

RHEOLOGICAL PROPERTIES OF DISPERSE SYSTEMS BASED ON HYDROLYZED LIGNIN AND OIL

T. A. Savitskaya,^a I. V. Reznikov,^a V. A. Shcheglov,^a
N. G. Tsygankova,^b G. M. Telysheva,^c and D. D. Grinshpan^b

UDC [66.081.3+665.7]:634.0.864

The rheological properties of oil dispersions of hydrophobized hydrolyzed lignin, which is an effective sorbent of oil and oil products, have been studied. It has been shown that at a lignin concentration of over 10%, free-disperse systems with Newton flow go over to coagulation thixotropic structures, demonstrating the pseudoplastic character of flow. The structural-mechanical characteristics of highly filled (lignin content of 40–45%) dispersions have been determined and the concentration region of existence of an oil-saturated sorbent in the form of a solid product easily removed from the water surface has been established.

Keywords: rheological properties, oil, lignin, dispersion.

Introduction. In spite of the existence of a large number of sorbents suitable for removing of oil and oil product spills from the water surface, the problem has not been solved completely and the properties and behavior of these sorbents under real conditions have not been studied comprehensively [1]. In particular, one of the effective, but little studied, oil sorbents is hydrophobized hydrolyzed lignin. It has an absorptive capacity of up to 4 g/g, is cheap, features buoyancy in the oil-saturated state, and forms with oil solid products which are easy to remove from the water surface and are suitable for obtaining fuel granules and pellets. Such granules and pellets containing in their composition occluded oil have a calorie content from 25 to 40 MJ/kg, whereas the caloric content of the source lignin is 17–22 MJ/kg [2–4]. This makes it possible to utilize the waste oil sorbent in the form of a solid fuel, which confers important advantages over other sorbents.

At the present time [5], in spite of the various proposals for using lignin, which is a large-tonnage by-product of the hydrolysis industry, it has not found wide application and is accumulated at enterprises, occupying large territories and threatening the environment. In the Republic of Belarus such an ecologically unfavorable situation takes place in Rechitsa and Bobruisk [4]. Therefore, there exists the necessity of investigating the structural-mechanical properties of dispersions in oil of this natural product which can be used on a large scale as an oil sorbent. Only a few works are known in which the colloidal-chemical properties of water dispersions of technical lignin are described [6, 7], and the dispersions of hydrolyzed hydrophobized lignins in oil have not been studied at all.

The aim of the present work is to study the rheological properties of dispersions of hydrophobized hydrolyzed lignin in oil at various component ratios.

Experimental. We used the hydrophobized lignin obtained from the dumps of the Republican unitary enterprise "Rechitskii pilot-production plant" (Republic of Belarus). The moisture content of the sample was 7%, the packed density was 240 kg/m³, the absolute density for helium was 1480 kg/m³, the ash content was 17.2%, the specific surface for nitrogen was 3000 m²/kg, and the total volume of pores was 4.5·10⁻⁵ m³/kg. For the dispersion medium, we used commercial petroleum with a density of 800 kg/m³.

Oil dispersions of lignin with a content of the dispersed phase from 10 to 45% were prepared by the gravimetric method with subsequent agitation in an IKA WERKE mechanical impeller agitator (Germany) for 10 min with a velocity of 500 rpm just before rheological measurements.

For dispersions with a lignin concentration of 10–39%, we used a "Rheotest-2" rheoviscosimeter (Germany) with a cylinder–cylinder operating assembly in the range of shear stresses 4–800 Pa. The highly filled dispersions with

^aBelarusian State University, 14 Leningradskaya Str., Minsk, 220030, Belarus; email: ta_savitskaya@mail.ru;

^bScientific-Research Institute of Physicochemical Problems, Belarusian State University, Minsk, Belarus; ^cLatvian State University of Wood Chemistry, Riga, Latvia. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 85, No. 3, pp. 611–616, May–June, 2012. Original article submitted August 29, 2011.

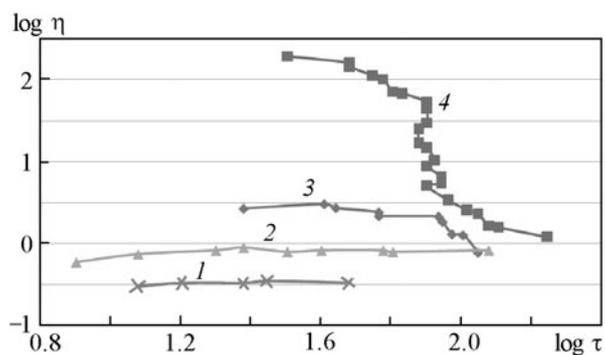


Fig. 1. Viscosity rheograms of oil (1) and oil dispersions of lignin at its concentration of 10% (2), 39 (3), and 20 (4).

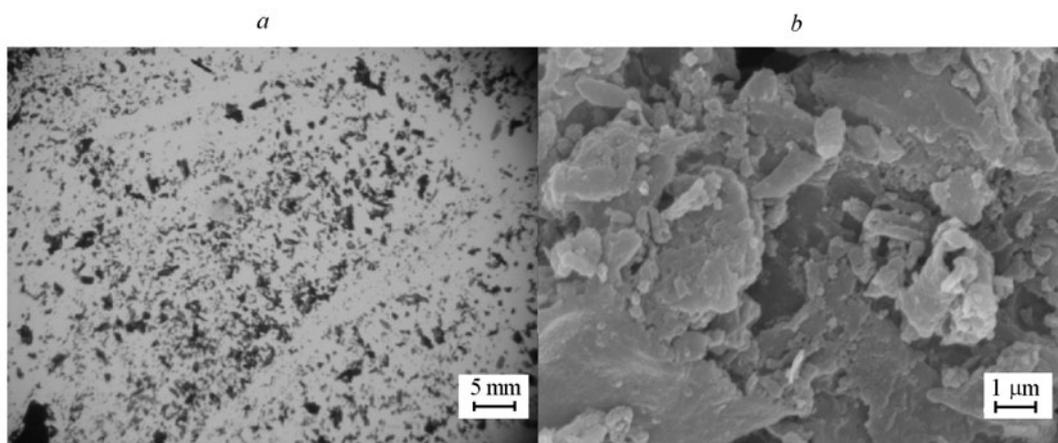


Fig. 2. Microphotographs: a) source lignin particles; b) fragment of the surface of an individual particle.

a lignin content over 40% were investigated on a "Brookfield" rotary rheometer (USA) with Rheo2000 software and a measuring system with CC25 coaxial cylinders in the 11.4–1140 Pa range of shear stresses. Measurements were made at a temperature of 298 ± 1 K in the regime of increasing shear stress which, upon reaching the limiting value, was decreased at the same rate. The duration of the experiment with measurements in one direction was 2 min with the use of the "Rheotest-2" rheometer and 20 s with the use of the "Brookfield" rheometer. The obtained data were represented in the form of flow curves $\dot{\gamma} = f(\tau)$ and viscosity rheograms $\eta = f(\tau)$. From the rheological curves, the dynamic yield stress τ_d the plastic viscosity η_{pl} [8], the initial viscosity of the practically nondestroyed η_0 [9], and the structural relaxation time θ_r [10] were determined. The force of single contacts F_1 was calculated in accordance with the model of concentrated suspensions in which it is assumed that the structure represents a three-dimensional lattice from aggregated particles [11]. The size distribution of particles in the source lignin was estimated with the aid of a HORIBA LA-300 particle analyzer, and that in dispersions was estimated by the microscopic method using an Amplival optical microscope (Germany) and a "LEO-1420" scanning electron microscope.

Results and Discussion. As follows from the viscosity rheograms presented in Fig. 1, the oil used for the investigation (curve 1) is a Newtonian fluid, which points to the absence from its composition of high-molecular paraffins forming supermolecular structures. The introduction of 10% of lignin practically does not change the character of the oil flow (Fig. 1, curve 2). Microscopic analysis has shown that with such a component ratio in the suspension, along with the individual lignin particles shown in Figs. 2 and 3, aggregates of them appear, inside of which the oil is occluded. The oil absorption by particles of hydrophobized hydrolyzed lignin can be explained by the presence in them of microscopic voids [12]. On the whole, in terms of the phase rheology [13], these oil-filled aggregates can be considered as particles of a new phase. The phase rheology, as opposed to the macrorheology, considers suspensions as two-phase systems whose flow mechanisms are determined by the dispersion medium and the dispersed phase in-

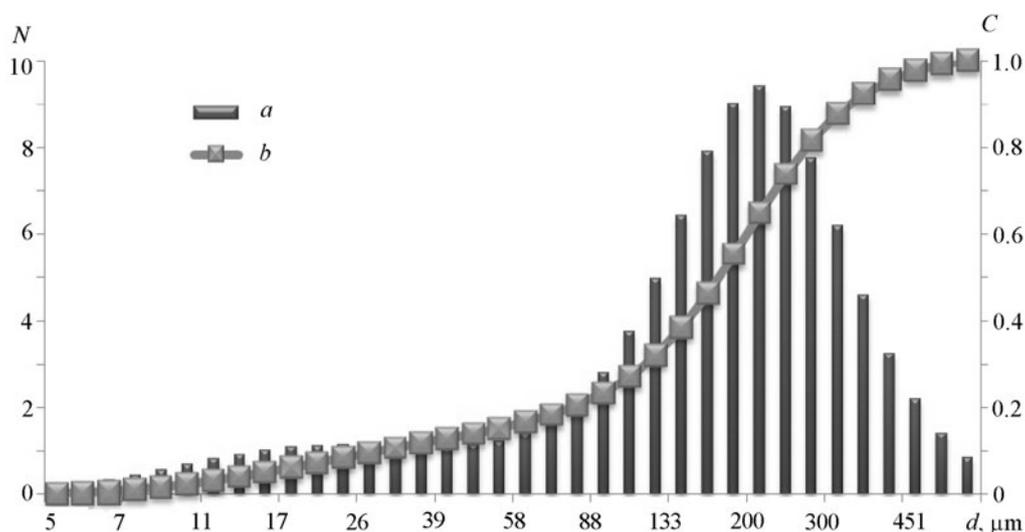


Fig. 3. Size distribution of lignin particles: a) particle occurrence rate in the field of the microscope; b) content of particles in the field of the microscope.

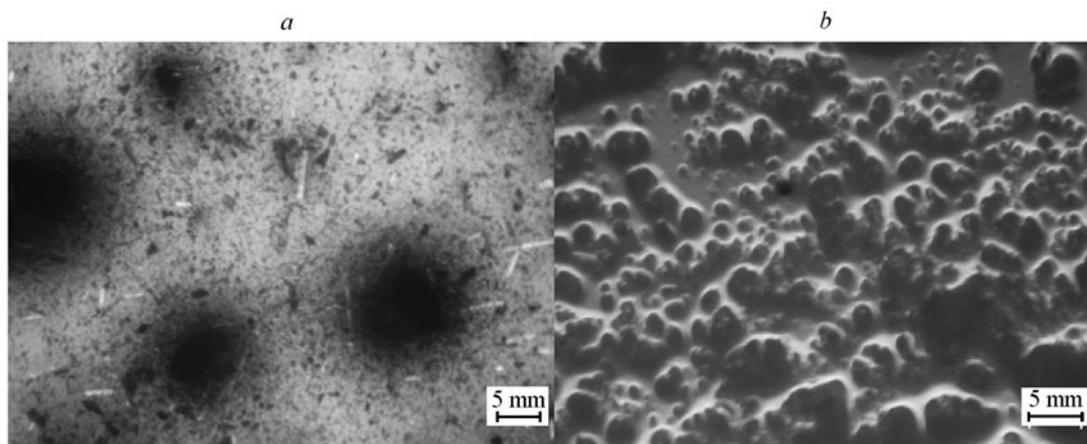


Fig. 4. Microphotographs of oil dispersions of lignin at its concentration of 20% (a) and 39% (b).

fluences the state of the dispersion medium rather than homogeneous systems whose rheological properties are determined by the contact interactions. It may be assumed that at the given content of lignin in the dispersion, collisions of dispersed phase particles with one another are so rare that their influence on the process of laminar flow of the dispersion medium is practically absent. In this case, shear stresses tend to deform the dispersed-phase particles and orient them in the flow in a certain way. In so doing, the orienting action is opposed by the Brownian motion. These processes counterbalance one another, as a result of which the viscosity of the system remains practically constant with increasing shear stress, i.e., Newtonian flow is realized.

As the lignin content is increased to 20%, the flow character of the system changes: it becomes non-Newtonian and, according to the data of Fig. 1 (curve 4), in the range of shear stresses up to 200 Pa, is described by the full rheological curve. In such a dispersion, the size of aggregates of lignin particles with occluded oil inside them increases to 10 μm (Fig. 4a). Simultaneously with the gathering of particles into oil-filled aggregates, the fibrous fragments of nonhydrolyzed cellulose always present in the source lignin particles but, unlike them, forming no aggregates with oil, are released, which is clearly seen in Fig. 4a.

A further increase in the content of the dispersed phase leads to a further change in the behavior of the flow curves. For instance, the viscosity rheogram of the suspension containing 39% of lignin in the range of shear stresses of up to 200 Pa assumes the form inherent in the flow of pseudoplastic systems (see Fig. 1, curve 3), the absolute

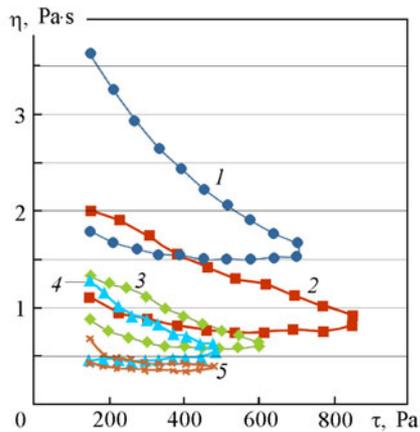


Fig. 5. Viscosity rheograms of oil dispersions of lignin at its concentration of 45% (1), 44 (2), 43 (3), 41 (4), and 40 (5).

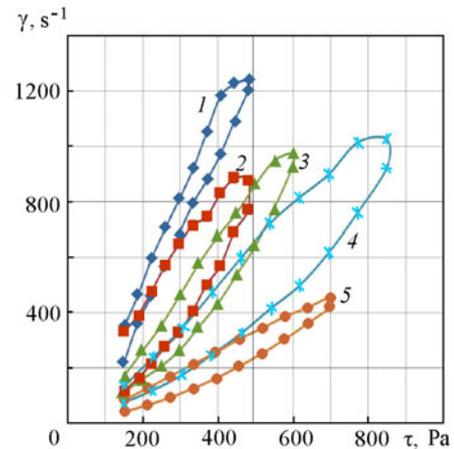


Fig. 6. Flow curves of oil dispersions of lignin at its concentration of 40% (1), 41 (2), 43 (3), 44 (4), and 45 (5).

value of this suspension viscosity turning out to be lower than that of the suspension with a content of 20% of lignin. Such a change in the rheological behavior can be characterized as the transition to a qualitatively new stage of the system in which practically the whole of oil turns out to be incorporated in lignin particles (Fig. 4b) in the form of added (solvate) layers, which leads to a transformation of the composition and structure of dispersed-phase particles and the suspension on the whole. The decrease in the viscosity with increasing shear stress taking place thereby can be explained by the bound-free transition of a certain quantity of oil under shearing conditions. When the lignin content in the system is increased to 40% or higher, it becomes impossible to take rheological measurements of such dispersions, which are actually high-viscosity pastes, under the shearing conditions provided by the "Rheotest-2" rheoviscosimeter. Therefore, to create higher rates of shear deformation, we used the "Brookfield" rheometer.

Figure 5 presents the dependence of the viscosity of highly filled dispersion of lignin in oil on the shear stress in the range of deformation rates from 40 to 1240 s^{-1} . As follows from this figure, the effective viscosity of the above dispersions increases naturally with increasing content of lignin. In accordance with the data of Table 1, the initial viscosity characterizing the viscosity of the system with a nondestructed structure and the plastic viscosity, which is a conditional quantity and characterizes the destruction rate of the structure, also increase [14]. The decrease in the viscosity with increasing shear stress observed for all dispersions can be attributed to the breakage of coagulation contacts both inside the aggregates of lignin particles and between them.

To describe the dependence of the effective viscosity of the dispersions under consideration on the volume fraction of the dispersed phase in them, we used the Mooney equation and determined the values of its coefficient K taking into account the effect of mutual overlap and hydrodynamic interactions of particles at various shear stresses [15]. The coefficient K determined in accordance with [16] is equal to 1.0 for emulsions and 2.5 for suspensions. As follows from the data of Table 2, the values of the coefficient K for highly filled dispersions of lignin in oil vary from 1.8 to 1.0, decreasing with increasing shear stress, the above data falling accurately onto the straight line determined by the equation: $f(K) = 2.439 - 0.0032\tau$. The reliability of approximation is 0.9972.

The distinguishing feature of oil dispersions of lignin at concentrations of the dispersed phase exceeding 40% showed up as a discrepancy between the viscosity rheograms and the flow curves obtained in the regime of increasing and decreasing the shear stress. As follows from Figs. 5 and 6, on the above curves obtained in such a regime there are hysteresis loops. This is due to the fact that after mechanical destruction the dispersion structure is restored thixotropically more slowly with time, and in the given regime of deformation the coagulation contacts between the dispersion structure elements have no time to be restored completely. In this case, the degree of thixotropy increases with increasing concentration of lignin in the dispersion, which is evidenced by the continuous increase in the area of the hysteresis loop on the viscosity rheograms (Fig. 5).

TABLE 1. Structural-Mechanical Characteristics of the Oil Dispersions of Lignin

| w_l , % | τ_d , Pa | η_{pl} , Pa·s | η_0 , Pa·s | F_1 , N | $\theta_r \cdot 10^3$, s |
|-----------|---------------|--------------------|-----------------|-----------|---------------------------|
| 40 | 82 | 0.30 | 0.57 | 0.57 | 2.1 |
| 41 | 74 | 0.68 | 1.72 | 0.42 | 4.6 |
| 43 | 42 | 0.98 | 1.74 | 0.14 | 4.8 |
| 44 | 39 | 1.53 | 2.40 | 0.080 | 5.6 |
| 45 | 53 | 2.38 | 4.34 | 0.057 | 10.8 |

TABLE 2. Values of the Coefficient K in the Mooney Equation of the Oil Dispersions of Lignin

| τ , Pa | 200 | 300 | 400 | 450 |
|-------------|-----|-----|-----|-----|
| K | 1.8 | 1.5 | 1.2 | 1.0 |

At the same time, for rheological curves in the range of lignin concentrations of 40–45%, the largest area of the hysteresis loop was registered for the dispersion containing 44% of lignin (Fig. 6, curve 4). This dispersion is characterized by the minimum value of the dynamic yield stress determining the shear strength of the structure and depending on both the number and force of coagulation contacts and the friction between the structure elements in flow (see Table 1).

It may be assumed that in this concentration range, as the content of the dispersed phase increases, the particles incorporate into the existing vacancies in the structure of oil-filled aggregates. At the same time, the decrease in such a rheological parameter as the dynamic yield stress τ_d may be due to kinetic reasons, which are reduced to the fact that in a high-viscosity dispersion the restructuring processes proceed slowly and under the experimental conditions do not reach full completion. In this case, the decrease in τ_d correlates with the decrease in the calculated values of the force of single contacts F_1 formed between the dispersed-phase particles (Table 1).

The subsequent increase in the dynamic yield stress when the lignin content is increased to 45% can be associated quite logically with the fact that there occurs a decrease in the quantity of the free dispersion medium to such a value that prerequisites are created for the appearance of a capillary contracting force between lignin and oil particles. As a result of the action of this force, the particles are attracted to each other and grow in size. The increase in the sizes of kinetic flow units is evidenced by the increase in the relaxation time of nondeconstructed structures, which in the given case will double (see Table 1). When the dispersed-phase concentration is increased still further by 1% or more, the particles lose individuality and the dispersion system gradually transforms into a solid-like continuous mass, whose rheological characteristics are beyond the capability of the measuring system used.

The bound-disperse system formed resembles gel in terms of the presence of a continuous space lattice and the absence of fluidity, but unlike true gel it is not prone to large reversible deformations. The system's integrity is probably determined by the action of the capillary contracting force depending on the quantity of liquid in the meniscus between particles. Such a contracting force arises when between particles the meniscus of the wetting liquid takes a certain form, the so-called "cup" [17]. For the investigated dispersions, it has been established that the range of lignin concentrations in which lignin suspensions in oil lose mobility is 50–70%. With increasing or decreasing quantity of liquid the contracting force decreases or disappears completely. For example, at a 40% concentration of lignin a viscous but fluid suspension is formed, and at a concentration of 80%, free-flowing powder, whose particles are not bound to one another, is formed.

We have established that oil incorporated into lignin is not extracted into the water phase even at prolonged (for over a month) contact and in the presence of surface-active substances in the water.

Conclusions. Lignin dispersions in oil containing up to 20% of lignin are free-disperse systems displaying the Newtonian character of flow. As the lignin content is increased from 20 to 40%, the dispersions become systems characterized by a decrease in the effective viscosity with increasing shear stress. At a concentration of lignin of over 50% due to the action of the capillary forces a solid bound-disperse system, or quasi-gel, is formed. This makes it possible to remove easily and practically without loss the oil-saturated sorbent from the water surface with the use of hydrophobized lignin for removing oil spills.

NOTATION

C , relative content of particles in the field of the microscope; d , particle size, μm ; F_1 , force of single contacts, N; w , mass concentration, %; $\dot{\gamma}$, shear velocity, s^{-1} ; η , viscosity, Pa·s; η_{pl} , plastic viscosity, Pa·s; η_0 , viscosity of the practically nondeconstructed structure, Pa·s; θ_r , time of structural relaxation, s; τ , shear stress, Pa; τ_d , dynamic yield stress, Pa. Subscripts: d, dynamic; pl, plastic; r, relaxation; l, lignin.

REFERENCES

1. M. Fingas, *Oil Spill Science and Technology*, Gulf Professional, New York (2010).
2. D. D. Grinshpan, G. M. Telysheva, T. N. Nevar, T. N. Dizhbite, N. G. Tsygankova, and A. S. Arshanina, Oil sorbent based on hydrolysis lignin, *Vestsi Nats. Akad. Navuk Belarusi, Ser. Khim. Navuk*, No. 2, 23–28 (2011).
3. A. F. Nadein and Yu. I. Kuz'min, *A Compound for Skimming Oil and Oil Products from Water Surface*, Patent 2051262 of the Russian Federation, Published 27.12.1995.
4. D. D. Grinshpan, N. G. Tsygankova, T. N. Nevar, and S. E. Makarevich, "Lignosorb" — a new sorbent for collecting oil and oil products, *Vestn. Belneftekh. Neftekhim. Kompl.*, No. 1 (4), 20–21 (2010).
5. N. V. Biryukova and A. E. Kozlova, *Development of Compositions and Investigation of Invert-Emulsion Drilling Muds for Opening Productive Pools. Drilling* [in Russian], VNIIOÉNG, Moscow (1982), No. 9, 35–37.
6. A. B. Dyagileva, Yu. M. Chernoberezhskii, Yu. L. Moreva, and I. S. Rudakova, Colloid-chemical properties of water dispersions of sulfatic (kraft) lignin, in: *Proc. 3rd Conf. on Colloid Chemistry and Physicochemical Mechanics Devoted to Two Centuries of the Discovery of Electrokinetic Phenomena by F. F. Reiss*, 24–28 June, 2008, Moscow, Legenda, Moscow (2008), p. 91 ISBN 978-5-0219-2.
7. D. S. Mitchell, Method of producing submicron lignin dispersions, *European Patent Application EP429723*, June 1991.
8. V. V. Nazarov, *Practical Work and Book of Mathematical Problems of Colloid Chemistry. Surface Phenomena and Disperse Systems* [in Russian], IKTs "Akademkniga," Moscow (2007).
9. G. V. Vinogradov and A. Ya. Malkin, *Rheology of Polymers* [in Russian], Khimiya, Moscow (1977).
10. K. E. Perepelkin (Ed.), *Carbon-Chain Synthetic Fibers* [in Russian], Khimiya, Moscow (1973).
11. E. V. Yakhnin and A. B. Taubman, Toward the problem of the structure formation in disperse systems, *Dokl. Akad. Nauk SSSR*, **155**, 179–182 (1964).
12. I. V. Gribkov, *Chemical Composition and Structure of Technical Hydrolyzed Lignin*, Author's Abstract of Candidate's Dissertation (in Chemistry), St. Petersburg (2008).
13. G. S. Khodakov, Rheology of suspensions. The theory of phase flow and its experimental justification, *Russ. Khim. Zh.*, **48**, No. 2, 33–44 (2003).
14. M. Reiner, *Advanced Rheology*, H. K. Lewis, London (1971).
15. V. D. Koshevar, *Organic-Mineral Dispersions. Regulation of Their Properties and Application* [in Russian], Belaruskaya Navuka, Minsk (2008).
16. A. I. Satamadze, *Formation of the Structure and Complex of Properties of Polymer Composite Materials Produced from Emulsions Based on Thermoreactive Oligomers*, Author's Abstract of Candidate's Dissertation (in Chemistry), Moscow (2011).
17. E. D. Shchukin, A. V. Pertsov, E. A. Amelina, and A. S. Zelenev, *Colloid and Surface Chemistry*, Elsevier, New York (2001).