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USAGE OF SILANES WHEN MAKING PROTECTIVE COATINGS FOR METAL BY UV CURING

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Adhesive strength of coatings depends on the nature and density of adhesive bonds. It has been shown that using silanes with olefinic carbon as an adhesive layer on metal substrates lets increase significantly protective effectiveness and life time of UV lacquer coatings due to formation of the Me-O-Si-C covalent bonds. Silanes show optimum properties when unimolecular film is formed on the surface.

Reducing the thickness of the paint coating to the persistence of high security features is one of the major trends in the paint industry.

Important role in this spectrum is the method to paint the material. In [1] data are presented on the conservation of protective coating characteristics as dependent on the application method.

Application methods for decreasing production of protective coating characteristics are as follows: electrostatic spraying, air spraying, airless spraying, inkjet poured, dipping, and brush. This difference is explained by the different structure of the coating formation with the density of its packing and size.

These relationships are of particular urgency when high anticorrosive properties are required at the film thickness of about 20 microns. In particular, anaphoretic coating allows for such a thickness to withstand the salt fog chamber for 250 to 500 hours, electrophoresis for 1000 hours or more [2]. Lower molecular weight oligomer in cataphoretic arrangement leads to an increase in the protective coating behavior [3].

Method of curing UV radiation received industrial development in the late 60-ies and is now considered to be one of the most promising. The advantages of this method are: relatively high performance, low energy costs, simple equipment. However, curing by UV radiation is applicable to a limited number of paints and varnishes. It is used mainly for obtaining coatings of materials capable of cured through polymerization reaction. The principle of cure is based on the ability of UV rays to initiate the polymerization of these oligomeric materials. The energy of UV radiation is high – 12.3 eV which is 2–4 times higher than the rays energy of visible light. This allows the solidification of coatings with a satisfactory rate at normal temperature.

The process of polymerization can be divided into stages of initiation, development, and completion. The initiation stage begins the process of formation of reactive particles (free radicals). During the irradiation of UV light, reactive radicals are formed by chemical decomposition of photoinitiator. The collapse of photoinitiator leads to the formation of free radicals which react with carbon-carbon double bonds of a film maker. As they are highly reactive and rapidly solidified, there may be high internal stresses that can lead to problems with adhesion to some substrates, in particular, on the metal. The molecular weight of film-forming coatings for UV-curing is of 500 to 2500 g/mol [4].

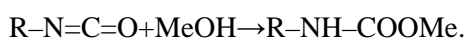
Adhesion strength of coatings depends on the nature and density of adhesive bonds. Bonds of different nature may occur dissimilar bodies: chemical (ionic, covalent, coordination) with energies from 65 to 1000 kJ/mol, hydrogen and van der Waals type (induction, dispersion, dipole, etc.), with energy not exceeding 50 kJ/mol in most cases. When coating, an interaction with the substrate occurs at the time of contact with the liquid paint material. However, the adhesion values of liquid paint and of finished with solid coating are usually not equal. When forming the coating, as well as during its operation, originally formed bonds can be stored, destroyed, or supplemented by new bonds.

The junction of two dissimilar materials – adhesives and substratum – perhaps is due to a spectrum of the molecular forces – attraction, repulsion, dispersion interaction. The result of this interaction is the adsorption of adhesive on the substrate surface. Depending on the operating forces, adsorption can be physical or chemical in nature. Formed during this interim at the interface or boundary layer, the polymer material has the structure and properties different from those of bulk polymer. These differ-

ences in properties are the result of restrictions of molecular mobility in the adsorption layers. The composition and structure of boundary layers exert a decisive influence on the magnitude of interfacial interaction and, accordingly, the adhesion of polymers to solid surfaces.

The increase in adhesive strength, according to the adsorption theory, is caused by changing the chemical nature of the polymer and increasing the polarity of the substrate, for example, through oxidation.

When using a binder having active functional groups, a chemisorption interaction can occur. Thus, the interaction of components of polyurethane formulations with metal oxides and hydroxides takes place at ambient temperature in the reaction:



The adhesion strength is a multivariate index dependent on the nature of polymer and substrate as well as the formation conditions of coverage. The coverage of monomeric and/or oligomeric binder converted into a polymer (three-dimensional) state directly on the substrate has the highest adhesion. Monomers and oligomers in some cases can be chemisorbed on the surface of metals; their subsequent polymerization or polycondensation leads to the formation of grafted polymers chemically bound to the metal.

The role of substrate in the adhesive interaction is as significant as that of the film material. The greatest difficulty is getting the adhesion-resistant coatings on smooth non-porous substrates (metals, glass) as well as on materials with low surface energy.

Currently, the leading foreign firms engaged in the development and manufacture of chemical means of surface preparation conduct extensive research and pilot projects to replace the highly toxic chromate reagents with processing compositions based on silanes [5, 6]. This provides a protection against corrosion due to the good barrier properties of silane films formed on the surface with a thickness of 4 to 20 nm which allows us to assign these strata to nanocoatings, and technologies of such a treatment – to nanotechnologies.

Trialkoxysilanes are environmentally friendly organometallic compounds produced at an industrial scale. They have a general formula $R'(CH_2)_nSi(OR)_3$ where R' is organo-functional group and OR is hydrolysed alkoxy-group: methoxy- (OCH_3), ethoxy- (OC_2H_5) or acetoxy- ($OCOCH_3$). Their structures are shown in Fig. 1.

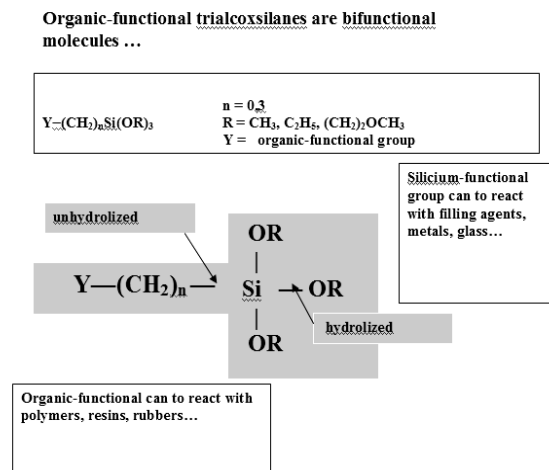
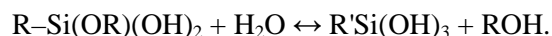


Fig. 1. Trialkoxysilane structures

Trialkoxysilanes used to form a protective coating on the metal surface should be hydrolyzed to form hydroxyl groups. It is an interaction of these hydroxyl groups with metal hydroxides present on metal surface resulting in bonding silanes with metal surface. Hydrolysis of an exposed alkoxy group (OR) in presence of water results in the formation of silanol group (SiOH). Hydrolysis usually occurs in dilute solutions of silanes as follows



As a result of hydrolysis, silane-triplets are formed. Mortar trialkoxysilanes become efficient due to achieving an effective concentration of silane-triplets. For the processing of inorganic surfaces, solutions of organo-alkoxy silanes are used in water or organic solvents, aerosols mixed with low-boiling solvents. When using aqueous solutions, a 0.1 to 0.5% solution is prepared and rapidly applied to the surface of material. To improve the condensing, surface is dried. During the subsequent hot drying of metal surfaces treated with aqueous solutions of silanes, two condensation reactions occur: one is between silanol groups of soluted trialkoxysilane and hydroxides of metal substrate resulted in the formation of covalent bonds ($MeOSi$) (Fig. 2). Another one occurs between silanol groups to form links $SiOSi$.

As a result of such treatment, poly-organo-siloxanes containing carbonyl functional groups are formed on the surface of inorganic materials chemically bound to it. The consumption of silanes depends on the surface area of the material treated, the content of hydroxyl groups on the surface, and the sizes of molecules of the adhesion promoter.

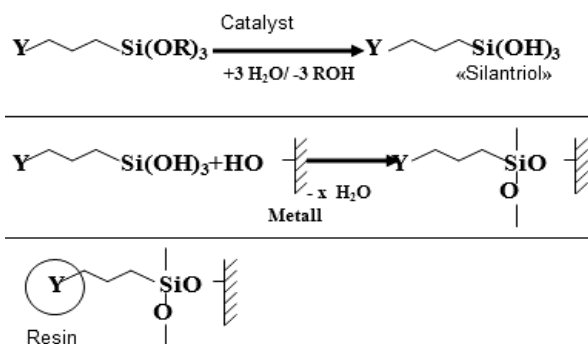


Fig. 2. Scheme of the formation of a covalent link Si–O–Me

Optimal properties of silanes appear in the formation of a monomolecular layer on the surface. In [7] calculations are made of the maximum consumption rates of some trialkoxysilanes a_0 (g/m²) needed for a monomolecular layer on the surface of the material (Table 1).

Table 1. Trialkoxysilanes with a double bond - adhesion promoters

No	Chemical type	Structure	Manufacturer	a_0 , g/m ²
1	vinyltrimethoxysilane	(CH ₃ O) ₃ SiCH=CH ₂	Momentive, Wacker	1.9×10^{-2}
2	vinyltriethoxysilane	(C ₂ H ₅ O) ₃ SiCH=CH ₂	Momentive, Wacker	2.4×10^{-2}
3	vinyltriacetoxysilane	(CH ₃ CO ₂) ₃ SiCH=CH ₂	Wacker	3.0×10^{-2}
4	vinylmethyldimethoxysilane	(CH ₃ O) ₂ CH ₃ SiCH=CH ₂	Wacker	
5	3-metacryloxypropyltrimethoxysilane		Dow Corning Evonik	3.2×10^{-2}
6	vinyltri(2-methoxyethoxy)silane	(CH ₃ OCH ₂ CH ₂ O) ₃ SiCH=CH ₂	Momentive, Wacker	3.6×10^{-2}

If the interaction occurs only with surface hydroxyl groups, the flow rate may be significantly lower. In practice, organo-alkoxy-silanes are used in quantities much larger than necessary for the formation of a monolayer. However, in this case a layered structure is formed.

The presence of a double bond in the organofunctional group Y (Fig. 1) allows the adhesive

layer to participate in the polymerization reaction of UV curing systems.

Table 1 shows the trialkoxysilanes forming adhesive monolayers on the surface of substrate.

Standard thin-plate cold-rolled steel grade 08ps 0.8 mm thick were used as objects under study stained with a pneumatic spray UV curable lacquer (see recipe in Table 2), and cures for installing an ORK-21M1 with a mercury lamp DRT [8]. Figure 3 shows photographs of plates during the test (0 hours, 50 hours, 72 hours) in the salt fog chamber (thickness of the film is of 25–35 microns), treated trialkoxysilane No 15.10.3 and without treatment No 15.10.6. (GOST 20.57.406-81 method 215-3).

Table 2. Formulations of UV varnish caused by air-spraying

No	Component and its characteristics	Application	Mass fraction
1	epoxy-acrylate MV 550, functionality 2	UV-film formation	40
2	dipropylene glycol-diacrylate	active thinner, regulation viscosity	20
3	1-hydroxycyclohexylfenilketone	photoinitiator	3
4	2, 4, 6-trimethylbenzoyldiphenyl phosphineoxide	photoinitiator	1
5	isobornil-acrylate	active thinner, regulation viscosity	36

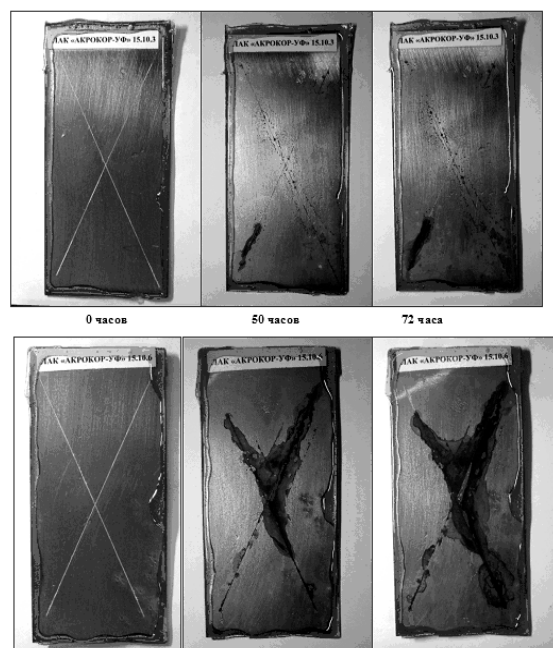


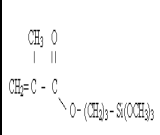
Fig. 3. Samples in the salt fog chamber

Photos plates demonstrate a significant increase in the protective characteristics of UV cured coatings by increasing the adhesion due to formation of covalent bonds Me–O–Si–C.

Table 3 shows the results of measurements of coating adhesion to the substrate (ISO 4624) depending on the number of trialkoxysilane per surface area (g/m^2). Fig. 4 shows the variation of adhesion as dependent on the number of layers of trialkoxysilane (N) on the surface. Using of trialkoxysilanes improves adhesion of lacquer UV curing to the steel plate with $7.5 \cdot 10^{-2} \text{ N}/\text{mm}^2$ (No 9) up to $9.3 \text{ N}/\text{mm}^2$ (No 3). Maximum amount adhesion observed in coatings, the quantity of trialkoxysilane on the surface protected does not exceed a monolayer.

Non-hydrolysed organo-functional groups with a double bond trialkoxysilane also affect the magnitude of adhesion. Examples: No 2, $12.5 \cdot 10^{-2} \text{ N}/\text{mm}^2$ and No 7, $8.5 \cdot 10^{-2} \text{ N}/\text{mm}^2$.

Table 3. Effect of trialkoxysilanes and their structures on the strength of UV-curing lacquer

No	Trialkoxysilane	Concentration of the trialkoxysilane solution $C_0, \%$	Number of applied adhesive layers of the trialkoxysilane solution	Adhesion N/mm^2	MV g/mol	a, g/m^2	N, number of silane monolayers
1		0.01	1	0.101	248	0.0006	0.018
2		0.1	1	0.125	248	0.006	0.18
3		1.0	1	0.093	248	0.06	1.87
4		1.0	2	0.094	248	0.12	3.75
5		1.0	3	0.093	248	0.18	5.6
6	$\text{H}_2\text{C}=\text{CH}-\text{S}:(\text{C}_2\text{H}_5\text{O})_3$	0.1	1	0.086	190	0.006	0.25
7	$\text{H}_2\text{C}=\text{CH}-\text{S}:(\text{CH}_3\text{OCH}_2\text{CH}_2\text{O})_3$	0.1	1	0.085	280	0.006	0.16
8	dynasilane DAMO	0.1	1	0.087	-	0.006	-
9	- without silane	-	-	0.075	-	-	-

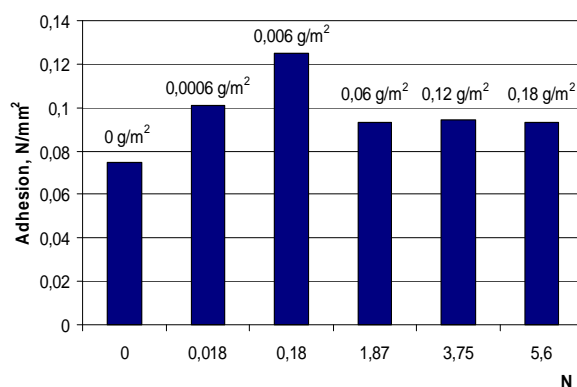


Fig. 4. Influence of silane quantity on adhesion of UV varnish on metal surfaces

Anticorrosive properties of coatings depend on the adhesion to a large extent. Passivation of the metal surface, inhibition of the anodic reaction, and slowing down the withdrawal of corrosion products are achieved with adhesive interaction. If we consider the metal corrosion as an adsorption process of corrosive substances at the vacant surface sites, it becomes evident that the greater the adhesion, the fewer of these vacant sites and, respectively, there is less opportunity for development of the corrosion process.

High adhesion coating may be a significant obstacle in the development of corrosion process due to slow drainage of corrosion products. In contrast, low adhesion is one of the reasons for violations of the coating and the appearance of underfilm corrosion. Therefore, all the factors which would produce coatings with high and stable in operation adhesion positively impact on the ability of protective coatings.

Earlier tests for applying UV-curable lacquer on the metal with the adhesive layer of trialkoxysilane without double bond (glicidoxypropyltrimethoxysilane, Dynasilane DAMO) showed no significant improvement in the protective characteristics of the coating.

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Використання силанів при приготуванні захисних покриттів для металів шляхом УФ-опромінювання

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Адгезійна міцність покриттів залежить від природи і щільності адгезійних зв'язків. Показано, що використання силанів з олефіновим вуглецем як адгезійного шару на металевих підкладках істотно поліпшує захисні властивості та довговічність покриттів, стабілізованих шляхом УФ-опромінювання, завдяки утворенню ковалентних зв'язків Me–O–Si–C. Силани виявляють оптимальні властивості при утворенні мономолекулярної плівки на поверхні.

Использование силанов при приготовлении защитных покрытий для металлов путем УФ-облучения

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Адгезионная прочность покрытий зависит от природы и плотности адгезионных связей. Показано, что использование силанов с олефиновым углеродом в качестве адгезионного слоя на металлических подложках существенно улучшает защитные свойства и долговечность покрытий, стабилизированных путем УФ-облучения, благодаря образованию ковалентных связей Me–O–Si–C. Силаны обнаруживают оптимальные свойства при образовании мономолекулярной пленки на поверхности.