

DURABILITY OF ORGANOSILICATE COATINGS FOR MOLD FUNGI

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Abstract

Index of organosilicate coatings durability for molds fungi depends on their chemical composition, method of formation, phase state and can be modified by a variety of physical and chemical factors of aging. Natural aging process magnifies the contamination of material by microorganisms and vice versa.

Key words: *organosilicate coating, polyorganosiloxanoles, layered hydrosilicates, pigments, fungal resistance, curing method, aging process, smooth aligned surface, surface roughness.*

1. INTRODUCTION

Organosilicate compositions are suspensions of finely dispersed fillers – layered hydrosilicates, pigments in solutions of organosilicon oligomers containing various target modifiers (hardening agents, plasticizers, etc.). Organosilicate materials based on organosilicate compositions have been widely used in various fields of material production as high adhesives, vacuum-tight sealant, pastes. Coatings based on organosilicate compositions have been successfully used as a weather resistant, anti-corrosion, radiation-resistant, anti-icing, heat-resistant and insulating [1 – 3].

During operation of organosilicate coatings in some cases there may be conditions favorable for the growth and development of fungi, bacteria and other microorganisms. It is known that the most common types of microscopic fungi affecting polymer coatings are fungi of the genus *Aspergillus* and *Penicillium*, and *Alternaria alternata*, *Fusarium moniliforme*, and *Trichoderma viride* [4]. For silicon coatings – *Aspergillus amstelodami*, *Aspergillus flavus*, *Aspergillus niger*, *Penicillium chermisinum* and *Penicillium sporum* [5]. Products of microscopic fungi metabolism on polymeric materials are different kinds of organic acids [4]. Propionic, succinic, apple, citric, oxalic, gallic and pyroracemic acids are most often found on the surface of the silicon coatings. The total concentration of them, depending on the polysiloxane may be $(0.99 – 3.05) \cdot 10^{-3} \text{ g / L}$ [5].

It is well known that the presence of non-fungi-resistant component in the coating formulation reduces the stability of the overall material. In this regard, there is need for careful selection of components for formulations of organosilicate fungus-resistant coatings.

On the processes of biodegradation of organosilicate coatings the following factors can affect: the chemical composition of the coating, method for forming the coating, the phase state and the processes of aging, when the course of which can vary chemical composition and phase state of the coating.

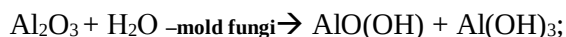
2. FACTORS AFFECTING BIOLOGICAL STABILITY OF ORGANOSILICATE COATINGS

In general, it is film-forming agents – synthetic unmodified and modified with organic resins polyorganosiloxanes – largely determine the biological stability of organosilicate coatings. It is well known that the fungus-resistance of synthetic film-forming materials and coatings decreases in the

following order: Epoxy> Polyurethane> Melaminoalkid> Organosilicon> Pentaftal. Modified polymeric thermosetting resins (Glyptal, Phenolic etc.) with drying oils or fatty acids, improving processing properties obtained with fatty paints and stoving enamels, resulting in a decrease in fungal resistance of protective coatings, due to the relatively low resistance to molds of modifying components.

The decisive role in the effects of mold on the organosilicon film-former is assigned to lateral hydrocarbon radicals [5]: organosilicon matters with ethyl radicals at the silicon atom have less fungal resistance than the polyorganosiloxanes with methyl and phenyl radicals. Action of microscopic fungi on polyorganosiloxanes with phenyl and ethylphenyl radicals is characterized mainly with destruction of hydrocarbons frameworks, including the phenyl ring cleavage. Degradation of hydrocarbon radicals leads to a marked decrease of hydrophobicity. For organosilicon polymers with methyl and phenyl radicals at the silicon atom microbial action reduces the strength of the Si–O–Si bond. The use of organosilicon coatings containing no fungicide groups is considered promising for increasing the resistance of materials to the action of fungi. However, such coatings during prolonged operation undergo significant decay associated with the cleavage of the Si–O–Si and Si–C bonds and their oxidation. Necessary fungal resistance can be achieved through the introduction of appropriate fillers.

Among the most common inorganic compounds which may be used in the organosilicate compositions, the most fungal resistance (after 28 days of test according to GOST 9.049-91 [6], media – distillate) Cu_2O , CuO , ZnO , MgO , BaO , and also B_2O_3 , TiO_2 , SnO_2 , PbO , WO_3 , Ni_2O_3 can be attributed [5]. For 60 days fungal resistance of Al_2O_3 increases with the score of 2 to 0 points, which is explained by the formation of hydroxides on the surface of the coating when exposed to micro-organisms on the anhydrous Al_2O_3 with subsequent inhibition of their growth by acid-base binding metabolites or direct processes of hydroxide formation on a partially-hydrated oxide. The chemical mechanism of the interaction of the species of Al_2O_3 with fungi can be schematically represented as follows (which may explain the long display of fungicidal properties) [5]:



Minimum resistance to fungi observed in silica (4 points) and iron oxide III (5 points). Oxides of cobalt III and chromium III are intermediate (fungus-resistance 2 – 3 points). With the increase in atomic weight of elements within II, III and IV of the periodic system the fungal resistance of oxides is significantly increased. Fungal growth on the dispersed oxides is accompanied by considerable waste products presented in the main by organic acids: hydroxy acids, monobasic, saturated and unsaturated dicarboxylic acids. Changing the properties of disperse oxides is mainly due to the growth of fungi directly, as well as the influence of metabolic products.

Action of fungi to disperse silicates is characterized by a decrease of the concentration of hydroxyl ions in the reaction medium. Depending on the type of material the pH is reduced to 0.05 – 0.56, the maximum increase in the concentration of hydrogen ions is observed in the least fungus-resistant silicates (perlite, fly ash thermal power plants, clay hydromicaceous).

The silicates destruction process starts with the leaching the least chemically stable elements Na and K when exposed acidic metabolic products, and with enrichment an aqueous solution with ions of H^+ ,

OH^- and H_3O^+ and then ions of magnesium, calcium, iron, and finally the silicon (the latter occurs when significant lesion of material by fungi). appear in the solution

Several silica fillers used in the organosilicate coating formulation containing 50 – 75 wt. % of SiO_2 are more susceptible to infection by microscopic fungi than layered hydrosilicates (talc, mica, muscovite, etc.) in which the decrease of SiO_2 (by increasing the content of Group I and Group II elements) leads to an increase in fungal resistance [5].

Usually smooth aligned, shiny film surface is harder polluted due to the absence of irregularities or roughness contributes to increased fungal resistance. In this regard, great importance is the ratio of polymer: filler in the formulation and method of organosilicate coating forming: hot curing coatings generally have a less rough surface. Figures 1a and 1b show the optical images of the surface of the organosilicate coatings of «hot» and «cold» cure [7]. Heat-cured coatings have a smooth aligned, shiny film surface is harder polluted due to the lack of (or minimizing) the irregularities and roughness, thereby reducing dirt retention in coatings, increase their fungal resistance. The curing method also determines the permeability and hardness of organosilicate coating. «Hot» curing, high drying speed of film-forming agent, reducing moisture absorption during curing tend to allow to achieve a higher resistance to degradation of coatings by microorganisms. However, the current technology to protect the majority of objects requires the use of curing agents at relatively low temperatures.



Fig. 1. The optical images of the organosilicate weather-resistant coating surfaces of «hot» (a) and «cold» curing (b), aminopropyltriethoxysilane as a hardener. Label – 25 microns [7]

3. GENERAL APPROACH TO THE CREATION OF FUNGUS-RESISTANT COATINGS

Resistance to contamination is one of the most important factors determining the fungal resistance of coatings, as well as various kinds of pollution can serve as nutritional substrates for the growth of bio-destructors.

One of the modern approaches to building easy-to-clean coatings is based on the three-parameter system [8]. It is believed that there are three defining parameters: mechanical properties, surface free energy and surface morphology of the coatings. Figure 2 shows the triangle of dirt retention / clean-ability, the shaded portion of which corresponds to the optimal values of key parameters.

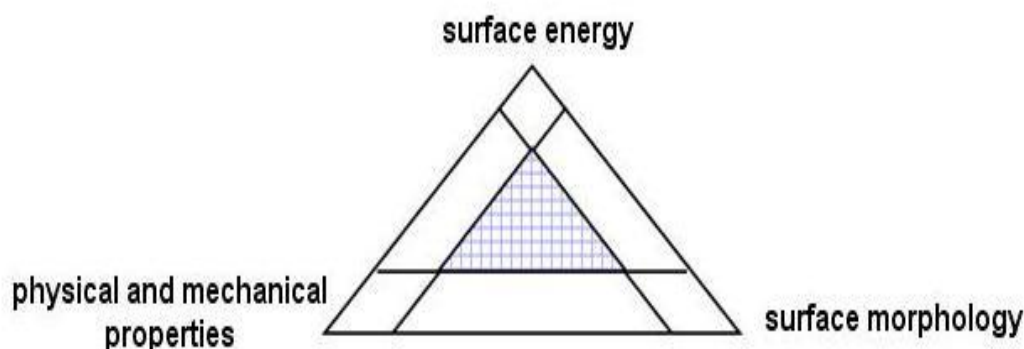


Fig. 2. The parameters defining the dirt retention / clean-ability of polymer coatings [8]

The optimal structure of easy-to-clean polymer coating is the coating with enough hard polymeric matrix, the minimum roughness and low surface energy. In many cases, chemical resistance [8] and, in general, – resistance to external (physical – for example, radiation, temperature, electric fields – and chemical) factors must be considered as the fourth parameter.

However such a parametric diagram is not exhaustive. It is known that some elastic silicone coating demonstrate low dirt retention and are also easily cleaned, and specific surface topography of the coating may give it even greater soil release properties than the smoothness of surface [9, 10].

4. FUNGAL RESISTANCE OF ORGANOSILICATE COATINGS

Study on fungal resistance for a number of electrical corrosion-protective organosilicate coatings (national standard GOST 9.050-75 [11]) shows, that the coatings exhibit fungi-static properties and retain all necessary characteristics after exposure to microscopic fungi (Table 1) [12].

The following characteristics combine all investigated coatings:

- a) Large coating hardness that is achieved due to the high degree of filling the organosilicate composite and operating in the presence of chromium III oxide in formulation as a pigment;
- b) Low permeability coatings with respect to a series of chemical agents that in turn is achieved by using film-former modified with polyester, and «hot» curing.

In the surface coating layers, carriers of hydrocarbon radicals are, giving low adsorption properties, and in the lower layers – carriers of polar groups that provide adhesion to the substrate. Examples are organosilicate coatings based on stratifying system of polyorganosiloxanes of different structure: a branched polydimethylphenylsiloxanes with gross formula $[(CH_3)_2SiO(C_6H_5SiO_{1.5})_{1.25}]_n$ and linear polydimethylsiloxane- α , ω -diol.

Gradient coatings based on stratifying mixture of organosilicon polymers were stable in different climatic zones, including in tropical climates. Fungal resistance of these coatings is evaluated by points 0 and maintained for a long period of time [13]

Table 1. Fungal resistance of electro-insulating organosilicate coatings

Properties	OS-91-26	OS-92-25	OS-82-05	OS-52-01
Volume resistivity, ρ_v , Ohm·cm, at 25°C	$6.0 \cdot 10^{15}$	$3.0 \cdot 10^{15}$	$4.9 \cdot 10^{16}$	$2.6 \cdot 10^{14}$
Electric strength, E, kW / mm, at 25°C	83.0	40.0	26.7	28.2
Permittivity, ϵ , at 10^6 Hz and 25°C	2.7	1.8	3.3	3.3
Dielectric loss tangent, $\text{tg } \delta$, at 10^6 Hz and 25°C	0.02	0.02	0.06	0.06
Impact strength, kgf · cm	50	50	50	50
Coefficient of thermal conductivity, λ , W / (m · deg)	0.58	0.58	0.3.	0.3
Moisture permeability/(cm·h·mmHg)	$7.1 \cdot 10^{-8}$	$7.4 \cdot 10^{-8}$	$1.0 \cdot 10^{-6}$	$1.7 \cdot 10^{-7}$
Fungal resistance, points	1	1	1	1
pH of water extract	7.0	6.4	7.65	7.9

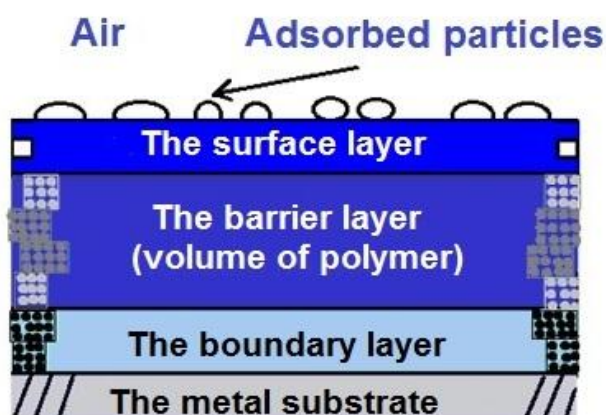


Fig. 3. Model of gradient organosilicate coating

6. CONCLUSION

In general, the application of organosilicate composites and coatings is promising for increasing the materials resistance to the action of fungi.

However, organosilicate coatings do not possess the fungicidal properties. Giving these properties to coating is possible by the introduction of appropriate fillers and additives into their formulations.

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