

The Influence of Low- and High-Molecular Hydroxyl-Containing Additives on the Stability of Sol–Gel Tetraethoxysilane-Based Systems and on the Structure of Hybrid Organic–Inorganic Coatings¹

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Abstract—Organic–inorganic composites are synthesized by introducing a number of low- and high-molecular water-soluble polyhydroxyl compounds (with different molecular weights and different molecular structures) into sols based on tetraethoxysilane. The coatings on nickel substrates are prepared by adding chromium dioxide as a finely disperse filler to the sols. The rheological properties of the sol–gel systems synthesized are investigated, and the surface condition and the microstructure of the coatings formed are examined. The xerogels and the coatings are studied by differential thermal and X-ray powder diffraction analyses.

INTRODUCTION

Hybrid organic–inorganic materials prepared by different methods either through the introduction of inorganic particles into organic matrices or, vice versa, through the plasticization of inorganic materials due to the incorporation of polymer molecules represent a new generation of designer materials. One of the efficient methods of synthesizing hybrid organic–inorganic nanomaterials is sol–gel processing. This technique provides conditions for the interaction of components on the molecular level, which makes it possible to produce materials with a high degree of homogeneity and a controlled chemical composition [1, 2].

Analysis of the data available in the literature [3–16] shows that there exist several approaches to the preparation of hybrid organic–inorganic materials with the use of the sol–gel process. The classical method involves the hydrolysis and condensation of alkoxy silanes and metal alkoxides in the presence of high-molecular compounds with active functional groups [such as poly(vinyl acetate), poly(methyl methacrylate), and poly(ethylene glycol)]. Moreover, the hydrolysis and condensation of alkoxides can be performed in polymer solutions. There is another approach, according to which the hydrolytic polycondensation of alkoxy compounds proceeds concurrently with the polymer-

ization of organic monomers. One of the newest techniques is based on the synthesis of the so-called silanized materials with the use of monomers or oligomers that are terminated by alkoxy silanes to provide their interaction with an inorganic network formed upon hydrolysis of alkoxy compounds.

The synthesis of hybrid organic–inorganic materials is an efficient way to improve the mechanical properties of substances. As was shown in [1, 8, 13, 17], the elasticity of synthesized hybrid monolithic materials, coatings, thin films, and membranes of different types is considerably higher than that of their purely ceramic or vitreous analogs. It is also known [18] that, in a number of cases, the introduction of modifying polymeric additives into ceramic mixes makes it possible to extend the range of methods for molding articles and to use procedures traditional in the technology of plastics.

One of the important practical problems is associated with the sol–gel deposition of temperature-resistant thin-layer hybrid organic–inorganic coatings on metals and alloys, which should be superior to purely silicate analogs in elasticity and moisture resistance and retain the high electrical and mechanical strengths. The first steps in this direction have already been made. The application of the sol–gel method of preparing silicate glass-ceramic coatings [19] and sols modified by water-soluble organic and inorganic additives permitted us to increase the thickness of coatings without deteriorating their elasticity and high electric strength [20–23]. However, the above problem calls for further

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Table 1. Characteristics of polyhydroxyl-containing low-molecular and oligomeric linear and branched compounds

Modifying additive	Molecular weight, g/mol	Number of OH ⁻ groups	Additive concentration, g per 100 g of sol
Glycerol	92	3	1.2
Poly(ethylene glycol)	300	2	1.2
Oligo(urethaneurea) $\text{CH}_2\text{O}-[\text{RO}]_x-[\text{R}'\text{O}]_y-\text{CONH}-\text{R}''-\text{CONHCON}(\text{CH}_2\text{CH}_2\text{OH})_2$ $\text{CH}-\text{O}-[\text{RO}]_x-[\text{R}'\text{O}]_y-\text{CONH}-\text{R}''-\text{CONHCON}(\text{CH}_2\text{CH}_2\text{OH})_2$ $\text{CH}_2\text{O}-[\text{RO}]_x-[\text{R}'\text{O}]_y-\text{CONH}-\text{R}''-\text{CONHCON}(\text{CH}_2\text{CH}_2\text{OH})_2$, where $R = \text{CH}_2\text{CH}(\text{CH}_3)$, $R' = \text{CH}_2\text{CH}_2$, $R'' = 2,4-, 2,6-\text{C}_6\text{H}_3(\text{CH}_3)$; $x + y = 19$	4200	6	0.6

Table 2. Characteristics of hyperbranched polymers

Additive	Type of core in hyperbranched polymer	Number of O-C(O) groups (indicators of repeating units in a ray)	Weight-average molecular weight M_w , g/mol	Number-average molecular weight M_n , g/mol	Approximate number of OH ⁻ groups in molecular shell	Additive concentration, g per 100 g of sol
HBP-49	Three-arm	9.3	1771	1681	12	0.4
HBP-64	Four-arm	21	5100	2772	64	0.4
HBP-16	Four-arm	11.5	2467	1681	16	0.4

investigation in order to improve practical results and to provide deeper insight into the nature of the processes occurring in sol-gel systems and hybrid coatings.

The purpose of the present work was to elucidate how low- and high-molecular organic compounds containing terminal OH⁻ groups affect (i) the stability of sols based on tetraethoxysilane (TEOS) against the gelation and (ii) the structure and physicochemical properties of hybrid coatings deposited on metals and alloys.

EXPERIMENTAL TECHNIQUE

Synthesis of sols and suspensions. Sol-gel systems containing hydrolyzed stabilized TEOS (modified by inorganic dopants and low- and high-molecular organic additives) and an oxide filler were chosen as objects of investigation. The initial components were taken in the ratio TEOS : H₂O : EtOH : HNO₃ = 1 : 24 : 1.5 : 0.002.

Dopants—modifying inorganic additives (metal nitrates and boric acid)—were introduced in amounts so as to produce a silicate coating of composition (wt %) 43SiO₂ · 24SrO · 23PbO · 5K₂O · 4B₂O₃ · 1CoO. Suspensions were prepared by adding a finely dispersed filler Cr₂O₃ (particle size, ~1 μm) to sols in the weight ratio sol : Cr₂O₃ = 2 : 1. The suspensions were obtained by mixing of the sols with the filler under ultrasonic action.

Choice of the modifying low- and high-molecular organic components. The sols were prepared using the classical approach (see Introduction) by performing the sol-gel synthesis through the hydrolysis of the TEOS precursor. The acid hydrolysis of TEOS was carried out in excess of water in the presence of the modifying inorganic compounds (dopants) and also low- and high-molecular organic components with active functional groups. The necessary condition in choosing low- and high-molecular organic components was their high solubility in water and ethanol. The introduction of these compounds into the homogenous sols should not lead to phase separation and precipitation. Since the sols should be used to apply coatings, the chosen organic components should not deteriorate the wetting and covering powers of the sols upon their application to substrates. The necessary condition was the requirement that a continuous xerogel layer without defects and cracks should be formed on the substrate surface after evaporation of a solvent in the course of application.

The amount of the introduced low- and high-molecular organic components was chosen reasoning from the necessity of preparing the sol that should be homogeneous (without indications of phase separation) and stable to gelation (for several days) and possess a good covering power (Tables 1, 2).

Glycerol involving two primary and one secondary hydroxyl groups was taken as a low-molecular organic compound.

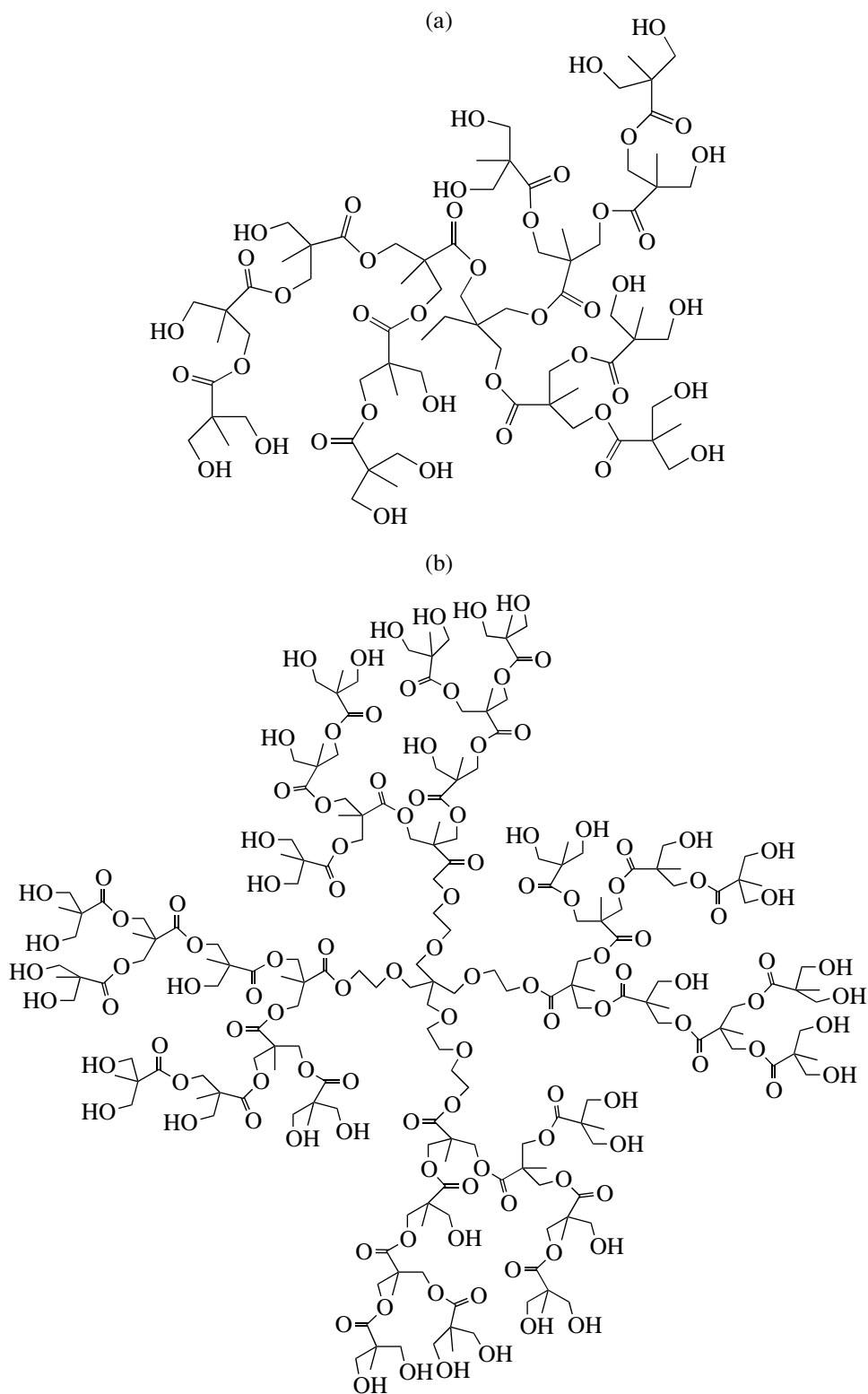


Fig. 1. Structures of (a) three-arm and (b) four-arm hyperbranched polymers.

Polyhydroxyl compounds with different molecular weights and molecular structures were used as high-molecular compounds. These were the oligomer

poly(ethylene glycol) (PEG-300) with a linear structure, oligo(urethaneurea) (OUU) with a branched structure, and hyperbranched aliphatic complex polyol poly-

ethers (HBP). The polymers of the last group differ in the molecular weight, the number of OH⁻ groups in the macromolecular shell, and the structure of the core of the hyperbranched molecule. As the cores, we used trimethylolpropane for the synthesis of HBP-49 and ethoxylated pentaerythrite for the synthesis of HBP-16 and HBP-64 (Fig. 1). The characteristics of the chosen organic compounds are presented in Tables 1 and 2.

The presence of primary hydroxyl groups in the compounds used is responsible for their interaction with products of the TEOS hydrolysis in the course of the sol-gel synthesis.

Coating formation. The initial sols and suspensions were applied with a brush. The applied layers were dried and calcined at 500–700°C. We examined the possibility of forming the coatings on nickel plates 10 × 10 and 50 × 50 mm² in size.

Characterization techniques. The structure and composition of xerogels were investigated by differential thermal analysis (DTA) on a Paulik–Paulik–Erdey derivatograph. The structure and composition of the formed coatings were studied using a scanning electron microscope and X-ray spectral microanalysis on a Camebax microanalyzer. X-ray powder diffraction analysis of the coating compositions was carried out on a Siemens X-ray diffractometer equipped with a position-sensitive detector. The rheological properties of the synthesized sols were examined with a Höppler rheoviscometer. The structural viscosity was calculated by the technique commonly used in the study of colloidal systems [24].

An important characteristic of sols is their relatively high stability, i.e., the ability to retain their homogeneity and mobility within a certain time interval. The precipitation, the appearance of visible liquid-liquid interfaces, and the decrease in the fluidity due to a gradual increase in the viscosity and the transformation of the sol into gel served as criteria for stability loss. In addition to visual observations, the stability of the sols was judged from the change in their structural viscosity with time.

The covering power is another important parameter of the sols and suspensions intended for depositing the coatings. The number of visually observed nonwetted regions and defects primarily associated with a nonuniform distribution of the sol or suspension over the substrate surface was the criterion of the covering power of the sols and suspensions on their base.

With the aim of elucidating the influence of the low- and high-molecular organic additives on the formation of thin-layer defect-free coatings, we analyzed the wetting power of the sols and suspensions under consideration. The wetting angles were measured with a horizontal microscope.

The effect of the modifying low- and high-molecular organic components on the structure of the formed coatings and also on their hydrophilic and hydrophobic properties was assessed from the angle of wetting the

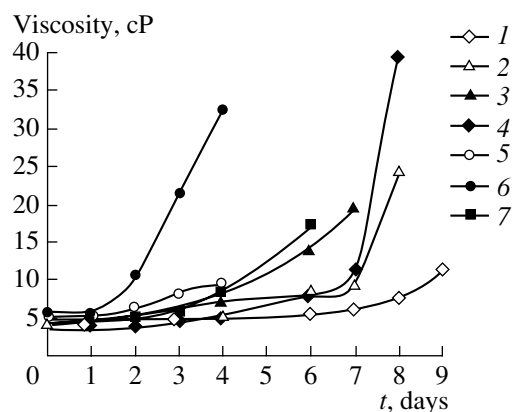


Fig. 2. Time dependences of the structural viscosity for the TEOS-based sols containing additives of different natures: (1) HBP-49, (2) glycerol, (3) without additive, (4) PEG, (5) OUU, (6) HBP-16, and (7) HBP-64.

coating surface by water with the use of the sessile drop method [25].

RESULTS AND DISCUSSION

Rheological properties of sol-gel systems. The TEOS-based sols are self-organizing and self-developing systems. The structure formation in the sols is accompanied by the appearance of a three-dimensional network. As a result, the system acquires a mechanical strength and its fluidity decreases. Therefore, the viscosity of sols increases as they “ripen.” The time dependences of the structural viscosity for the sols are depicted in Fig. 2. The histogram of the “lifetime” of the sols from their preparation to the transformation into the gel is represented in Fig. 3. This transformation is attended by a sharp increase in the structural viscosity (Fig. 2).

It follows from the data obtained that, at room temperature, the lifetimes of all the sols under investigation are relatively short (from five to ten days). Note that the time of the transformation from the sol to the gel can increase and decrease depending on the nature of the organic additive. Among the studied organic additives, the PEG additive leads to the formation of the most stable sol. In this case, the gel is formed only within ten days. The sol involving the HBP-16 additive has the least stability. It is of interest that the sol containing no organic additives is intermediate in the gelation rate between the most and the least stable sols.

Ravanie *et al.* [3] investigated the sol-gel system TEOS : (PEG)_n : HX = 1 : (0.5–4.5) : 0.005 (where X = CH₃COO⁻, NO₃⁻, Cl⁻, SO₄²⁻, and ClO₄⁻) similar to that studied in the present work. According to the data obtained in [3] (which agree with our experimental results), ethoxy groups of TEOS in this system interact

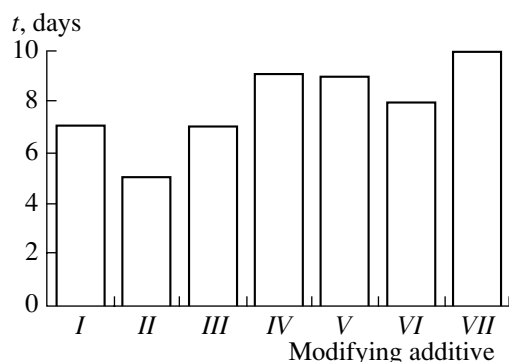
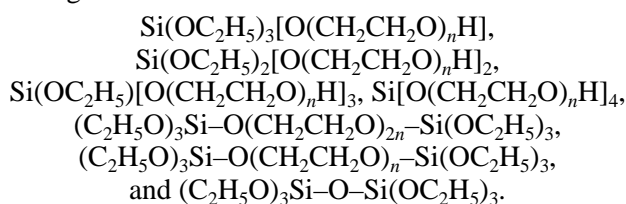


Fig. 3. Histogram of the lifetime t of the TEOS-based sols containing different modifying additives: (I) without additive, (II) HBP-16, (III) HBP-64, (IV) HBP-49, (V) glycerol, (VI) OUU, and (VII) PEG.

with hydroxyl groups to give the products with different degrees of substitution in PEG and TEOS:



This is accompanied by the release of the corresponding amount of ethanol. Such a reaction scheme in the sol-gel system suggests that, in the inorganic network, bridging poly(ethylene oxide) fragments are formed owing to the formation of the Si-O-C chemical bonds, i.e., the organically modified inorganic polymers are formed. In [3], the synthesized hybrid organic-inorganic material was referred to as the ORMOSIL, which means the organically modified silicate material prepared by mixing of TEOS with poly(ethylene glycol).

The use of glycerol in the sol-gel synthesis also retards the gelation (Figs. 2, 3). Note that the influence of glycerol, as PEG, can be likely associated with its high viscosity. At the same time, the gelation rate of the sols containing glycerol is higher than that of the sols involving PEG. This can be explained by the fact that the number of OH⁻ groups per unit molecular weight in glycerol is substantially larger than the corresponding number OH⁻ groups in PEG. As a consequence, the interaction with the products of TEOS hydrolysis and the formation of the three-dimensional network occur at a higher rate.

It is interesting that the opposite effect on the gelation time is observed for the HBP additives depending on their topology, the number of OH⁻ groups, and the molecular weight. The highest gelation rate is found for the sol containing the four-arm HBP-16 modifier in which the shell involves only 16 OH⁻ groups (Table 2). The HBP-64 modifier with the same topology as in HBP-16 but with a greater number of OH⁻ groups in the shell and an appreciably larger size has a somewhat

weaker effect on the gelation rate. By contrast, the three-arm HBP-49 modifier with a relatively small number of OH⁻ groups stabilizes the sol. In this case, the influence of the HBP structure clearly manifests itself. Moreover, compared to the four-arm HBP molecules, the three-arm HBP molecule is more hydrophobic, because it has a smaller number of hydroxyl groups and a more hydrophobic core.

Van der Waals, hydrogen, and hydrophobic bonds can participate in the formation of a three-dimensional structure of gels. The hydrophobic bonds are formed upon association of nonpolar molecular groups with each other at distances considerably larger than the sum of their van der Waals radii. This leads to the formation of aggregates composed of nonpolar molecular segments with the minimum number of contacts between water molecules and nonpolar groups [26].

The three-arm HBP-49 modifier, whose structure is more compact than that of the four-arm HBP-16 and HBP-64 modifiers, possesses a lower viscosity as compared to the initial sol (without organic additive). As a result, the HBP-49 modifier interacts faster with the hydrolysis products and modifies them. Since one HBP molecule has several active centers, the particles are efficiently stabilized at a smaller amount of the modifier as compared to the PEG additive.

Owing to the nonuniform and more directed arrangement of OH⁻ groups at the periphery of the molecule, an increase in the gelation rate in the sol containing the four-arm HBP-16 modifier is associated with the formation of chain structures. In the case of these relatively hydrophilic molecules, hydrogen and van der Waals bonds play the decisive role. Since the molecular weight of the HBP-64 modifier is higher than that of the HBP-16 modifier, the number of HBP-64 molecules in the sol is smaller compared to the number of HBP-16 molecules. This is responsible for the less pronounced decrease in the stability to the gelation for the HBP-64 modifier.

Among the organic modifiers under consideration, the OUU additive is of special interest. The introduction of this additive into the sol already within five days results in the formation of an extremely strong structural network, which retains a rheoviscometer ball at the liquid (sol) surface in a measuring vessel, whereas the transformation of the sol into the gel (the loss of the sol mobility) is observed as late as within eight days. Apparently, this is explained, first, by the occurrence of strong intermolecular interactions, which are characteristic of oligourethanes and polyurethanes with a segmental structure [27], including the used OUU modifier, and, second, by the interaction of both OH⁻ and urethane groups with the products of TEOS hydrolysis. The branched structure of the OUU molecule and the presence of CONH groups can favor the formation of bridges through hydrogen and van der Waals bonds, which leads to an increase in the viscosity of the system. Note also that the structure of flexible OUU seg-

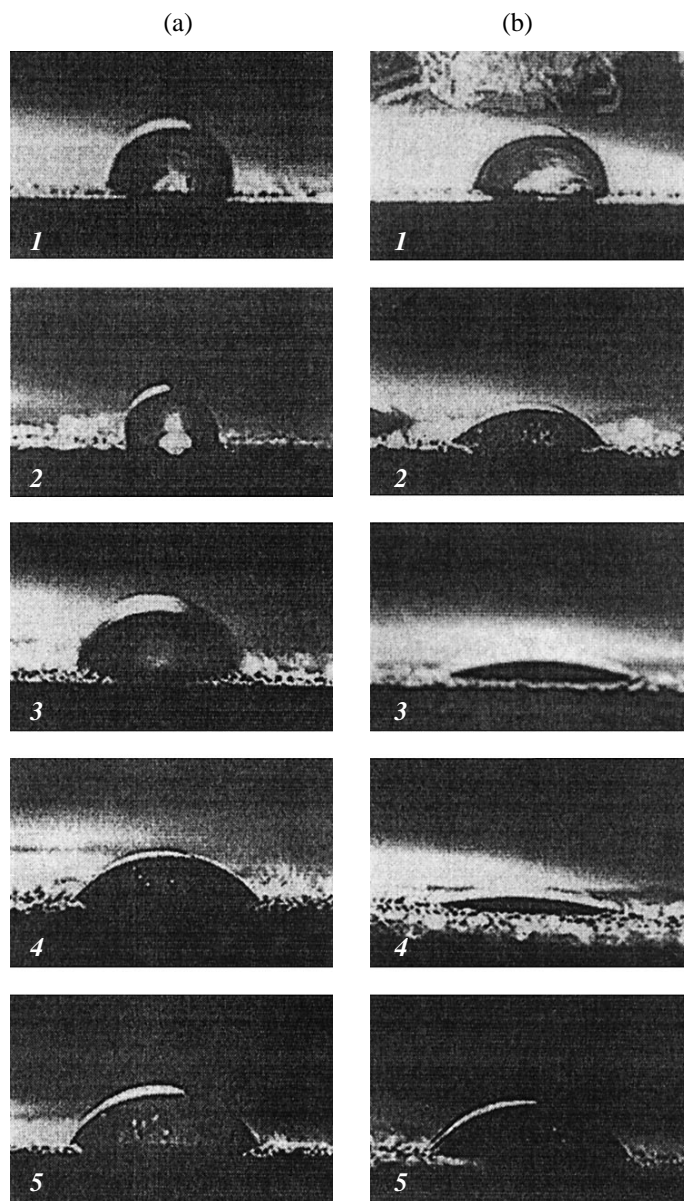


Fig. 4. Images of the water drops (a) immediately after the application and (b) within five or six seconds after the application to the surface of coatings based on the sols containing different additives: (1) PEG, (2) OUU, (3) without additive, (4) glycerol, and (5) HBP-49.

ments exhibits a pronounced diphilicity, namely, the hydrophilic [oligo(ethylene oxide)] and hydrophobic [oligo(propylene oxide)] components.

Covering power of suspensions. The wetting of the substrate surface by a liquid is the most important factor determining the adhesion of a coating to a substrate [28, 29]. As is known, metals have hydrophobic surfaces. However, the preliminary oxidation provides a way of producing a thin oxide surface film whose polar nature ensures the wetting of the surface by sols [19, 25, 28–31].

Visual examination shows that the sols without additives and with the glycerol and HBP additives spread well over the surface of nickel plates subjected to preliminary oxidation. At the same time, the sols containing the OUU and PEG additives do not spread as well. Nonwetted regions are formed on the plate surface. These observations are confirmed by the measured angles θ of wetting the substrate by the sol (Table 3).

It can be seen from Table 3 that, after introduction of the Cr_2O_3 filler into the sols and preparation of the suspensions, the angle θ decreases only for the suspen-

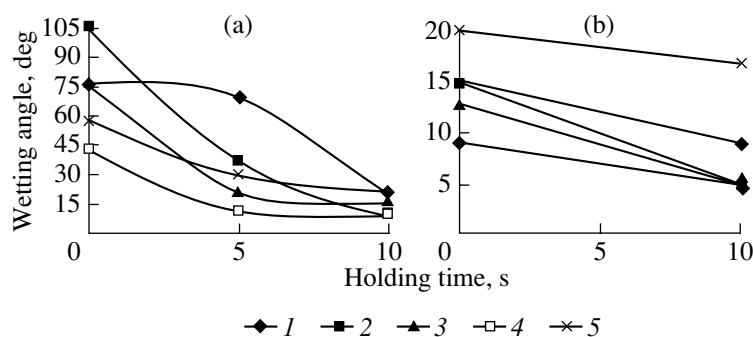


Fig. 5. Dependences of the wetting angle on the time of holding water drops on the surfaces of different coatings prepared with modifying organic additives and treated at temperatures of (a) 500 and (b) 700°C. Modifying organic additives: (1) PEG, (2) OUU, (3) without additive, (4) glycerol, and (5) HBP-49.

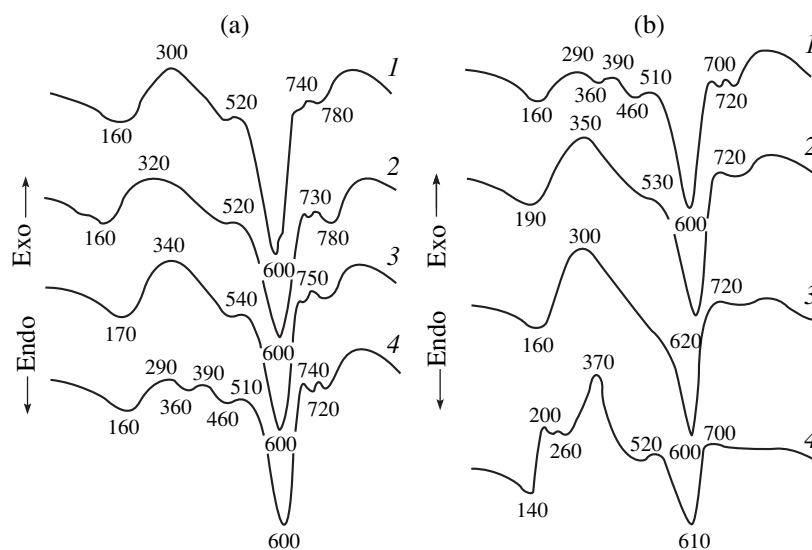


Fig. 6. DTA curves for the xerogels obtained during ageing of the sols with different additives: (a) (1) HBP-16, (2) HBP-64, (3) HBP-49, and (4) without additive; (b) (1) without additive, (2) glycerol, (3) OUU, and (4) PEG.

sions containing the high-molecular additives. It is of interest that a sharp decrease in the angle θ is observed for the suspension involving the HBP-49 additive, which is undeniably associated with the specific structural features of this polymer.

It seems likely that these effects are caused by the interaction of the low- and high-molecular organic compounds not only with sol particles surrounding powder particles but also with filler particles; as a result, the degree of hydrophobicity of the filler decreases.

Analysis of the wetting angles for the sols and suspensions of different compositions allows us to draw the inference that the low- and high-molecular organic modifiers considerably affect the wetting angle and, hence, the covering power of the suspensions. It should

be noted that the wetting angle for all the suspensions is less than 90°.

Surface morphology and the structure of the formed coatings. In a number of cases, the application of coatings with the use of suspensions is attended by undesirable effects, such as the cracking, the peeling, and the formation of defects due to a nonuniform distribution of the filler. For example, the addition of the HBP-49 modifier possessing hydrophobic properties favors the formation of a crack network over the entire surface, which decreases the adhesion strength between the coating and the substrate. By contrast, the addition of the more hydrophilic HBP-64 modifier and glycerol leads to a decrease in the number of defects and a substantial improvement of the coating quality. Our investigations reveal that the homogenization of suspensions

upon ultrasonic treatment is an efficient method that enables one to eliminate the above disadvantages. The ultrasonic treatment results in an increase in the stability of suspensions to the sedimentation and a noticeable enhancement of their covering power. The denser and more structurally homogeneous coatings were prepared after ultrasonic treatment of suspensions.

A comparison of the results obtained shows that the effect of the HBP-64 modifier on the uniformity of the filler distribution is identical to that of the ultrasonic treatment. Most likely, this is due to the ability of the HBP-64 molecule to interact simultaneously with a large number of filler particles, which, in turn, is associated with a large number of active centers in a strongly branched structure of this polymer.

Therefore, the structure of the formed coatings is affected by the HBP topology (determined by the structure of the polyols used as cores in the synthesis) and the number of OH groups in the HBP shell. In this case, the HBP modifier likely plays the role of a certain controller whose structure and a large number of OH active functional groups control the coating structure.

Hydrophilicity and hydrophobicity of coatings.

The results of investigations into the hydrophilicity (hydrophobicity) of coatings with the use of the sessile drop method were recorded in dynamics with a picture camera. The photographs obtained for the coatings heat treated at 500°C are presented in Fig. 4. The images of water drops immediately after application to the coating surface are shown at the left (Fig. 4a), and the images of these drops within five or six seconds after application are represented at the right (Fig. 4b). Immediately after application of a water drop, the coating based on the sol containing the OUU additive is characterized by hydrophobic properties (the wetting angle $\theta > 90^\circ$). However, the wetting angle decreases after holding for 5–10 s. Consequently, even this coating cannot be treated as hydrophobic. The other coatings are hydrophilic. Note that the hydrophilicity of the purely silicate coating and the coating based on the sol with the PEG additive is lower than that of the coating based on the sol containing glycerol. The drop shape considerably changes with time on all the coatings, including the purely silicate and hybrid coatings and, especially, on the coatings based on the suspensions with the glycerol additive. Within 5–10 s after application, the water drop almost completely spreads over the surface (Fig. 4). On the other hand, the drop shape more slowly changes on the surface of the coatings prepared with the use of the suspensions containing the high-molecular additives and remains virtually unchanged in the case of the PEG modifier. The observed effects can be attributed to the occurrence of pores that hinder the formation of an equilibrium wetting angle on the sample surface. Moreover, these effects can also be associated with the influence of the surface roughness, which enhances both the hydrophilic and hydrophobic properties of the coating surface [30]. Similar experiments

Table 3. Wetting angles (sol–nickel substrate)

Additive	Wetting angle θ , angular deg	
	sols	suspensions
Without additive	20	25
Glycerol	25	25
HBP-49	27	11
OUU	60	40
PEG	30	30

Table 4. Temperatures of the thermal effects observed upon heating of gels and the gelation times of sols used for their preparation

Additive	Gelation time, days	Temperature of thermal effect, °C	
		removal of physically bound water and alcohol T_1	thermal destruction of polyorganosiloxanes T_2
HBP-16	5	160	300
HBP-64	7	160	320
OUU	8	160	300
HBP-49	9	170	340
Glycerol	9	190	350
PEG	10	~200	370

were performed with the coatings heat treated at 700°C. The experimental data in the graphic form are depicted in Fig. 5. As can be seen from this figure, the above assumptions are in agreement with the fact that a considerable decrease in the wetting angle is observed for the coatings treated at a higher temperature of 700°C. This is explained by the densification of the coatings, the decrease in their roughness and porosity, and the increase in the fraction of the crystalline phase upon high-temperature treatment.

Consequently, the nature of the additive has a substantial effect on the degree of hydrophilicity of the surface. An increase in the heat treatment temperature leads to a considerable weakening of this effect, which can be associated with the destructive processes that proceed in organic fragments incorporated into the structure of the produced hybrid coatings.

DTA data. The processes occurring in the coatings during their heat treatment were indirectly investigated using thermal analysis of the gels prepared by ageing the sols and suspensions. Figure 6 shows the DTA curves of the gels produced from the sols with different low- and high-molecular additives and without additives. All the DTA curves in the temperature range 140–190°C exhibit endothermic minima associated with the

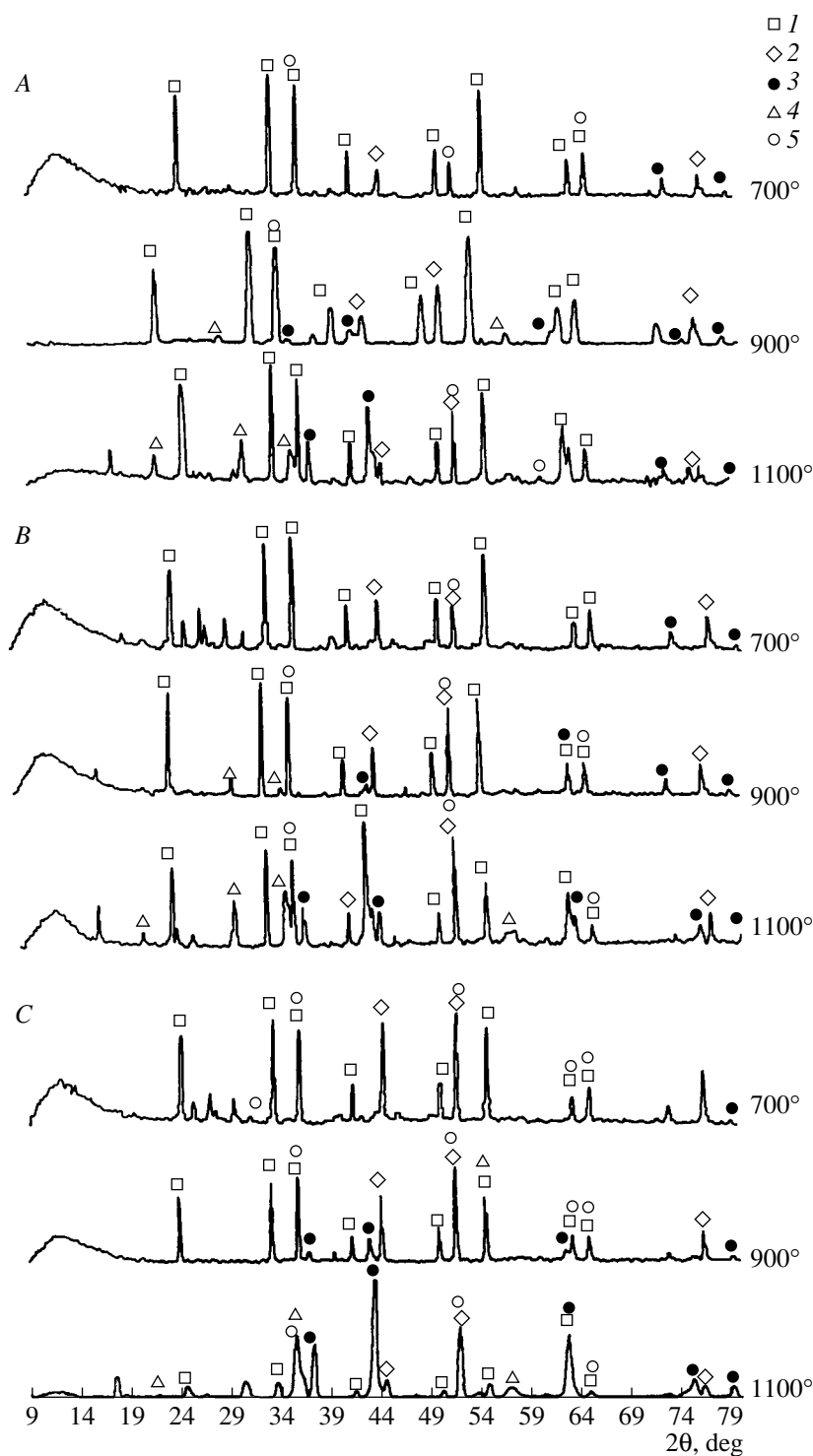


Fig. 7. X-ray diffraction patterns of (A) glass-ceramic coating applied using the sol without additives and the hybrid coatings produced from the sols containing (B) glycerol and (C) HBP-49 additives.

removal of crystallization water and alcohol [1, 2, 19, 32, 33]. The characteristic exothermic maxima at 290–390°C are observed in all the DTA curves. This effect is most pronounced for the sol containing the PEG additive

and least pronounced for the sol without additives. According to [33], the exothermic effect under consideration is attributed to the structural transformation of polyorganosiloxanes and the formation of amorphous silica.

Numerous endothermic and exothermic effects observed in the temperature range 200–400°C in the DTA curves for the gel without organic modifying additives can be associated with the decomposition of the inorganic modifying additives (metal salts) [19, 34]. These effects are often masked by the effects due to the organic modifying additives. The introduction of the organic and polymeric additives results in an appreciable increase in the area of the observed peaks, which suggests the complete decomposition of the gels and the formation of a homogeneous mixture of reactive amorphous oxides [33]. Therefore, the DTA curves for the xerogels obtained from the sols containing different additives differ noticeably. This indicates that the low- and high-molecular compounds substantially affect the TEOS hydrolysis, the subsequent polycondensation of the hydrolysis products (resulting in the formation of the inorganic polymer network), and the attachment of the organic fragments to the inorganic network.

It is of interest to compare the DTA data for the gels, which reflect the correlation between the bond strength in the organic–inorganic composite and the stability of the sols (forming the composite) to the gelation (Table 4).

As can be seen from Table 4, crystallization and adsorbed water and alcohol in the gels prepared from more stable sols containing the PEG, glycerol, and HBP-49 additives are removed at higher temperatures T_1 as compared to the gels obtained from the sols with a lower stability. This implies that the formed bonds are stronger in the more stable sols and the gels on their basis. On the other hand, it is known that an increase in the temperature leads to a weakening of hydrogen and van der Waals bonds and a strengthening of hydrophobic bonds. Therefore, the formation of a stronger structural network requires a longer time and this network can undergo destruction at a higher temperature. This regularity even more clearly manifests itself in the temperature range corresponding to the thermal destruction of the organic components and the onset of the structural transformation of polyorganosiloxanes with the formation of silicon–oxygen tetrahedra (T_2). The behavior of the gels produced from the sols containing the OUU modifier with urethane groups (in addition to hydroxyl groups) slightly deviates from the above regularity.

X-ray powder diffraction data. The X-ray diffraction patterns of the glass-ceramic and hybrid coatings are shown in Fig. 7. All the coatings were deposited on nickel plates and were then annealed for 1 h at 700, 900, and 1100°C. Numerous weakly pronounced maxima and amorphous halos are observed in all the X-ray diffraction patterns (Fig. 7). This suggests that crystalline and amorphous phases coexist in the studied materials. As can be judged from the X-ray diffraction patterns, the content of the amorphous phase is relatively low. Most likely, a considerable width of maxima indicates

that coherent-scattering regions (crystals) are small in size. All the X-ray diffraction patterns contain clearly defined diffraction maxima corresponding to the Cr_2O_3 filler (interplanar distances, 0.267, 0.248, and 0.167 nm). It is found that crystalline SiO_2 is formed in the form of α -cristobalite (interplanar distances, 0.405, 0.312, and 0.247 nm). Note that the content of the crystalline phase likely increases with an increase in the temperature. There are the diffraction maxima associated with Ni (interplanar distances, 0.203, 0.176, and 0.125 nm), NiO (interplanar distances, 0.209, 0.241, and 0.148 nm), and SrO (interplanar distances, 0.252, 0.208, and 0.181 nm). As can be seen from the X-ray diffraction patterns, the amorphous (vitreous) phase is formed at 700°C in all the coatings, which can be judged from the amorphous halo at scattering angles in the range characteristic of the cristobalite [35]. The introduced additives, such as HBP-49 and, especially, glycerol, favor the retention of the vitreous phase with an increase in the temperature, which improves the gas impermeability and corrosive resistance of the coatings. Similar results were obtained for the coatings based on the sols containing the OUU additive [23].

Therefore, from analyzing the X-ray powder diffraction data, it can be concluded that the silicate glass-ceramic coatings are formed from the suspensions with and without low- and high-molecular organic additives. The main difference lies in the content of the vitreous phase formed, especially, upon treatment at high temperatures (above 900°C).

CONCLUSIONS

Thus, the results of the above investigation allowed us to draw the inference that the introduction of polyhydroxyl low- and high-molecular organic compounds into the TEOS-based sols doped with metal nitrates makes it possible to control a number of characteristics of the sol–gel systems and the coatings formed on their basis. These characteristics are as follows: (i) the time stability of the sols (retardation or promotion of their transformation into the gel) and the strength of fragments of the structural gel network formed in the sol, (ii) the wetting power of the sols and suspensions produced by adding finely disperse Cr_2O_3 to the sols, (iii) the degree of hydrophilicity of the surface of the formed hybrid coatings, and (iv) the structure and the phase composition of the hybrid organic–inorganic coatings.

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