boric acid, cetyl pyridinium chloride and organomodified montmorillonite as the optimal system.

A comparison was performed of the periods of half-lives of paraoxon and methylparathion in the studied micellar systems with the known, and applied in NATO subdivisions, decontamination systems. It was concluded that the rates of decontamination in the proposed systems are higher or not less than the rates in the known systems. At the same time, the proposed systems based on solid source of hydrogen peroxide have advantages in terms of environmental safety, manufacturability, and stability.

The parameters of the decontamination rate and the degree of decomposition of paraoxon and methyl parathion gives us possibility to recommend the micellar systems as promising for individual deactivation of organophosphorus compounds.

The development of fast-acting decontamination formulations, which are mild in their effects on a human body and are environmentally friendly, is a necessary and urgent task among a number of technological solutions for neutralization of toxic organophosphorus substrates, such as pesticides, chemical weapons components and active pharmaceutical ingredients.

Keywords: decontamination system, hydrogen peroxide, carbamide peroxysolvate, paraoxon, methyl parathion, peroxoborate, deactivation, organophosphorus compounds.

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FEATURES OF COMPLEX FORMATION OF A FIBROUS COMPLEXITE WITH NICKEL IONS IN WATER–DIOXANE MIXTURES (p. 15–22)

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The study deals with the complex-forming properties of a fibrous complexing agent (complexite) NAG with respect to nickel(II) ions in a mixed solvent water-1,4-dioxane. Spectral tests indicate that the absorption of nickel(II) ions by the NAG fibrous complexer occurs according to the mechanism of complexation. The factors affecting the complex formation of the NAG complexite with nickel(II) ions in water-1,4-dioxane mixtures are established, and the stability constants of hydroxamic and amidoxime groups are calculated depending on the pH values of the medium and the composition of the solvent.

The influence of the solvation parameter on the composition and stability of the complexes under study with nickel(II) ions has been established. The solvation characteristics of the NAG complexite and complexes with nickel(II) ions depend on the nature of the mixed solvent in which the complexation reaction takes place. The solvation effects in the water-1,4-dioxane mixture with a molar fraction of dioxane of 0.00–0.17 level the stability of the resulting complexes.

It is shown that the pH range of 6.2–3.8 mixed solvent creates the conditions for the formation of a wider composition and structure of the range of coordination units with different proportions of their content in the polymer. Apart from the hydroxamic, deprotonated amidoxime groups take part in the complexation. The preferred fixation of functional groups on the surface of NAG fibres leads to a high local concentration of the reaction centres and enhances the cooperativeness of the process, facilitating easy orientation of the groups during the formation of mixed-ligand coordination nodes. The stability constants of the deprotonated amidoxime groups of the the NAG complexite with nickel(II) ions are estimated. The study has proved dependence on the composition of the solvent.

Keywords: polyacrylonitrile fibre, complexation, solvation, stability constants, water-1,4-dioxane.

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INFLUENCE OF PLASTICIZERS ON FIRE RETARDING PROPERTIES OF CARBON FOAMS OF INTUMESCENT COATINGS (p. 22–28)

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The studies were conducted using the triple intumescent system based on Exolit AP 740 F, which is a synergetic system based on ammonium polyphosphate with the addition of nitrogen-containing compounds. Styrene-acrylic polymer was used as a binder, titanium dioxide acted as a pigment. Plasticizers in the study were selected to assess the influence of their molecular weight on the structure of the foams. Dibutyl phthalate and polybutene oligomers, such as Indopol H 1200, Indopol H 6000 and Indopol H 18000 were selected as plasticizers.

The results were presented in the form of images from electronic microscopy, the time of reaching critical temperatures during testing with the help of Bunsen burner, coefficients of expansion factor of the composition, as well as the diagrams of thermo-gravimetric analysis.

The influence of plasticizers on the porous structure of fire resistance of carbon foams of intumescent coatings was established. Using polybutene aliphatic materials as an example, the temperature intervals of the thermo-oxidative destruction of plasticizers were determined, the dependence of their stability during thermal treatment on the value of molecular weight was established. It was shown that the use of plasticizers of different molecular weight enables the change of dimensions of cells of foams by decreasing the indicator of yield limit of the melt, which leads to an increase in the dimensions of these cells. At an increase in molecular weight, the ability of the plasticizer to form associative structures increases, which increases the yield limit of the melt and decreases the value of the average diameter of the foam cells, as well as to change the character of forming formation of contractional cracks in the structure. It was found that the indicator of fire resistance of coatings depends on the type and molecular weight of the used plasticizers. The dependence of fire resistance on molecular weight of the plasticizer for the studied intumescent system based on styrene-acrylic polymer was detected.

The results of this research can be used when developing the formulations of fire protective intumescent systems.

Keywords: intumescent coating, carbon foam, plasticizer, thermal insulation, carbon layer structure, fire protection.

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CONSTRUCTION AND INVESTIGATION OF THE COMPUTER MODEL OF DISTRIBUTION OF THE COMPOSITION OF PRODUCTS FROM EQUILIBRIUM CONDENSATION TELOMOMERIZATION (p. 28–35)

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Based on the mechanism of the course of polycondensation, we have built a scheme of reaction for the equilibrium condensation telomerization as a polycondensation process whose chain is disrupted by a monofunctional telogen chain. Given this scheme, we constructed the material balance equations for structural elements, which include an infinite number of terms. If a Flory principle about equal reactivity of terminal groups is fulfilled, the infinite sums represent geometric progressions with the same denominator. This makes it possible to collapse the process model into a closed system of four non-linear algebraic equations.

Our research into properties of the model that involved mathematical analysis and computer experiments has established the following:

– the distribution of telomerization products is a superposition of geometric distributions of base structural components with the same denominator of progression, but different magnitudes of starting concentrations. A Flory distribution for homopolycondensation can be considered as a special case of this distribution;

– the system of model's equations can have up to 4 real roots. At a single solution to the system with a random selection of initial approximation, ~74 % of cases yield a false positive root. To verify the validity of the root, we have developed a criterion based on the magnitude of denominator in a converging geometric progression, and proposed a procedure of computer solution to the system, making it possible to find the true root;

– the model has been found to demonstrate regularities in the influence of reactants concentration on the composition of an equilibrium mixture at a constant concentration of the low-molecular by-side product of condensation. It is shown that when this concentration tends to zero the composition ceases to depend on the values for equilibrium constants.

The constructed model makes it possible to calculate a composition of the equilibrium mixture of oligomers depending on the ratio of monomer concentrations, telogen, and a low-molecular condensation product. That makes it useful in practice for preliminary quantifying the composition of equilibrium mixtures of oligomers when planning syntheses using a method of condensation telomerization.

Keywords: equilibrium condensation telomerization, nonlinear algebraic equations, computer simulation, composition of oligomers.

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INFLUENCE OF THE CaO-CONTAINING MODIFIERS ON THE PROPERTIES OF ALKALINE ALYUMOSILICATE BINDERS (p. 36–42)

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The basis for ensuring the resistance of artificial stone based on alkaline aluminosilicate binders to variable environmental conditions is the formation of zeolite- and mica-like hydrate neo-formations.

It is possible to control the structure forming processes and, as a result, the operational properties of alkaline hydro aluminum silicates using the variation of the ratio of basic oxides of the binder, dispersiveness of particles and hardening conditions. It was noted that in order to obtain high operational characteristics of a stone based on alkali aluminosilicate binders, there is a need for elevated temperature of their hardening.

The research shows that it is possible to ensure water resistance of artificial stone at hardening under normal conditions at the expense of the modification of the binder by Ca-containing additives.

The influence of CaO-containing modifiers of different phase composition on physical and mechanical properties of artificial stone based on alkali aluminosilicate binders was explored. Ensuring water resistance of artificial stone at its hardening under conditions of normal temperatures was proved by experimental research and its phase composition was studied. The kind and the optimal amount of CaO-containing modifiers to provide for operational properties of artificial stone were determined. The use of CaO-containing modifiers of alkaline aluminosilicate binders ensures the acceleration of their structure formation and contributes to an increase in water resistance and strength under normal conditions.

The influence of CaO-containing modifiers of various morphological type on physical and mechanical properties of artificial stone based on alkaline aluminosilicate binders was studied. It was established that on day 28 of hardening at ambient temperature of 20±2 °C regardless of the type of introduction of Ca-containing modifiers, artificial stone is characterized by strength at compression from 14.2 to 42.8 MPa with a coefficient of water resistance from 0.81 to 1.05 due to the formation in combustion products of the mixture of high- and low-base calcium hydro silicates and zeolite-like neo-formations of the hybrid type – calcium-sodium hydroaluminosilicates with an insignificant content of Na- and K-heulandite. It was shown that water resistance of artificial stone in the early periods of hardening at ambient temperature of 20±2 °C is ensured due to the formation in hydration products of the binder of high- and low-base calcium hydro silicates, formed due to hydration of Portland cement, ground slag and slaked lime. It is possible to accelerate the kinetics of strength gaining with ensuring the water resistance of artificial stone using liquid glass with silicate module of 2.0–2.6 and lime content in the amount of 2.0–3.0 % percent of the weight of alkaline aluminosilicate binder as an alkaline component. It was noted that hydraulic activity of Ca-containing modifiers decreases in the series Slag>$Ca(OH)_2$>$CaCO_3$>Portland cement>Alumina cement.

Keywords: alkaline aluminosilicate, CaO-containing modifier, artificial stone, phase composition, structure formation.

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ESTIMATION OF THE EFFECT OF TEMPERATURE, THE CONCENTRATION OF OXYGEN AND CATALYSTS ON THE OXIDATION OF THE THERMOANTHRACITE CARBON MATERIAL (p. 43–50)

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The effect of temperature, oxygen concentration and gas-air mixture flow rate on the oxidation efficiency of thermoanthracite carbon granular material with the formation of carbon monoxide and dioxide is considered. The modeled installation implies heating of the carbon material sample in a heat chamber with constant passing of the gas-air mixture obtained by adjusting the supply of air and carbon dioxide through the heating zone. The temperature range was 20–850 °C.

It is found that noticeable oxidation of carbon material in a heat chamber during purging of gas-air mixtures with an oxygen content of 8–21 % begins at temperatures above 500 °C, and significant concentrations of carbon monoxide are formed at temperatures of 600–800 °C. It is determined that, at an oxygen concentration of 14 %, the content of carbon monoxide in flue gases is minimal in the chosen range of oxygen concentrations of 8–21 %.

It is shown that the use of the gas mixture saturated with water vapor increases the efficiency of carbon monoxide reoxidation at temperatures of 650–850 °C, but when using the manganese catalyst, the catalytic effect of water vapor is not observed.

The use of the manganese catalyst applied as microcrystals on the carbon material surface is proposed, which provides a significant reduction of CO concentrations at temperatures of 500–850 °C. The disadvantage of the process is a 1.6–2.0 times increase in carbon material losses due to the acceleration of coal oxidation to CO and CO_2.

The possibility to create certain conditions for the technological process of oxidation of thermoanthracite carbon granular material at enterprises to provide a reduction of the carbon monoxide content in oxidation products is presented.

Keywords: carbon monoxide, flue gases, thermoanthracite charge, graphitization, carbon material, manganese dioxide, oxidation, environmental catalysis.

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EFFECT OF STEP HEAT TREATMENT MODES ON THE PHYSICAL-MECHANICAL PROPERTIES OF CONCRETE (p. 51–57)

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Heat treatment of waterproof heavy concrete samples using heated air in step modes is carried out. It is indicated that these experiments are an integral part of the research of the method of heat treatment of concrete and reinforced concrete products using the air heated in a solar energy collector (the products are in closed forms). It is noted that on cloudy days and in the cold period of the year, an electric heater is used.

It is emphasized that in certain cases, the time of intermittent clouds during the day will be relatively short, and it can be assumed that under such conditions the decrease in concrete hardening intensity due to the break in the heated air flow to the chamber will be negligible.

It is indicated that simulation of the air heating process in the solar energy collector is carried out using an infrared heater.

It is determined that the investigated step modes of heat treatment of heavy concrete with heated air give an opportunity to increase the compressive strength of concrete 1.59...1.76 times compared with hardening in air conditions. It is shown that the higher the heating intensity of the concrete of the studied composition during the first hour of heat treatment (in the range from 4 to 8 °C), the greater the concrete compressive strength at 1 day.

It is recommended not to use an electric air heater for the purpose of energy saving in the warm period of the year in conditions of intermittent clouds.

It is found that in the investigated cases, concrete temperature after heat treatment in step modes after 4 hours 15 minutes was 30 °C, and concrete temperature after 22 hours of hardening in the chamber was 26.3...27.2 °C. It is specified that this concrete temperature at the end of hardening in the chamber indicates that relatively intensive hydration of cement occurs. It is recommended for similar cases to analyze the expediency of extending the period of concrete thermosetting in the chamber.

Keywords: heavy concrete, solar heat treatment, heated air, step modes, compressive strength.

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INVESTIGATION OF CHARACTERISTICS OF DOUBLE Ni–Co AND TERNARY Ni–Co–Al LAYERED HYDROXIDES FOR SUPERCAPACITOR APPLICATION (p. 58–66)

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Nickel hydroxides are widely used as the active material in supercapacitors. To improvise electrochemical activity, activators, namely Co and Al compounds, are introduced into the structure of nickel hydroxide. The most effective is the introduction of activators directly into the structure of nickel hydroxide. Characteristics of double Ni–Co (Ni:Co=8:1) and triple Ni–Co–Al (Ni:Co:Al=8:1:2) hydroxides, synthesized by single-stage reverse titration method were studied. Crystal structure of the samples was studied by means of X-ray diffraction analysis, thermogravimetry and differential scanning calorimetry, electrochemical characteristics were studied by means of cyclic voltammetry and galvanostatic charge-discharge cyclic in supercapacitor regime. Comparative analysis of characteristics of double

Ni–Co and triple Ni–Co–Al hydroxide was conducted. By means of XRD analysis, thermogravimetry, and differential scanning calorimetry it was found that Ni–Co–Al is layered triple hydroxide with the structure of α-$Ni(OH)_2$ with high crystallinity. Ni-Co hydroxide is double Ni–Co hydroxide with the crystal lattice of β-$Ni(OH)_2$, in which part of Ni^{2+} is isostructurally substituted by Co^{2+}, and low crystallinity. By means of cyclic voltammetry and galvanostatic charge-discharge cycling, high electrochemical activity of Ni–Co hydroxide was found. By means of cyclic voltammetry, an abnormal, α-like behavior of Ni–Co with β-$Ni(OH)_2$ lattice was found. The electrochemical activity of triple Ni–Co–Al hydroxide was found to be significantly lower than that of double Ni–Co hydroxide (maximum specific capacities are 550.4 F/g and 741.5 F/g, respectively), despite the structure of pure layered double hydroxide and presence of two activators. A hypothesis was proposed on the poisoning of Ni–Co–Al LTH with free aluminum compounds during reverse titration synthesis.

Keywords: double Ni–Co hydroxide, triple Ni–Co–Al hydroxide, layered triple hydroxide, specific capacity, supercapacitor.

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