

CHEMICAL PROBLEMS OF THE DEVELOPMENT OF NEW MATERIALS AND TECHNOLOGIES

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**A. I. Lesnikovich,
S. A. Vorobyova**

**PREPARATION AND INVESTIGATION
OF THE HETEROGENEOUS SYSTEMS, CONTAINING HIGHLY
DISPERSED COMPONENTS**

The investigations of the structural and sorption properties of inorganic substances were began under the direction of N.F.Ermolenko at the chair of the inorganic chemistry of the Belarusian State University and then were successfully developed under the supervision of V.V.Sviridov at the chair of the inorganic chemistry of the Belarusian State University and in the Research Institute for Physical & Chemical Problem of the Belarusian State University. These investigations were transformed into the fundamental and applied works, corresponding of the present-day requirements later on. The preparation of the highly dispersed inorganic substances and composite materials, containing ones, was the reference direction of these investigations.

The retrospective analysis of the results obtained under investigation of the heterogeneous systems, containing highly dispersed components, testifies that there were three main lines of investigations, which were developed in the laboratory of the highly temperature reactions of the Research Institute for Physical & Chemical Problems. They are the preparation and investigation of the highly dispersed governors of the rocket propellant burning rate, the development of the novel civil materials based on highly dispersed components and interphase synthesis of the metals, hydroxides and salts nanoparticles.

**1. HIGHLY DISPERSED GOVERNORS OF THE ROCKET
PROPELLANT BURNING RATE**

The preparation and investigation of the highly effective governors of the composite rocket propellant's burning rate was the priority direction of the explorations which were performed in the laboratory of the highly temperature reactions beginning in 1972. These investigations were carried out over thirty years and several effective catalysts and inhibitors were developed. It should be noted that there is at least two chemical techniques to prepare highly effective governors of the composite rocket propellants burning rate. They are the synthesis of the new chemical compounds and the modification of the known governors. The correlation between the parameters of the burning rate law $U = \beta p^{\nu}$ were established by analyzing of the published data [1]. Using this correlation, the limits of the

burning rate regulation at given limits of the pressure index v were determined [2]. Taking into account these results it has been concluded that the first of the above-mentioned techniques and search for «supergovernors» have no reliable basis for solution. The second approach is more justified. It was proposed to obtain highest possible effect of the known governors at the smallest contents of ones. To investigate the capabilities of the known governor's modification the investigation of the influence of the physical state of governors on their activity were started in 1974. In this case, by physical state of governors were meant the aggregative state of the governors, their shape and size, the form of their localization in propellant and in combustion zone.

The film, colloidal and fiber catalysts and inhibitors were prepared to study the effect of the physical state of activators on the combustion of composite rocket propellants [3–5].

The film catalysts were prepared by pyrolysis of the metal's acetylacetonates over an ammonium perchlorate. As a result, both individual and mixed ferrous, copper, chromium and cobalt oxides were deposited on the surface of the ammonium perchlorate particles. It was found that the catalytic activity of the film catalysts is distinct from that of the powder catalysts. At the same time, the activity of the film catalysts is determined by their chemical composition, concentration and structure. Detailed investigation of the film catalysts and combustion of the rocket propellant containing them shows that the square of the triple contact of the oxidizer, catalyst and binder is a condition of the high catalytic efficiency. Using iron- and chromium-containing catalysts, it was shown that, in some cases, changes in the degree of dispersion of the catalytic additives and the character of their localization in propellants influence their effectiveness at small concentrations (up to 0.5 %) of the additive in the propellant. Some aspects of the mechanism of the catalytic combustion of the ammonium perchlorate rocket propellants were studied using film and colloidal catalysts. It was found that the condensed phase is the site of the action of chromium-containing catalysts. In contrast, the gas phase is the site of the action of ferrous-containing catalysts.

The effect of inhibitors added as powders and as colloidal solutions to propellants on the combustion of ammonium perchlorate composite rocket propellants was also investigated. The study performed shows that conversion of inhibitors of composite rocket propellant combustion into an ultradisperse state increases the effectiveness of the governors and decreases their concentration in the propellant, provided that particle aggregation is prevented in the synthesis of the governors and during preparation of the propellant. Practical implementation of the method involves preparation of colloidal dispersions in the binder plasticizers. Some variants of ultradisperse governors are also possible. In particular, we established that the removal of the dispersion medium without destruction of the surfactant layer on the surface of colloidal particles produces ultradisperse powders that are not worse in activity than colloidal solutions. This is due to the fact that, since such powders are lyophilic to binder components, dispersion of them in a propellant leads to almost the same particle distribution in the propellant as with addition of colloidal solutions. One factor responsible for the high activity of the additives studied, namely their disaggregated state in propellants, is rather obvious and is confirmed by the experimental data. However, this factor, related to an increase in the particle surface, which has a significant effect on combustion processes,

is not the sole one. Actually, there is a stronger exponential dependence, which can be regarded as evidence for the «pure» dimensional effect related to the change in the reactivity of the additive in the ultradisperse state. As is known, for solids in this state, many properties including lattice parameters, position of the Fermi level, presence of defects, specific excess internal energy, melting point, thermodynamic potential change significantly.

Thus, it is concluded that some deterioration of the physico-mechanical properties of propellants upon addition of heterogeneous governors of the burning rate is compensated by the decrease in their concentration in the propellant due to the high effectiveness of colloidal governors of the burning rate.

To introduce the highly dispersed catalysts in the gas phase of the burning rocket propellant and to activate the gas phase reactions, the carbon and graphite fibers prepared in collaboration with the scientists of the Institute of Inorganic Chemistry of National Academy of Science of Belarus were used. The carbon and graphite fibers as known don't burn in the fire of the ammonium perchlorate propellants. As a result, the propellants having extremal high burning rates were produced. It was shown that this result is a combined effect of the catalysis of the gas phase reactions, thermal conductivity and gas-permeability of the propellant's charge.

The results obtained under investigation the composite propellants are covered more than 20 patents.

2. NOVEL CIVIL MATERIALS BASED ON HIGHLY DISPERSED COMPONENTS

The knowledge and experience acquired under development and investigation of the highly dispersed catalysts and inhibitors of the composite rocket propellants were successfully used to develop the novel civil materials.

X-ray contrast neutron capturing ferromagnetic liquid was developed in collaboration with Research Institute for Medical Radiology (Obninsk, Russia) [6, 7]. This liquid can be transfer and confine under the magnetic field. As a result, it can be admitted in the easily accessible detail's cavity for flaw detection of their walls and in internal human organs for medical treatment of the malignant formations. X-Ray contrast neutron capturing ferromagnetic liquids can be used for neutron capturing therapy under X-ray control. In this case, the common irradiation of human is decreased as a result of the source localization in the area of tumor. The degree of the X-ray contrast neutron capturing ferromagnetic liquids is 95 % as related to barium sulphate and miodil that are traditionally used as X-ray contrast reagents.

The magnetic abrasive materials were developed in collaboration with Physical & Technical Institute of National Academy of Science of Belarus. These materials were prepared by surface modification of the known abrasive components. The titanium or silicon carbides were used as abrasive components. To give the magnetic properties, the abrasive components were modified with ferromagnetic fluids. It was found that obtained material has highly magnetic, cutting and abrasive properties [8].

Using the ferromagnetic liquids, the non-ignitable nylon-6 was obtained [9, 10]. Combustion studies showed that ferric/ferrous oxides are synergistic with red phosphorus. Nylon 6 formulations containing red phosphorus coated by colloidal Fe_3O_4 release phosphine 4.5 times more slowly than formulations containing plain red phosphorus.

The magnetic sorbents for the purification of the waste water of the industrial enterprises were developed and investigated. It was shown that magnetic sorbents make it possible to clean the water from the different pollutant. In addition the time of the purification is reduced and the bulk of the deposit is decreased as compared to the conventional precipitation technique.

The antifriction and antiwear additives to the mineral oils were elaborated with participation of the Ministry of Transport and Communications of Belarus. As known [11], using the powder metals and some their compounds as the additive to the mineral oils and lubricants the friction and wear of the rubbing elements can be decreased. To prepare these additives, the physical methods are traditionally used. In contrast to the physical methods of the additives preparation, we have used the chemical deposition to prepare ones. At the first stage the metal or oxide particles are precipitated. Then obtained particles are stabilized by surfactant. As is obvious, the chemical technique has the advantage over the physical methods. Firstly, using chemical deposition the smaller particles can be prepared. Secondly, the primary particles obtained by chemical deposition are stabilized in situ. The motor oil and oleic acid were used as disperse medium and surfactant respectively. Previously we have shown [12–17], that the stabilization of the obtained additives is a result of the surfactant's chemisorption by the metals or oxides surfaces. The additives with highly dispersed nickel, copper, cobalt and copper oxide were prepared and closely investigated. The laboratory stands and operating tests were carried out. According to the obtained results the additive containing the highly disperse nickel particles has the best operating characteristics. This additive was called as «NIKMA». «NIKMA» is desirable for diesel and carburetor internal combustion engines, compressors, pumps, reducers and bearings. It's best for depreciating units and aggregates. «NIKMA» elevates the compression of the internal combustion engines by 2.1–8.4 %, power – by 2.7–6.7 %, motoresource by 15000–35000 km, reduces expenditure of fuel by 1–2 H_2O mm, decreases the oil consumption to refuel by 15–22 %, decreases the pressure of the gases by 1–2 H_2O mm, restores compressors, pumps, reducers, bearings, improves antifriction properties of the oils by 12 %, antiwear by 25 %, increases the alkaline number by 3.6%, decrease the content of the wear products a 20–80 times, decreases the content of CO in the reaction gases of the motor cars by 5–42 %.

Highly dispersed oxides prepared by novel technique are the basic components of the black and white developers for latent fingerprint visualization on wet, greasy and adhesive surfaces. These developers were elaborated with participation of the State Expert & Forensic Science Center Ministry of Internal Affairs of Republic Belarus and were named as «DAKTI» and «DAKTI-2». DAKTI developers are used for latent fingerprint visualization on black and light-colored wet, greasy and adhesive ceramic, metal, glass and polymeric surfaces. The distinctive characteristic of DAKTI developers is that no surface pretreatment or drying is necessary.

Different gas-generating systems for sickness diagnostics were developed together with the Research Institute of Epidemiology and Microbiology [18, 19].

The gas-generating systems «Anaeropak H_2+CO_2 » and «Kapnopak_{aqua}» were designed for creation and control of the atmosphere in 2.5l jar produced by BioMerieux, Becton Dickinson, Oxoid. The gas-generating system «Anaeropak H_2+CO_2 » is used for anaerobic bacteria cultivation and investigation in the bacteriological laboratories and scientific institutes. Gas-generating system contains 10 gas-generating bags, 2 highly dispersed catalysts and 10 indicated test-straps. Using the gas-generating system «Anaeropak H_2+CO_2 » full oxygen binding and evolution of 7–8 vol.% carbon dioxide are observed. The gas-generating system «Kapnopak_{aqua}» is designed for creation of excess CO_2 concentration for optimal cultivation of the capnophilic microorganisms. About 7-8 vol.% of carbon dioxide is eliminated as a result of the utilization of the gas-generating system «Kapnopak_{aqua}». At the present time, the hospitals of Belarus use the above-mentioned gas-generating systems.

The techniques of the preparation of Ag and Ag/Pd alloy powders for microelectronics with predetermined morphology characteristics were developed. These powders can be used to prepare conducting pastes [20].

3. INTERPHASE SYNTHESIS OF THE METALS, HYDROXIDES AND SALTS NANOPARTICLES

In 1996 the copper oxide nanoparticles were prepared for the first time by the interphase interaction of the copper oleate and sodium hydroxide which were dissolved in the different immixible phases of the two-phase reaction system [21–23]. This novel technique was called as interphase synthesis. Fig. 1 shows the overall scheme of the interphase synthesis.

The solution of one of the reagents in non-polar solvents is added to aqueous solution of another reagent and resulting two-phase system is stirred without disturbing of the interface. In contrast to traditional one-phase synthesis, at the interphase synthesis the interaction may occur at different phases: water, organic, at the interphase both on the source of water or organic phase depending on conditions of the reactions. The interaction conditions at the each of the above mentioned phases are differentiated. These differences are manifested themselves in va-

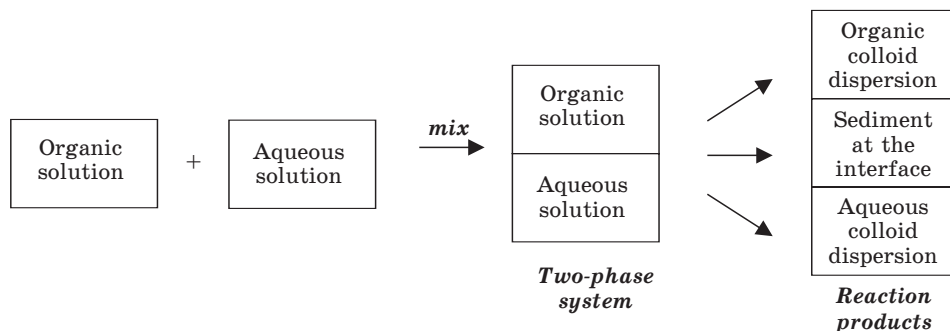


Fig. 1. Overall scheme of the interphase synthesis

rious reagent concentrations, different diffusion conditions, mutual molecular position, solvation. The different conditions of the crystal's formation and growth at the each of the above mentioned phases are the prerequisite for formation the metals and their inorganic compounds with properties differentiated from one's deposited from homogeneous solutions. As in the case of microemulsion and above-mentioned two-phase synthesis, the interaction of reagents dissolved in the different phases of the two-phase systems, is the principle of the interphase synthesis. In contrast to microemulsion synthesis, during interphase synthesis both phases should not intermixed. Another distinction of the proposed technique is that the stable metal, oxide and sulphide colloidal dispersions are obtained without additional surfactants. In solution the particles, which are formed during chemical deposition, are mobile and will coalesce due to van der Waals forces unless they are protected. Consequently, the synthesis of nanoparticles involves rapid nucleation, homogeneous growth and a final encapsulation stage with polymers, ions, complexing ligands or surfactants to prevent the growth of larger crystals. In the case of the interphase synthesis the nanosized metals and their compounds, synthesis of which in homogeneous solutions are impossible or difficult, may be synthesized without any addition of surfactants by the interaction of the reagents dissolved at different phases of two-phase systems. In so doing the stabilizing agents and surfactants should be formed as a result of the interphase interaction and stabilize the colloidal dispersion «in situ». The essence of the interphase synthesis is the interaction of the reagents dissolved in different immiscible phases of the two-phase system.

At the present time the colloidal dispersions of the gold [24–26], silver [27–29], palladium and silver/palladium [30] were prepared by interphase interaction without using of tiols and amines, which are traditionally used to stabilize the organosols of the noble metals. The stable colloidal dispersions of precious metals in non-polar solvents were obtained by the interphase reduction of the noble metal's complexes with quaternary ammonium salt by sodium borohydride dissolved in organic and water phases, respectively. The N,N,N-tridecil(3-aza-3-decyltridecan)ammonium iodide was used as the quaternary ammonium salt to transfer noble metals into organic phase. The N,N,N-tridecil(3-aza-3-decyltridecan)ammonium iodide was synthesised by the specialists of the chair of analytical chemistry of the Byelorussian State University for the first time. The sodium borohydride was used as reducing agents. The non-polar solvents were used as organic phase.

The overall reactions of the interphase preparation of the noble metal's dispersions and some their properties are summarised in Table 1. The obtained results show that under interphase reduction of the noble metal's complex with quaternary ammonium salt, the colloidal dispersions of noble metals are formed in the organic non-polar phase and at the interface. In contrast to the colloidal solution of silver and palladium, a gold film was deposited at the walls of the reaction vessel in aqueous phase simultaneously with the formation of gold hexane colloidal dispersion. The lifetime of the obtained non-polar dispersions ranges from 3 h (Pd) to 8 month (Au). In agreement with the X-ray diffraction and X-ray photoelectron spectroscopy, the prepared colloidal dispersions contain crystalline metals. The diffraction peaks are broaden. The observed peaks broadening are due to the high dispersity of the obtained particles. Transmission electron microscopy shows that the shape of the prepared metal's particles is spherical. In most cases, the primary

Table 1

**The overall reaction equations and some properties
of the noble metal's colloidal dispersions prepared by interphase reduction**

Metal	The reaction equation	The results obtained					
		Phase of sediment localization	State of reaction's product	The life-time of the dispersion	Particle's mean diameter, nm	Standard deviation	Adsorption maximum, nm
Ag	$\text{KI} + \text{AgI} \rightarrow \text{K}[\text{AgI}_2]$ $\text{K}[\text{AgI}_2] (\text{aq}) + [\text{N}(\text{R}^1)_3\text{R}^{11}] \text{I}(\text{decane}) \rightarrow$ $[\text{N}(\text{R}^1)_3\text{R}^{11}][\text{AgI}_2] (\text{decane}) + \text{KI} (\text{aq})$ $m[\text{N}(\text{R}^1)_3\text{R}^{11}][\text{AgI}_2] (\text{decane}) + m \text{e}^- (\text{aq}) \rightarrow$ $m \text{ Ag (decane)} + m [\text{N}(\text{R}^1)_3\text{R}^{11}] \text{I}(\text{decane}) +$ $m \text{ I}^- (\text{aq})$	decane	reddish-brown colloidal dispersion	7 days	20–110	0.30–0.67	420–480
Au	$\text{K}[\text{Au}(\text{CN})_2] (\text{aq}) + \text{N}(\text{R}^1)_3\text{R}^{11}\text{I} (\text{hexane}) \rightarrow$ $\text{N}(\text{R}^1)_3\text{R}^{11}\text{Au}(\text{CN})_2 (\text{hexane}) + \text{KI} (\text{aq})$ $m \text{ N}(\text{R}^1)_3\text{R}^{11}\text{Au}(\text{CN})_2 (\text{hexane}) + m \text{e}^- (\text{aq}) \rightarrow$ $m \text{ Au (hexane, aq)} + m \text{CN}^- (\text{aq}) +$ $m \text{ N}(\text{R}^1)_3\text{R}^{11}\text{CN} (\text{hexane})$	hexane	crimson colloidal dispersion	8 month	2.6	0.47	514
Pd	$4\text{KI} + \text{Pd}(\text{NO}_3)_2 \rightarrow \text{K}_2[\text{PdI}_4] + 2\text{KNO}_3$ $\text{K}_2[\text{PdI}_4](\text{aq}) + 2[\text{N}(\text{R}^1)_3\text{R}^{11}] \text{I}(\text{hexane, chloroform}) \rightarrow$ $[\text{N}(\text{R}^1)_3\text{R}^{11}]_2[\text{PdI}_4] (\text{hexane, chloroform}) + 2\text{KI}(\text{aq})$ $m [\text{N}(\text{R}^1)_3\text{R}^{11}]_2[\text{PdI}_4] (\text{hexane, chloroform}) + m \text{e}^- (\text{aq}) \rightarrow$ $m \text{ Pd (hexane, chloroform)} + m \text{I}^- (\text{aq}) + 2m$ $[\text{N}(\text{R}^1)_3\text{R}^{11}] \text{I} (\text{hexane, chloroform})$	hexane	black colloidal dispersion	3 h	1.4	0.29	unstructured adsorption
Ag/Pd		hexane	colloidal dispersion	3 h	2.2	0.17	400–450

particles are aggregated. In accordance with the transmission electron microscopy (TEM) data, the mean diameters of Au, Pd and Ag/Pd primary particles are distributed from 1.4 to 2.6 nm. The particle size distributions of the palladium and silver/palladium are narrow and standard deviations have small numerical value. These results testify that Pd and Ag/Pd particles are uniform. The particle size distribution of the gold colloids is broader, the standard deviation is equal to 0.47. The silver particle's mean diameter and standard deviation as a whole depend on the reaction time.

The UV-vis adsorption spectrum of the freshly prepared silver dispersion shows the broad absorption peak with the maximum at 460-480 nm. During storage the adsorption maxima are shifted to short-wave spectral region. Along with the displacement of the absorption maxima, the variation of their intensity and shape are observed. Simultaneously with the decreasing of the intensity of the absorption peaks, their narrowing are observed. The displacement and narrowing of the absorption maximum can be assigned to the sedimentation of some large Ag particles. As the result, the fraction of smaller particles increases and the absorption maxima are shifted to the shorter wavelength and became a narrower. The concentrations of the colloidal solutions are decreases and the intensities of the maxima are decreases too.

The position of the gold dispersions absorption peak is practically invariable at 514 nm on the different stages of preparation and storage of the gold dispersion.

The UV-vis spectra of the black palladium colloidal dispersion in organic phase are characterized by unstructured adsorption.

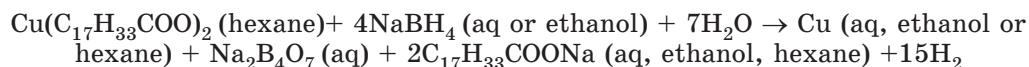
The UV-vis spectra of the colloidal silver/palladium dispersion after 30 min have a shoulder at 400-450 nm corresponding to the metallic silver. The UV-vis spectra of the Ag/Pd dispersions obtained at the later stages of the reaction are identical to the spectra of the individual palladium dispersions. The adsorption corresponding to the metallic silver is absent. Evidently, it is due to the formation the palladium cores on the silver particle's surface. As a result, the silver spectrum is concealed by spectrum of the palladium colloid. The UV-vis spectrum of the film formed at the interface is identical to ones of the colloidal dispersion.

The colloidal dispersions of the noble metals destroy slowly under storage. According to the transmission electron microscopy data, the sediment deposited during gold hexane dispersion storage consists of non-aggregated spherical particles. The mean diameter of the particle size distribution is 2.5 nm and similar to one of the colloidal dispersion. The standard deviation is 0.61. The primary gold particles are assembled. The palladium and silver/palladium sediments consist of the spherical particles. Their sizes are distributed from 1.5 to 3.5 nm.

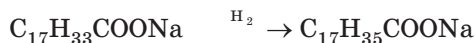
In contrast to the colloidal solution of silver, a gold film was deposited at the walls of the reaction vessel in aqueous phase simultaneously with the formation of gold hexane colloidal dispersion. The film deposited at the walls of the reaction vessel contacting with aqueous phase consists of spherical gold particles. The mean diameter of the particle size distribution and standard deviation are 8.2 nm and 0.57, respectively. The primary particles are integrated into aggregates.

In order to create inhomogeneities of electric field in the thin film organic volume, silver nanoparticles prepared by interphase interaction were used. Thin films were prepared by spin coating method. It was found that silver nanoparticles mixed with MEH-PPV result in the increase of electroluminescence brightness and efficiency [29].

As differentiated from the precious metals, the copper dispersions and powders were prepared by the interphase reduction of the copper oleate which were dissolved in hexane [31, 32].



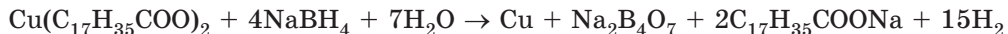
X-Ray evident that the mixture of the metallic copper and copper (I) oxide are formed as a result of this reaction. The phase of the localization of the reaction products and there state depend on the reaction conditions (concentration and ratio of the reagents, pH, water phase volume). Varying the composition of the two-phase system and the reagent's concentration, the state of the reaction products (sediment or colloidal dispersion) and phase of the localization (hexane, water or ethanol) are also varied. When employing hexane/water two phase system and otherwise identical conditions, the colloidal dispersion in water or sediment in hexane are formed. Using the hexane/ethanol two-phase system the reaction products are formed in the polar organic solvent (ethanol). During storage of the weak copper aqueous colloidal dispersion, the colorless of one is observed. This process is accompanied by the precipitation of the blue sediment. According to the results of the liquid chromatography and ^1H NMR spectroscopy, the blue sediment is the copper stearate. Evidently, the low-temperature hydrogenation of the double bond of the oleate-ion occurs. The metallic copper precipitated by the copper oleate interphase reduction catalyses the hydrogenation.



Then the sodium stearate reacts with the metallic copper and copper stearate is formed.



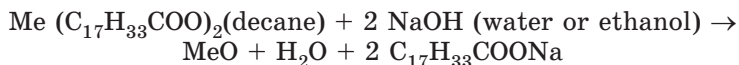
The copper stearate is reduced and colloid dispersion of the metallic copper is formed under addition fresh sodium borohydride solution to the reaction system.



Thus, the low-temperature hydrogenation of oleate-ion occurs in copper colloidal solution prepared by interphase reduction of copper oleate. This effect is very interesting because the low-temperature hydrogenation is known to occur at room temperature only over supported catalyst based on noble metals, in particular, on platinum. The transition metals, for example, Renee nickel, catalyse the olephin hydrogenation only at high temperature.

A number of oxides, hydroxides and salts were also prepared by interphase interaction.

The zinc and copper oxides were prepared by the interphase interaction of zinc or copper oleate and sodium hydroxide, which were dissolved in decane and water or ethanol, accordingly.



Me \equiv Zn, Cu

The different ZnO samples were obtained by the variation of the experimental conditions (temperature, ratio of the reactants) and two-phase system composition (decane-water, decane-ethyl alcohol) [33, 34].

Varying the reaction conditions the copper oxide colloidal solution or sediments, having different shape and composition, were obtained by the interphase interaction of copper oleate and sodium hydroxide [21–23, 35]. The blue sediment of the Cu(OH)_2 is precipitated in water phase of the decane/water two-phase system by the interphase interaction of the copper oleate and sodium hydroxide. It consists of the needle shape particles. At the same time, the spherical Cu(OH)_2 particles are precipitated in homogeneous water solutions. With ethanol is placed of water in octane/water two-phase system the copper (II) oxide is formed in ethanol after 2 h aging at room temperature. The aging conditions in the two-phase system as shown is softer then ones in homogeneous solutions. Under rise in temperature on 95 °C the colloidal dispersion of CuO is formed in hexane. In agreement with the results of the X-ray disperse phase of colloidal solution contains crystals of CuO. The average size of the coherent scattering regions of the copper (II) oxide were evaluated. It is about 3.2 nm. The characteristic bands of the carboxylate ion (1560, 1410, 1313, 1274 cm^{-1}) in the FT-IR spectra indicate that the dispersed phase of the colloidal solution contains also copper (II) oleate. The results of the chemical analysis and estimations from IR-spectroscopy revealed that the mole ratio of $\text{CuO}:\text{Cu(C}_{17}\text{H}_{33}\text{COO)}_2$ is 5.4:1.0. It is likely that copper (II) oleate is a stabilizer for the obtained colloidal solutions similar to iron (II,III) oleates which are formed at the chemical sorption of oleic acid by iron oxides (II,III) [15]. However, in contrast to the iron oleates, copper(II) oleate is not the product of chemical sorption. It is an active reagent, which simultaneously maintains stability of the colloidal solution. To ensure the stability, an excess of copper (II) oleate respective to the exchange reaction with sodium hydroxide should be used. Thus, if one of the reagents is a derivative of the surfactant that was used in excess, the chemical deposition in two-phase systems might be considered as a method for synthesis of colloids in one of these phases. The TEM investigation shows that the disperse phase of the colloidal solution consists of crystal spherical particles of copper oxide (II) of average diameter ca. 6 nm ($\sigma = 1.65$).

Copper, zinc and cadmium sulphide were also prepared [36–38]. The copper sulphide was synthesised by the interphase interaction of the copper oleate and sodium sulphide (hydrogen sulphide), which were dissolved in organic and water phases of the hexane-water two-phase system accordingly.



Me \equiv Cu, Cd, Zn

The effect of the precipitant nature and initial molar $\text{Cd}^{2+}/\text{S}^{2-}$ ratio on the CdS nanoparticles and obtained dispersions optical properties were investigated. As evi-

dent from the obtained results, the nature of the precipitant influence the reaction product's phase of localization and their form. Therefore, using the hydrogen sulphide aqueous solution as precipitant, the product of the interphase interaction is CdS colloidal dispersion in hexane. However, if the sodium sulphide aqueous solution is used as precipitant, the CdS colloidal dispersions are formed in water and hexane phases simultaneously. Furthermore, the cadmium sulphide sediment is precipitated on the hexane/water interphase. Probably, these distinctions are due to the differences between surface-active properties of the oleic acid and sodium oleate generating during the interphase interaction. The $\text{Cd}^{2+}/\text{S}^{2-}$ ratio hasn't influence the interphase reaction product's phase localization. The blue shift is common to optical spectra of the obtained CdS dispersions. As known, it may be a reflection of the very small CdS particles. So, the CdS particle size determined from the onset of light absorption based on the previously published calibration curve is equal to 2 nm. This result is remarkably close to those obtained from X-Ray analysis. The sharpness of the UV peak shows that the CdS nanoparticles have a narrow size distribution. The sole exception is the colloidal dispersion obtained by precipitation with sodium sulphide and molar ratio 0.3:1. The luminescence peak position shift to short wavelength from ~ 534 to ~ 311 nm are characterized to hexane colloidal dispersions prepared by interphase precipitation with sodium and hydrogen sulphide as precipitants and molar ratio 0.3:1. To analyze the purpose of these results the more sophisticated investigation must be developed.

To prepare CdS thin films in polystyrene the obtained CdS colloidal dispersions in toluene solution of the polystyrene were poured out on substrate and dried on air at room temperature. The data obtained demonstrate the possibility of the developed technique to prepare CdS colloidal dispersions and thin films in polystyrene. As in the case of the hexane colloidal dispersion the CdS nanoparticles in polystyrene films are equal to ~ 2 nm.

CONCLUSION

Based on the obtained data the common recommendations of the nonaggregated nanoparticle's preparation can be formulated. They are the prevention the coalescence on the primary particles in the act of forming or disintegration of the globule's aggregates. These recommendations are utilized in practice by chemists. The surfactants are traditionally used for that. The preparation of the particles having predetermined shape and orientation in the dispersion medium is also very important for the preparation of the composite materials. This problem has no common resolution. In the case of ferrofluids the covering of magnetic field during synthesis is the effective method of the governing of shape and orientation of magnetite particles [39]. The interaction of the magnetic dipoles promote oriented intergrowth of the primary particles without using of the magnetic field [13, 15, 40].

The purposeful synthesis of the unisometrical particles of the diamagnetic substances is the more complicated problem. To accomplish this task the pseudomorphose of the primary substance can be prepared. These pseudomorphoses transform to resulting products and hold the shape of precursors. So, crystalline copper (II) hydroxide and copper (II) oxide obtained from the last, are needles in shape. The preparation of these particles has no particular hardship. At the same time, the preparati-

on of the isometrical copper (II) oxide particles is the more difficult problem. To resolve the problem CuO were prepared by interphase synthesis [21–23, 35].

Furthermore, the reaction at the interface is interesting for the preparation of films, colloidal oleosols or aquasols without introducing of additional surfactants, powders with predetermined sizes. For example, the colloidal gold prepared by interphase synthesis, is formed in organic phase as colloidal dispersion and is simultaneously deposited on walls of reactor in aqueous phase. The reasons of the selective deposition in one of the phases are not always clear. Evidently, besides from the differences in Au particle's sizes, the solvofilic of ones determine the phase of the reaction product's localization.

The distinction of the developed method is that the stable metal, oxide and sulphide colloidal dispersions are obtained without any additional surfactants. However, the surfactants can be produced as a result of the interphase interaction. Depending on the quantity of surfactants, the micelles of hydrophilic or hydrophobic sols can be arisen. The nature of the micelles determines the phase of the localisation of the reaction products. Evidently, changing the quality of the N,N,N-tridecil(3-aza-3-decyiltridecan)ammonium iodide or oleate-ion, the desired distribution between the phases of the two-phase system can be achieved. Under stoichiometric proportion of the reagents, the surfactant formed is not enough to transfer all particles to non-polar phase. As a result, part of them, stabilized by double electric layer remain in aqueous phase and form colloidal dispersion, film or deposit. Due to the deficiency of the surfactant, the colloidal dispersions prepared by interphase synthesis has no reasonable sedimentation stability. This deficiency can be eliminate by addition of the surfactant. The thin fractionation of the dispersed phase can be carrying out by surfactant addition or by deposit peptization after fixed time intervals. Due to this technique, the stable colloidal dispersions having small standard deviation and high structure uniformity can be prepared.

The formation of thin films of noble metals at the interface is of fundamental importance. This fact is indicative of surfactant forms at the interface both continuous and discrete layer of polar molecules. Under small quantity of surfactant in the phase of the non-polar solvent, oleophilic micelles are transformed to liophilic-liophobic structures which can be named as semimicelles. Under sufficient quantity of them the continuous layer is formed. This layer facilitate to the film formation. Under small quantity of the semimicelles, the microheterogeneities of the interface give rise to the surface tension modification and to the geometrical microirregularity of the interface. The size of these microirregularities cause the size of the primary particles formed. The particles formed give rise to force balance at the interface. As a result the particles pass into organic or aqueous phase depending on the proportion of the interaction energy of the particles formed with the double electric layer (in water phase) and adsorption layer (in organic phase). The proposed scheme can be used to explain the experimental data obtained.

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