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# ORGANOSILICATE ADHESIVES:
# COMPOSITION – STRUCTURE – PROPERTIES – APPLICATION

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**Abstract**

*Organosilicate composites (OSC) are widely used as weather- and corrosion-proof, electrically insulating, radiation- and heat-resistant adhesives.*

*OSC represent suspensions of finely dispersed layered silicates (mica, talc, chrysotile), inorganic or organic pigments in solutions of organosilicon oligomers, containing various special modifiers (curing agents, plasticizers, vitreous additives etc.)*

*The peculiarities of their manufacturing and forming are responsible for their structure, properties and application areas.*

**Key words:** *coating, formation, interphase interaction, organosilicate composition, thermooxidative destruction, solid-phase reactions, structural transformations in the material, polyorganosiloxanes, dehydroxylation of layered hydrosilicates,*

## 1. INTRODUCTION

Organosilicate composites (OSC) are widely used as coatings, glues and vacuum-tight sealants and press-materials in our country and abroad as materials that possess unique functional properties [1].

More often OSC are used as organosilicate coatings (OSCt). OSCt, on the one hand, can play a role of a barrier layer which limits chemical processes of oxidation and corrosion or slow down diffusion processes (corrosion-proof coatings); or give to a substrate new electric and magnetic properties by creation of electro conducting or electro insulating, magnetic or antimagnetic layers (electrical conducting or electrical insulating); or disseminate or absorb radiation (radiation-resistant), ets. The majority of OSCt properties are manifestations of characteristics of a bulk material. In particular, the anticorrosive properties can be considered as a function of adhesive-cohesive interactions, permeability of the coating with respect to different reactants, and the glass transition temperature of the coating. The heat resistance depends on the bond energy of components, structural regularity, molecular mobility, and intermolecular interaction in the bulk of the material

On the other hand, the coating can give new properties to a substrate due to special properties of its surface, for example, the ability to be deactivated or self-cleaning**,** to reflect streams of energy and light (reflecting) and others**.**

There are a number of properties predominantly associated with the low-energy character of the surface of OSCts (such as low dirt-holding capacity, decontamination ability, hydrofobicity, etc.). At present, it has been universally accepted that the surface energy of the coating reflects not only the chemical nature of the film former but also a change in its composition and properties in the course of formation and operation [2, 3].

In this report the main physical and chemical regularities of correlations "organosilicate composite composition – technology for production and application – structure – properties" are considered.

## 2. STRUCTURE and PROPERTIES of ORGANOSILICATE COMPOSITES

OSC represent suspensions of finely dispersed layered hydrosilicates, inorganic or organic pigments in solutions of organosilicon oligomers, containing various special modifiers (curing agents, plasticizers, additives, etc.) [4].

At present, film formers are represented by commercial organosilicon varnishes prepared by hydrolytic copolycondensation of mixtures of bi- and thrifunctional organochlorosilanes. Synthesized by this method oligomers have rather complex structure with random distribution of linear, branched, cyclolinear, and ladder fragments. Polyorganosiloxanes (POS) contain methyl and phenyl radicals at silicon atoms, and are characterized by a broad distribution of molecular masses, have silanol terminal groups. Both unmodified organosilicon polymers and those modified during so-called reactionary mixture of components by organic polymers, for example, by polyesters, alkyd and epoxy resins, are used extensively.

Numerous properties of POS are considered to be features associated, first, with the presence of the siloxane bond in the backbone, and, second, with the chemical structure. The presence of siloxane bonds in the aforementioned organosilicon film formers assumes an opportunity of two operating modes of OSCt [4].

1) At temperatures below the destruction temperature of the organosilicon film former the coating operates as paint and varnish coating; glues and sealants – as polymeric composite material with a wide temperature interval of application (up from minus 60 to 300 – 400°C).

2) At temperatures above the destruction temperature – as high-temperature inorganic coating which is formed through interactions of products of thermooxidative destruction of POS with mineral components, solid-phase reactions, and structural changes occurring in the material.

The structural features of macrochains of these POS are also responsible for a number of disadvantages inherent in the film formers under consideration. First and foremost, these are low physicomechanical properties, unsatisfactory resistance in liquid corrosive media and solvents, and the necessity of high-temperature curing and the presence of toxic aromatic solvents.

These disadvantages can be eliminated with the use of following techniques: filling and reinforcement of polymers; blending with different organic pitches containing polar groups; using various curious agents; introduction of functional groups into the organic fragments of the molecule, etc.

Inorganic pigments and fillers are introduced into the composition of OSC for heat-resistant protective coatings.

For OS-materials the choice of pigments is governed by the field of application and the corresponding operating properties. The main characteristics are given below (Table).

By present time a great positive experience of using organic pigments and dyes in composition of weatherproof OSCt has been accumulated. In formulations of chemically proof, heat-resistant, electro insulating OSCt inorganic pigments such as oxides and salts of transition metals have been predominantly used. The most widespread fillers of OSCt are the following mechanically dispersed natural fillers: chrysotile asbestos, muscovite mica, talc, barite, and synthetic filler Aerosil, modified sepiolites.

Modern rheologic additives have been extensively used to increase the sedimentation stability in the

course of storage and flow of OC-suspensions.

### 3. PROCESSES of ORGANOSILICATE COATINGS

By now, it has been revealed that OSCt can be efficiently cured at relatively low temperatures of heat treatment under natural conditions with the use of a number of agents [3, 4]. The most widely used curing agents are as follows:

– tetrabutoxytitanate (TBT) and poly(butyl titanate) (PBT);

– 1-amino-hexamethylene-6-aminomethylenetriethoxy-silane (AGM-3);

– a mixture of γ-aminopropyltriethoxysilane with β- aminisoopropyltriethoxysilane (AGM-9);

– diethylamine (DEA) in combination with tetraethoxysilane (TEOS) or TBT;

– polymethylsilazane (MSN-7);

– polymethylphenylsilazane (MFSN-5);

– boron-containing polymethylphenylsilazane (MFSN-B).

**Table –** Properties of cured coatings

| | |
|---|---|
| Heat resistance, °C | |
| short-term | 300 – 700 |
| long-term | 1200 |
| Impact strength according to GOST (National Standard 4765, N·cm (kgf·cm) | 250 – 500 |
| Flexural Strength according to GOST (National Standard ) 6806, mm | (25 – 50) |
| | 3 – 15 |
| Hardness according to GOST (National Standard) 5283, arb. units. | 0.3 – 0.7 |
| Adhesion to steel, aluminum according to GOST (National Standard ) 15140, (cross-hatch test), points | 1 – 2 |
| Adhesion to steel according to the 90º peel test, MPa | 2 – 7 |
| Volume electrical resistivity, Ω cm: | |
| at 20 °C | $10^{12} – 10^{15}$ |
| at 500 °C | up to $10^{9}$ |
| Dielectric strength at 20 °C, kV/mm | 10 – 50 and more |
| Dielectric loss tangent | 0.008 – 0.1 |
| Dielectric permittivity | 3.0 – 6.0 |
| Temperature coefficient of linear expansion in an interval of 20 – 300 °C, $K^{-1}$ | |

| | |
|---|---|
| | $(1 – 2) \times 10^{-5}$ |
| Heat conductivity, W/ (m K) | 0.3 – 0.6 |
| Specific heat capacity, kJ /(kg K) | 0.6 – 1.5 |
| Radiation resistance: | |
| in beta and gamma radiations fields | $10^6 – 10^8$ |
| at doses, Gr (rad) | $(10^8 – 10^{10})$ |
| in neutron fields (air–vapor medium) | |
| at integral dose, thermal neutrons/cm$^2$: | |
| > 20 000 h, 280 °C | $1 \times 10^{14}$ |
| > 10 000 h, 150 °C | $1 \times 10^{21}$ |
| Diffuse reflectance of light from coatings: | |
| white color and light tones | 85 – 92 |
| red, green, blue, brown, orange colors | 60 – 80 |
| black color | 50 – 55 |
| Hydrophobic properties (contact angle), degree | 90 – 110 |

Almost all the studied curing agents accelerating the curing process result in a decrease in the heat resistance and elasticity of the coating approximately to the same extent, viability of OSC containing the curing agent is satisfactory only for few from them.

It is known, that at application of curing agents in OSM there can be following physical and chemical processes:

– the acceleration of homocondensation of OH-groups of polymers resulting in their cross-linking;

– the condensation of OH-groups of polymer molecules with functional groups of a curing agents;

– an increase of thermo stability of cross-linked polymers due to the introduction of heteroatoms or heteroatomic groupings of curing agents into the polymer network;

–an increase in the thermooxidative stability due to the introduction of groupings possessing the antioxidant properties.

The specified processes are characteristic for all types of curing agents, but for each agent it is possible to find prevailing.

As in the case of the TBT, PBT agents the presence of reactive ethoxy groups in AGM-3 and AGM-9 curing agents results in the condensation of silanol groups of polyorganosiloxanes with functional groups of the curing agents. However, since AGM-3, AGM-9 and AM-2 molecules contain amino groups the curing ability of these products is a little bit higher than that of the TBT or PBT agents

The advantage of OSC involving polyorganosilazanes manifests itself in decreasing the formation time, the preparation of films with high hardness and adhesion, and the ability of materials produced by cold curing to remain in an unsoftening state upon heating. In some cases appears the alcohol and gasoline resistance, in all cases the water absorption decreases as a result of an increase in the gel fraction contents. The application of several layers enables one to decrease the time of drying between

the application of layers and the time of complete drying. At the same time, viability of OSC with introduced polyorganosilazanes in some cases appears to be insufficient: viability of mixtures of composites with MFSN-B reaches 5 – 7 days, with MFSN-5 – 3 – 24 h, and with MSN-7 – from 30 min up to 2 h.

At use of a complex curing agent the structuring of polymethylphenylsiloxanes is caused by amine, and also by TEOS which, in turn, is activated by amine due to the interaction of not divided electron pair of the nitrogen atom and *d*-orbitales of the silicon atom. It is considered, that in these conditions there is a formation of cross-linked structure in POS due to the amine-induced homocondensation of silanol groups, and the interaction of silanol groups with hydroxyl groups of TEOS derivatives formed upon hydrolysis of the curing agent. In other words, at application of this curing agent processes I and II are prevailing. At introduction of 1 wt % of the complex curing agent (TEOS+DEA) in the ratio of 1:0.4 into polydimethylphenylsiloxanes or polymethylphenylsiloxanes the gel fraction content achieves 85 – 95 wt% for 24 – 36 h.

The humidity of surrounding air also affects the curing rate. In dry air the process goes faster as curing process is associated with the removal of moisture from the system. For the same reason, the curing rate of OSCt goes faster in a thin layer, than in a thick one.

The type of film former and the curing parameters affect the technological properties (the viscosity, durability, flow properties, drying time); hardness, adhesion, impact strength, flexural strength, and other physicomechanical properties; sol–gel fraction content; protective properties; heat resistance; and electrically insulating properties. As a rule, the set of these properties determines the service life and service reliability of OSCts. The energy characteristics of the surface of OSCts and the related decontamination ability, a low dirt-holding capacity, hydrophobicity, and anti-icing effect, i.e., the surface properties of OSCts, should be sensitive to a change in the chemical composition of the surface layer and its texture.

The curing of OSCts in the course of heat treatment, as a rule, is associated with the condensation of silanol terminal groups of POS and the removal of $H_2O$ thus formed from the coating. An increase in the temperature accelerates these processes and makes it possible to achieve a more complete curing. The kinetics of curing and aging of organosilicate composites is affected by oxidants of the environment (for example, oxygen) and the oxidizing and reducing agents introduced into the composition of organosilicate composites.

## 4. PROCESSES OF ORGANOSILICATE MATERIAL AGEING

Ageing of OSCt under various operating conditions manifests itself in the loss of gloss, chalking, cracking and peeling and under-film corrosion. Change of conditions of ageing determines a kind and a degree of destruction of OS-materials. Ageing is accompanied not only by chemical transformations, but also by the processes of structuring playing the important role in destruction of original organosilicate polymeric materials and forming new organic-inorganic and inorganic glass-ceramic material.

As for the second mode of operating and ageing [5], both in inert, and in the oxidizing atmospheres the main volatile products of decomposition of OS-coatings are methane, benzene, hydrogen, water and cyclic siloxanes. In an interval of temperatures 300 – 1000 °C (and above) the structure of volatile products remains constant, their only relative content varies. In oxygen and air atmospheres in addition there are carbon dioxides and carbon monooxides, the water content increases as a result of secondary processes – oxidation of benzene, hydrogen, and methane, formic acid and formaldehyde.

As destruction of organosilicon binders leads to decrease in water repellency, increase of porosity

which manifests itself in deterioration of protective, electro-insulating, physical mechanical properties of OSCt fusible additives are used in formulations of OSC.

## 5. EXAMPLES OF SOME FUNCTIONAL ORGANOSILICATE COATINGS

*5.1 Corrosion protective OSCts*

According to the mechanism of protective effect under conditions of the first mode of operating and ageing, that is up to temperatures 300 – 400 °C, OSCts for the most part belong to the mixed barrier-adhesion type since they produce a good diffusion barrier, on the one hand, and prevent the development of underfilm corrosion, due to satisfactory adhesion, on the other hand. The barrier effect of protective effect of OSCts is enhanced by increased water repellency and is determined by structural morphological features of their surface. The determining factor of corrosion destruction of OSCts is the contact with moisture. The optimum thickness of OSCts, intended for operation under these conditions, on metal surfaces is equal to 150 – 200 μm and no less than 100 μm at painting on concrete, brick, plaster surfaces.

*5.2 Radiation-resistant OSCts*

OSCts, rendered on carbonaceous steel or on a layer of aluminum which possesses high radiation-thermal resistance in vapor atmosphere up to an integrated doze of an irradiation equal to 2.8 MGr, irrespective of capacity of a doze are developed. According to the radiation resistance (2.8 MGr) OSCts can be applied for protection of surfaces of rooms in served and unattended zones of the atomic power station which can contact with vapor-gas mix at heavy failures and failures such as "small" or the "big" leak (LOCA, LLOCA).

*5.3 Electrical insulating OSCts*

Electrical insulating OSCts are characterized by the following parameters:

– a range of working temperatures: from a minus 60 up to (350 – 500) °C;

– volume electrical resistivity ($\rho_v$), Ω·cm

at 20 °C: $10^{12}$–$10^{15}$

at 200 °C: $10^{10}$–$10^{12}$

after influence of a damp atmosphere: $10^{9}$–$10^{11}$;

– dielectric durability (E), kV/mm no less than 20;

–dielectric loss tangent (tg δ): less than 0.08;

(at change of temperature from 20 up to 400 °C tg δ grows from 0.02 till 0.38).

For comparison: alkyd enamels: (GF-571, GF-916, GF-5109) have lower values of $\rho_v$ ($10^{8\text{-}12}$ Ω·cm), narrower range of working temperatures (from a minus 60 up to plus 80 °C).

Epoxy enamels (EP-56) and composites for electrical insulating purposes (EP -115, EP -153) work in a temperature range (from a minus 60 up to plus 200 °C), at 20 °C have good parameters of $\rho_v = 10^{14\text{-}15}$ Ω·cm; E = 20 – 25 kV/mm, ε =4, tg δ = 0.02. But at rise in temperature up to 100 °C deterioration of properties is observed: $\rho_v$ changes on 4 orders up to $10^{9}$ Ω·cm, tg δ grows by the order – at 100 °C tg δ = 0.1.

The resulted comparison of parameters for coatings of the different nature shows advantages of OSCts in comparison with organic enamels, caused by characteristic for OSM's combination of resistance to

high temperatures and sufficient level of dielectric properties.

Dielectric OSCts are applied to protect of various radio components and radio engineering devices (resistors, condensers, small-sized transformers and etc).

*5.4 Gradient OSCts*

Energy characteristics of surface of OSCts and connected with them ability of self-cleaning, deactivation, low dust-holding, water repellency, anti-icing properties [6], reflecting effect, that is properties of surface of OSCts, are adjusted by a chemical formulation of a surface layer and its texture. The choice of structures of OSCts and special modes of curing allow creating coatings in which a surface of a coating carries one function and the volume phase –another. In anti-icing [6] and radiation-resistant deactivated OSCts the gradient of composition and structure is essential.

In a basis of layer-to-layer-non-uniform structure of the majority of OSCts the following feature of organosilicon varnishes lays: at drawing there is an orientation of macrochains to a substrate, the inorganic part of polymers (Si─O─Si bridges) cooperates with a surface of a substrate in such a manner that organic groups of POS settle down on a surface of a coating as small umbrellas and give to a coating low adsorbic properties. Properties of a surface are determined by rather thin layer of a coating (no less than 1 – 3 μm) and set by low values of surface energy. For steady characteristics for weatherproof OSCts the optimum values of surface energy are no less than 40, for radiation resistant deactivated OSCts – 30 and for anti-icing OSCts – 25 $mJ/m^2$.

*5.5 Application of organosilicate composites in tensometry*

OSC are used in tensometry as high-temperature glues and binding for manufacturing and adhesion of tensoresistors (strain gauges).

A number of requirements, many of which are difficultly compatible, especially such as high adhesion to various constructional materials and high electric resistance in a wide range of temperatures, are imposed for binders for high-temperature tensoresistors. High-temperature tensoresistors with OSC are used for measurement of stresses on details and units of machines of nuclear power installations in a range of temperatures from a minus 60 up to +900 – 1200 °C. Adhesive seams and coatings on the basis of these OSC are temperature stable at rather high temperatures.

*5.6 Organosilicate sealant pastes*

Organosilicate sealant pastes have a consistence of dense sour cream. The consistence of pastes is determined by the contents of a thinner and can be easily changed by its decreasing or increasing. Thus it is necessary to keep the uniformity of a material as a whole not to be broken.

It is established, that at the contents of volatile phase in paste within the limits of 5 – 7 wt % the paste easily can be applied with injector, and the paste fills narrow (1 – 2 mm) clearance under action of small pressure and allows rather small shrinkage in process of curing.

Sealant pastes have found wide application for hydrophobic thermo- electrical insulating protection of precision wire resistors.

*5.7 Glues for pasting electric technical steels*

Glues for pasting electric technical steels are applied at manufacturing of packages of magnetic circuits. The feature of application of OSC as temperature resistant glues and pastes is the requirement to a degree of grinding: depressiveness of particles should be high, no less than 5 – 25 μm.

*5.8 OSC for restoration works*

Choice of OSC for restoration works is determined by several requirements, basic of which is the

durability. The volume of restoration works is great, in this connection repeated restorations of buildings and constructions are not planned, choose, as a rule, the most durable material. OSC meet these requirements. The application of OSC in restoration of historical and cultural monuments in Russia has almost thirty-year experience. OSC were used as protective-decorative coatings on plaster, concrete and brick building facades, and for protection of black and nonferrous metal structures, as impregnation materials for strongly destroyed wood.

*5.9 Organosilicate press-materials*

Organosilicate press-materials are rather new kind of heat resistant constructional materials of heat and electric insulating purposes, received upon technology of plastics. By present time practical application was found for two kinds of it: organosilicate composite-silica fabric press-material and organosilicate molding fibro material.

## 6. CONCLUSIONS

Thus, the design of functional coatings still is a key stage in the development of new materials with desired properties. Stated differently, a layer of organosilicate composite fulfills a function not typical of the substrate material and conventionally provides protection against various chemical and physical factors.

Naturally, functional properties of coatings are governed by the set of factors: coating composition and physicochemical and mechanical properties of constituents, preparation procedure, curing and application methods.

The reliability and duration of organosilicate adhesives are highly affected by operating conditions and substrate nature.

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