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Abstract
Adsorption of vinyl triethoxysilane and γ-aminopropyltriethoxysilane on the surface of aluminium from aqueous solutions was studied by quartz nanobalance technique. Adsorption isotherms were obtained. It was shown that during adsorption silanes displace adsorbed water from the surface. To interpret the adsorption data, we used the well-known approaches of adsorption data: Langmuir, BET, Flory-Higgins, Langmuir multimeter, Temkin, Freundlich adsorption isotherms. The surface orientation of adsorbed molecules was determined. The silanes adsorption heats were calculated by different ways. It was shown that silanes are chemisorbed on the aluminium surface. By means of quartz nanobalance, atomic force microscopy, scanning electron microscope, Fourier transform IR spectroscopy it has been shown that a uniform, self-assembled, anti-corrosion vinylsiloxane nanolayer is formed on the aluminium surface during adsorption of vinyl silane from aqueous solution. This layer covalently bonded to the hydroxyl groups of the metal. The thickness of the surface nanolayer can be controlled by changing the deposition conditions. The effect of the vinylsiloxane nanolayer on the dissolution of aluminium in chloride-containing solutions has been studied. It was established that an ordered vinylsiloxanenanolayer, up to five molecular layers thickness, effectively inhibits the uniform and localized aluminium corrosion. It was shown that after 10 days of corrosion tests vinylsiloxanenanolayer is preserved on the aluminium surface, indicating its resistance to water and corrosive components.

Keywords: Aluminium; Adsorption; Alkoxysilane; Organosilicon Self-Assembled Nanolayers; Heterogeneous Processes; Corrosion; Electrode Reactions; Corrosion Test

Introduction
It is known that [1] aluminium and alloys based on it have found application in many areas, such as the aviation industry, engineering, shipbuilding, energy etc., as they combine lightness and strength, high thermal conductivity and electrical conductivity, reflect light and heat well and in addition, are hygienic and non-toxic. A wide variety of forms of these materials are produced in contributes to their various use. At the same time, being stable under conditions of uniform corrosion, they have low corrosion resistance in chloride-containing media, because they are prone to pitting corrosion [2]. Pitting corrosion is one of the most dangerous types of metal structures destruction and occurs on metals covered with an oxide film in the places of the passive film damage. Due to the implementation of high metal dissolution rates in local areas, the result of pitting corrosion may be failure of the entire structure. Despite the increased interest of researchers in the aluminium and its alloys pitting formation, observed for several decades [2-6], the problem of developing effective methods of aluminium and its alloys protection from pitting corrosion is relevant.

Usually, during the operation, aluminium and its alloys products are protected from corrosion by polymer and paint coatings, which are well established as one of the most effective ways to reduce corrosion risk in various conditions [7]. Often, when they are used, the metal surface is subjected to preliminary chemical treatment (finishing) to improve corrosion resistance and increase the paint (polymer) coating adhesion to the metal. Until recently, the metal surface was chemically treated with hexavalent chromium compounds. Chromic layers effectively protect the metal from corrosion while providing high coating adhesion. However, hexavalent chromium, which is part of the components, is toxic and environmentally harmful element, the use of which is currently highly undesirable and in the future is subject to a complete ban [8]. In recent years, the efforts of researchers have been aimed at replacing chromic technologies, in particular in aluminium and its alloys processing [9,10]. However, the problem has not been solved, and the development of more efficient and environmentally friendly methods of aluminium surfaces pre-treatment is an urgent scientific and technical task. Toxic chromium compounds were replaced by organosilanes, whose general formula is as follows - RnSi(R')4-n.
are non-toxic and can be adsorbed on the aluminium surface, forming surface self-assembled siloxanenanolayers[11-13]. At the same time, on the one hand, strong and hydrolytically stable bonds of Al-O-Si (Ranuni et al. 2012) with the hydroxylated metal surface are formed and, on the other, it is possible to provide a high affinity of the nanolayer to a wide range of polymeric and paint materials due to the variation of the organic radical R chemical nature.

Despite the great long-term interest in the study of organosiliconnanolayers on inorganic surfaces [11,14], the mechanism of organosilanes adsorption on aluminium and their influence on the corrosion properties of this metal have not been sufficiently investigated. In this regard, the aim of this work is to study the adsorption of vinyl and amino-containing trialkoxysilanes on the aluminium surface and to study the influence of surface siloxane nanolayers on the corrosion and electrochemical behavior of aluminium in chloride-containing electrolytes.

**Experimental**

A995 aluminium foil [15] with a thickness of 100 µ and thermally deposited (from vacuum) A99: aluminium were used in the work. The aluminium sheathing was placed in a tungsten evaporator and heated to an evaporation temperature by passing 70 A current in 10⁻⁴ mm of mercury vacuum, achievable by using vacuum post VUP-4 (made in Russia). Two types of substrates were used for the aluminium layer application: 1) quartz resonator brand QC-10-AuBU gold plated, with AT-cut, and basic frequency of 10 MHz (Elchema, USA) and 2) glass plates with 3 mm thickness and a size 15x30 mm were used. The substrates surface was degreased with alcohol, washed with water and dried in air at room temperature.

The thickness of the metal layer was determined by electrochemical piezoelectric quartznanobalance[13,16] on the EQCN 700 unit (Elchema, USA), measuring the change in the frequency of the quartz resonator during the spraying process and calculating the change in mass during metal deposition and the value of the true metal surface by the method described in [13]. All calculations were carried out taking into account the true value of the metal surface.

Organosiliconnanolayers based on vinyltriethoxysilaneCH₂=C HSi(OC₂H₅)₃ (VS) ultrapure

(Witco Co, Switzerland) and aminopropyltrietoxysilane NH₂-(CH₃)₃Si(OC₂H₅)₃ (AS) ultrapure

(Witco Co, Switzerland) were formed on the aluminium surface. Organosilanes were applied on the surface by dipping the samples into aqueous solution, which was prepared by adding organosilane to bidistilled water. The aqueous solutions with an interval of 10⁻⁵ - 10⁻¹ M concentration were used.

Before using, the solution was kept for 60 minutes for silane hydrolysis. The samples were dipped in the solution and kept for 10 minutes, after which the excess organosilane was washed away by holding in water for 1 minute and dried in air at room temperature. After applying an organosilane layer, the surface was characterized using a piezoelectricquartznanobalance, Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), Fourier transformed Infrared Spectroscopy (FT-IR).

Solver P47 (NT MDT, Russia) scanning probe microscope was used for AFM studies. Infrared reflection spectra were obtained using Perkin Elmer 2000 Fourier spectrometer in the range of 400-4000 cm⁻¹, with a resolution of 4 cm⁻¹, the number of scans 400. A mirror reflection attachment with an angle of incidence of 80° was used. Scanning electron microscopy of the samples surface before and after corrosion tests and X-ray Spectral Microanalysis (XSMA) were carried out at the Camebax SX50 unit (Samesa, France).

Corrosion tests of aluminium foil samples were carried out in sodium chloride solutions (ultrapure NaCl) with a concentration of 0.001 - 0.1 M and in a climatic chamber (Taiwan) RH 90%, t=60°C for 30 days. Corrosion of aluminium was studied using “in situ” methods: piezoelectric quartznanobalance[13], resistometry[17] and scanning reflectometry[18].

During resistometric studies of aluminium corrosion, both Al foil(with 100 µm thickness)or thermally-deposited Al samples were used. The working element of the resistometric thermally deposited indicator was an aluminium layer 1 mm thick, deposited to the glass surface. Such indicators are used for rapid assessment (within 1-2 days) of corrosive aggressiveness of the medium in the study of the metal behavior in natural conditions[17]. The resistometric indicator is characterized by high sensitivity and response speed (about 30 minutes). The reliability of the corrosion rates obtained using indicators with a working element made of thermally deposited aluminium was confirmed by the gravimetric method on foil samples [17].

The change in the resistance of the corroding metal was measured and the change in the layer thickness was calculated by the formula

\[ \Delta d = d_0 - d_z = \frac{\rho I}{h} \left( \frac{1}{R_0} - \frac{1}{R_z} \right) \]

where \( t \) is the time of testing, \( d_z \) is the initial sample thickness (µm), \( d_0 \) is the thickness of the sample at time \( t \), \( \rho \) is the aluminium resistivity, \( I \) is the sample length, \( h \) is the sample width. \( R_0 \) is the initial resistance of the sample. \( R_z \) is the sample resistance at time \( t \).

The sample resistance during the corrosion test was measured continuously with a frequency of one measurement in 10 min with an accuracy of 0.01 Ohm by APPA109N multimeter (APPA, Taiwan), allowing automatic recording of the measured values. The test duration was 100 and 300 hours for sprayed and foil samples respectively. The amount of corrosion was determined by gravimetrically with quartz nanobalance[19] technique on the EQCN 700 unit (Elchema, USA) by measuring the frequency change of the quartz resonator in the spraying process and calculating the mass change at the metal corrosion by the formula:
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\[ \Delta m = -\frac{NpS\Delta f}{f_0^2} \] (2)

\( f_0 \) is the basic frequency of 10000 kHz; \( \Delta m \) is the change in the silane mass (g); \( \Delta f \) is the change in the frequency of the piezoelectric resonator (kHz), \( N \) is the frequency constant (for AT-cut crystals, \( N = 1670 \) kHz-mm); \( S \) is the working quartz area, equal to 0.72 cm².

Studies of corrosion using scanning reflectometry were performed by processing the electrode surface diffuse reflection reflectogram obtained during corrosion tests. They were recorded on a standard computer scanner (Epson Perfection 3200 Photo, Epson, Japan) with optical resolution of 3200 dpi and at the same time recorded the change in the corrosion potential of samples continuously for 10 days. The metal corrosion was evaluated by changing the area of the corroded surface during the test. A glass cylindrical cuvette with a smooth, optically transparent bottom was used for testing. The sample was placed on the bottom of the cell, working surface down, providing a gap between the metal surface and the cuvette bottom with a glass stop. The angle between the metal surface and the scanner glass was selected in such a way as to obtain a white image of the sample [18]. The potential was measured relative to the chloride reference electrode using an APPA 109N multimeter (Appa Co, Taiwan).

The calculation of the degree of the surface coverage with defects and the average size of a single defect was carried out using the original software for digital image processing, written in the Ruby 1.9.0 programming language and the RMagic 2.1.2.0 program (ImageMagick 6.5.6-8). Three-dimensional visualization of surface defects was performed using software developed on the basis of Surfer 9.0 program.

The study of the organosilicon nanolayers effect on the electrochemical behavior of aluminum was carried out by polarization method (Kelly 2002). A three-electrode cell with a chloride-silver reference electrode was used. The measurements were carried out using the PI-50-1 potentiostat (Gomel plant of Measuring Devices, Belorus) at fixed potentials or potentiodynamically with a potential sweep rate of 0.1 mV/s. The experiments were carried out on disk (0.8 cm²) and cylindrical (12.14 cm²) aluminum electrodes.

The pitting formation critical potential (Epit), i.e. the potential above which the metal pitting dissolution occurs and stablepittings spread [20], was determined by anodic polarization curves from the fracture on the curve, as the potential upon reaching which a sharp increase in the current is observed (Figure 1) [20,21].

The study of the aluminum surface morphology with surface siloxane nanolayers was carried out using the “Solver-Pro” atomic force microscope («Micro and Nanoholographicsystems» Company, Ltd, China) “ex situ” (in the air) in a contact mode. Data processing for image and roughness data was performed using the following software: NOVA Solver Pro (NT-MDT, Russia).

This processing was carried out using a software package for 3d-images [22].

Results and discussion

Ethoxysilanes adsorption on the aluminum surface was determined by measuring the change in the frequency of the quartz resonator and recalculating it in the mass change by formula (2) when ethoxysilane was introduced into the solution. The addition of a small amount of VS corresponding to the solution concentration of 10⁻⁵ M into the water first leads to a light decrease in the mass of the sample followed by its increase (Figure 2).

This may indicate the processes of competing adsorption at the metal-solution interface, as a result of which the adsorbed ethoxysilane displaces the solvent molecules, i.e. water, from the surface. Similar effects have been observed previously on copper [19] and they have been observed during the adsorption of corrosion inhibitors on the surface of iron and gold [23]. The sample weight reduction is insignificant in the case of VS (10⁻⁵ M) and is 16.4 ng/cm² which may correspond to the displacement of 13-14 H₂O molecules.

At the same time, about 6 VS molecules are adsorbed on the surface, i.e. during adsorption, each silane molecule displaces 2 or more water molecules. Increasing the amount of silane to concentrations of 10⁻³ also leads to displacement of water from the surface. In the case of aminosilane the same effect was observed, but the introduction of AS into the solution leads to the displacement of more solvent from the surface. The reduction in mass was 25.7 ng/cm² at a solution concentration of 10⁻³ M which corresponds to the displacement of 20-22 H₂O molecules.

Silane adsorption was calculated taking into account the mass of the displaced water. Increasing the concentration of alkoxysilane solution in water leads to an increase in its adsorption (Figure 3 and 4). Besides, it was found that the sorbed phase VS and AS consists of reversible and irreversible parts. The
Figure 2: Kinetics of vinylsilane adsorption on the surface of freshly sprayed aluminium from aqueous solution

Figure 3: Isotherm of vinylsilane irreversible adsorption on the surface of freshly sprayed aluminium from aqueous solution

Figure 4: Isotherm of aminosilane adsorption on the surface of freshly sprayed aluminium from aqueous solution

reversibly sorbed layer is easily removed from the surface when the sample is kept in clean water for 10 minutes and is about 10% of the total amount of adsorbate. The irreversibly sorbed part of silane is water resistant for at least 8 hours, i.e. the adsorbed molecules of silane are dissolved in clean water during at least 8 hours, while maintaining the metal sample with irreversible sorbed VS and AS in the pure (without silane) water.

Figures 3 and 4 show the adsorption isotherms of vinyl - and the amino-silanes (Figure 4). Figure 3 presents the isotherm of vinylsilane irreversible adsorption on the surface of freshly sprayed aluminium in a wide range of VS concentrations. The type of adsorption isotherm corresponds to the Langmuir isotherm.
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which may indicate that VS molecules are adsorbed monolayerly. The conversion of the mass into the number of molecules showed that at VS solution concentrations less than 0.001 M per 1 nm² of the surface, about 21 silane molecules were adsorbed, and the thickness of the monolayer can be calculated from the bond lengths and is about 0.9 nm. The increase in the VS solution concentration above 0.001 M leads to a polymolecular coverage of the surface and during adsorption from the 0.1 M solution on the surface forms a vinylsiloxane layer with a thickness of 10 molecular layers.

The shape of the aminosilane adsorption isotherm corresponds to a multi-molecular adsorption (Figure 4). Moreover, the conversion of the adsorbed AS mass into the number of molecules shows that even at low concentrations of 10⁻⁴ M per 1 nm² of the surface 158 aminosilane molecules are adsorbed. The calculation using bond lengths shows that with dense monolayer coverage, there can be no more than 49 molecules on the surface, i.e. at AS solution concentration of 10⁻⁴ M the metal surface is covered with more than 3 tightly packed vertically oriented molecular layers of aminosilane.

To study the adsorption mechanism of silanes adsorption data were processed in terms of known adsorption approaches: Langmuir (eq. 3), BET (eq. 4), Frumkin, Temkin, Flory-Higgsens:

\[
\frac{1}{C} = \frac{1}{m_{na}} + C \left( \frac{1}{b m_{na}} \right) \\
\frac{C}{m} (1 - C) = \frac{1}{k m_{na}} + C \left( \frac{k - 1}{k m_{na}} \right)
\]

where C is the VS (M) concentration, m is the mass of adsorbed VS (ng), mm is the mass of a tightly filled monolayer ng, b and k are constants.

It was found that the surface coverage with silane molecules of less than one monolayer, there is no interaction between neighboring adsorbed molecules, which allows the use of these isotherms in the description of adsorption.

The solution of equations (3) and (4) makes it possible to determine the area occupied by an individual molecule (“landing site”) and the heat of VS molecules adsorption at adsorption of the first layer. The values of “landing sites” were 0.05 and 1.23 nm² molecule in the calculation by the Langmuir and BET isotherm, respectively. i.e. from 19 to 25 molecules are adsorbed per 1 nm² at a monolayer coverage. This coverage may indicate the horizontal position of silane molecules on the surface (Figure 5).

In case of monolayer adsorption, neighboring molecules most likely do not interact. Apparently, for condensation of a neighboring molecules and formation of self-assembled siloxanenanolayer polymolecular adsorption is required. Using equation (5):

\[
K = \frac{1}{55.5 \times \exp \left( - \frac{\Delta G_{ads}}{RT} \right)}
\]

where R is the universal gas constant, T is the temperature, 55.5 is the mol water concentration in 1 liter of the solution, calculated the K coefficient, from which, in turn, the VS and AS adsorption heats were calculated (Table 1, 2) whose values lie in the range from 20 to 46 kJ/mol which exceeds the values recorded for specific adsorption of organic compounds on metals. However, it is believed that the chemisorption corresponds to the value of 100 kJ/mol. Which was determined using ethiols adsorption on gold [24]. At the same time, it is considered [25] that the heats values of the substantive adsorption determined by quartz balance are strongly underestimated, since the interaction energy of the water displaced from the surface on metals with high hydrogen overvoltage is much higher than on precious metals. Therefore, we can say that VS is chemisorbed on the aluminum surface. In addition, the obtained values of adsorption energies correspond to the hydrogen bond energies [26].

In the aminosilane adsorption the analysis of adsorption data using the Langmuir and BET approaches showed (Table 2) not 158 (as we mentioned above), but 19.7 and 25 molecules are located per 1 nm². This means that the aminosilane molecules are also located horizontally on the aluminium surface. The value of x in the Flory-Higgins equation was 3.6, which indicates that VS molecules are adsorbed on the surface from the 0.1 M solution on the surface more than 53 adsorption places (Table 2) and apparently AS molecules are connected by hydrogen bonds with surface hydroxyl groups of neighboring molecules (Figure 6).

Since alkoxysilanes were adsorbed from the solution, and Langmuir and BET isotherms are usually used for adsorption from gas media, adsorption data were processed using isotherms used to describe adsorption in liquid media. As noted above, during adsorption ethoxy silanols replace water on the surface. So if the interaction between the adsorbate molecules and water occurs on the surface, the reaction is realized:

\[
A_{aq} + x(H₂O_{ads}) \rightarrow A_{ads} + x(H₂O_{aq})
\]
Table 1: Using the known adsorption approaches for the description of VS adsorption from dilute water solutions.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Langmuir</th>
<th>BET</th>
<th>BET</th>
<th>Temkin</th>
<th>Langmuir multicentre</th>
<th>Flory-Huggins</th>
<th>Frumkin</th>
<th>Langmuir Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td>Correlation R</td>
<td>0.995</td>
<td>1.000</td>
<td>1.000</td>
<td>0.961</td>
<td>0.999</td>
<td>0.999</td>
<td>0.992</td>
<td>0.999</td>
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<tr>
<td>Correlation R²</td>
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<td>1.000</td>
<td>1.000</td>
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<td>1.00</td>
<td>1.00</td>
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<td>Monolayer capacity, molecule/ nm²</td>
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<tr>
<td>Molecule’s “landing site”, nm²/ molecule</td>
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<td>1.23</td>
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<td>ƒ in Temkin equation</td>
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<td>Interaction energy kJ/mol</td>
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<td>24.05</td>
<td>46.61</td>
<td>44.54</td>
<td>40.73</td>
<td>37.96</td>
<td>20.13</td>
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Table 2: Use of known adsorption approaches to describe AS adsorption from diluted water solutions

<table>
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<tr>
<th>Isotherm</th>
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<th>BET</th>
<th>Temkin</th>
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Figure 5: Orientation of VS molecules on the aluminium surface during adsorption from aqueous solution
Adsorption of Organosilanes and Formation of Organo silicon Self-Assembled Nanolayer on the Aluminum Surface. Influence of Surface Nanolayer on Corrosion and Electrochemical Behavior of the Metal

Figure 6: Orientation of AS molecules on the aluminium surface during adsorption from aqueous solution

x H₂O molecules are displaced from the surface. To describe the so-called “substitute” adsorption, a number of authors [9,27] use the Flory-Higgens isotherm:

\[
\frac{\theta}{e^{(x-1)(1-\theta)^x}} = KC
\]  

(7)

where C is the concentration, \( \theta \) is the degree of surface coverage, x is the substitutive factor, the number of substituted water molecules, K is the constant of adsorption equilibrium.

The transformation of equation (7) leads to (8) allowing to present the adsorption data a linear form and calculate x and K:

\[
\ln\left(\frac{\theta}{C}\right) = (x - 1) + \ln K + x \cdot \ln(1 - \theta)
\]

(8)

From Tables 1 and 2 it can be seen that the adsorption data are straightened in the coordinates of the Flory-Higgens isotherm with high fin correlation coefficients. Processing of equation (8) allowed to find for VS the value of x equal to 2.54 cm (Table 1) and the adsorption equilibrium constant. The data obtained confirm the results described above that VS displaces more than 2.5 water molecules from the surface during adsorption. In this case, the silane molecule can occupy more than one adsorption place on the surface. So-called multicenter adsorption isotherms are used to describe such situations [9]. In our case, to determine the orientation of the adsorbed molecules on the surface, the multicenter Langmuir adsorption isotherm was used, where the assumption is that there are \( n \) adsorption centers on the surface. Then the classical Langmuir isotherm is converted to (9), and into a linear form (10):

\[
\frac{\theta}{(1 - \theta)^n} = KC
\]

(9)

\[
\log\left(\frac{\theta}{C}\right) = \log K + n \cdot \log(1 - \theta)
\]

(10)

Construction of adsorption data in the linearization coordinates of the equation (10) showed a rectilinear dependence with a correlation coefficient close to one (Table 1), indicating the applicability of the Langmuir multicenter adsorption isotherm to VS. The value of n was 2.54, i.e. on average, each vinylsilane molecule occupies 2.54 adsorption centers, which confirms the assumption of the horizontal orientation of VS molecules on the surface (Figure 5).

Thus, the analysis of VS adsorption isotherms showed that at the initial stages VS adsorption occurs with the displacement of the adsorbed water, while the silane molecule occupies more than two adsorption places on the surface and is located horizontally. However, the question about the transformation of a silane molecule, the interaction of neighboring molecules and the formation of connections with the surface remains open. Temkin, Frumkin and Freundlich isotherms take into account the heterogeneity of the surface, the interaction of adsorbate molecules with each other and dissociative adsorption.

The representation of adsorption isotherm in the coordinates of the surface coverage degree-logarithm concentration showed a linear relationship in a wide range of VS concentrations (Table 1). The obtained data are confirmed by AFM studies of the modified surface. Figure 7 shows atomic force images of the thermally deposited aluminium surface after modification from VS water solutions with concentration of 10⁻⁵ and 10⁻¹ M. At low concentrations, under conditions of pre-bedding, an uneven distribution of the adsorbate on the metal surface was observed. VS is adsorbed in the form of separate islands with a height of about 2 nm (Figure 7. a).

Increasing the concentration of the solution to 10⁻³ M leads to a more even coverage of the surface with a layer of VS with the thickness of about 1-2 nm which corresponds to 1-2 molecular layers (Figure 7. b). Further increase in concentration leads to a polymolecular coverage of the surface and during adsorption...
from the 0.1 M of the solution, close-packed vinylsiloxane layer with the thickness of 10 molecular layers is already being formed (Figure 7. c).

Electron microscopy of aluminium samples with VS adsorbed layer of about 2 nm thickness, deposited from a solution with the concentration of 0.1 M showed (Figure 8) mostly uniform surface coverage, but also heterogeneities associated, apparently, with the formation of polycondensed siloxane layers in excess of the monolayer coverage are also observed.

To study the chemical processes occurring in the formation of organosilicon nanolayers, the FT-IR spectroscopic study of the aluminium surface, with a vinylsiloxane nanolayer, of about 3 monolayers thick, deposited from the solution with the concentration of 10⁻² M (Figure 9).

FT-IR spectrum of the aluminium surface treated with VS solution (Figure 9) contains a number of bands related to the vinylsiloxane layer formed during hydrolysis and polycondensation of silane molecules on the surface. Thus, the intense band of 1030 cm⁻¹ lies in the region of the Si-O-Si group oscillations and the band of 905 cm⁻¹ corresponds to oscillations in the bonds of the bridge oxygen atom in the Si-O-Si fragment. In addition, a band lying in the region of 1000 cm⁻¹ was found in the spectrum which can be attributed to the oscillations of -Al-O-Si-surface groups. The bands at 1411 and 1600 cm⁻¹ lie in regions close to the oscillations of the -CH=CH: double bond and at 2950 cm⁻¹ corresponds to oscillations of the Si-C bonds. A wide but low-intensity band of about 3370 cm⁻¹ was found in the spectrum which can be attributed to the oscillations of the -OC₂H₅ group.

Spectrum analysis allows us to determine the nature of chemical processes occurring on the surface during the self-assembled nanolayer formation. Thus, the first stage of the process is the hydrolysis of vinylsilane molecules with the silanol formation. It should be noted that no bands corresponding to the Si-O-C groups oscillations were found in the spectrum which indicates the absence of nonhydrolyzed silane molecules on the surface. The low-intensity oscillation band of the -OC₂H₅ fragment indicates trace amounts of ethyl alcohol remaining on the surface after washing. The conducted research allows to propose the following scheme for the formation of self-assembled vinylsiloxane nanolayer on the aluminium surface (Figure 10, a-c). At the first stage, when vinylsilane is introduced into the solution, its hydrolysis occurs with the formation of silanol (Figure 10. a). Further, the silanol molecules diffuse to the metal oxide-hydroxide surface, displace the adsorbed solvent molecules (H₂Oads) from the surface and interact with the hydroxyl groups of the surface, first forming hydrogen bonds (Figure 10, a). Next, the silanol molecule enters into the condensation reaction with surface hydroxyl groups. In this case, the formation of metal-siloxane Al-O-Si bonds between the adsorbed molecules and the surface layer of the metal occurs (Figure 10, b). At the last stage, neighboring adsorbed molecules enter the polycondensation reaction, forming hydrolysis-resistant bridging Si-O-Si bonds (Figure 10, c), and a vinylsiloxane nanolayer is formed on the surface, firmly bonded to the surface. Thus, during VS adsorption on the aluminium surface, self-assembling of the adsorbate molecules is observed. It is caused by high affinity of the vinylsilane molecules to the surface reactive groups of the oxide-hydroxide layer of the metal and to the neighboring adsorbate molecules. Due to this affinity, silanemolecules without external specific action are self-assembled on the surface so that as a result, an oligomeric-polymeric vinylsiloxane nanolayer associated with surface metal atoms is formed.

However, the thickness of the surface nanolayer is determined by the VS concentration in the solution. Table 3 presents data on
Adsorption of Organosilanes and Formation of Organosilicon Self-Assembled Nanolayer on the Aluminum Surface. Influence of Surface Nanolayer on Corrosion and Electrochemical Behavior of the Metal

**Figure 8:** Scanning electron microscopy of aluminium samples with an adsorbed VS layer of about 2 nm thick, deposited from the solution with the concentration of 0.1 M VS.

**Figure 9:** Reflective FP-IR spectra of the thermally deposited aluminium surface with the 3 molecular layers thick vinylsiloxane film, adsorbed from aqueous solution of 10-2 M VS.

**Table 3:** Thickness of the organosilicon nanolayer depending on the modifying solution concentration

<table>
<thead>
<tr>
<th>Vinylsiloxane solution concentration, M</th>
<th>The degree of surface coverage of vinylsilane molecule, n</th>
<th>Thickness of the layer molecular layers</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0,00001</td>
<td>0,00010</td>
</tr>
<tr>
<td>0,00001</td>
<td>0,069</td>
<td>0,100</td>
</tr>
<tr>
<td>0,00010</td>
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<td>1,21</td>
</tr>
<tr>
<td>0,00050</td>
<td>1,21</td>
<td>1,30</td>
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<td>1,45</td>
</tr>
<tr>
<td>0,00400</td>
<td></td>
<td>0,01000</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Concentration (M)</th>
<th>Thickness (Å)</th>
<th>Thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00000</td>
<td>2.00</td>
<td>2.50</td>
</tr>
<tr>
<td>0.05000</td>
<td>3.05</td>
<td>3.81</td>
</tr>
<tr>
<td>0.07000</td>
<td>7.66</td>
<td>9.57</td>
</tr>
<tr>
<td>0.10000</td>
<td>15.45</td>
<td>19.31</td>
</tr>
</tbody>
</table>

The thickness of siloxane layers formed in VS adsorption from water solutions of different concentrations. At low concentrations the formation of a monolayer was observed on the surface and with its increase above 0.001 M multilayer adsorption begins. Thus, during the VS adsorption from the water solution, a uniform, self-assembled covalent-bound to the surface groups of the metal vinylsiloxanenanolayer is formed on the aluminium surface, the thickness of which can be controlled by changing the application conditions, for example, the vinylsilane solution concentration. As a result, the change in the VS concentration in the solution allows the intended formation of a siloxane nanolayer with any given thickness in the range from 1 to 19.3 molecular layers (Table 3).

The study of the influence of surface organosilicon nanolayers on the corrosion and electrochemical behavior of aluminium was carried out. It is known that a necessary condition for the corrosion processes on the metal is the presence of adsorbed or phase water layer on its surface. In this regard, the interaction between the surface siloxane layer and water was studied in detail. For this purpose, the influence of the surface nanolayer on the water adsorption from the vapor phase was studied (Figure 11). It was shown that one siloxane monolayer reduces both reversible and irreversible water adsorption. A greater effect was observed in the case of a more hydrophobic vinylsiloxane layer (Figure 11, curve 3) when the amount of (both reversibly and irreversibly) adsorbed water was reduced by almost half. The presence of a more hydrophilic amine-containing layer on the aluminium surface led to a 17% decrease in reversibly and 39% irreversibly adsorbed water compared to the aluminium surface without an organosilicon layer (Figure 11. curves 1 and 3).

The data obtained indicate that the polymolecular organosilicon layer formed as a result of the monolayer chemisorption of organosilane is able to reduce the corrosion rate of aluminium...
in water. Therefore, in addition to the water adsorption on the aluminium surface from the vapor phase, the influence of surface siloxane layers on the hydration rate of the Al₂O₃ oxide film on aluminium with the formation of Al (III) and Al corrosion in distilled water was studied. For this purpose, a single layer of VS and AS (from a diluted water solution) was applied to the quartz resonator covered with a freshly deposited layer of aluminium. The sample was placed in water and the mass change was measured over time, the rate of hydrate formation and aluminium corrosion was estimated by weight gain (Figure 12). It was established that the aluminium surface without the organosilicon layer in the water quickly hydrated (Figure 12, curve 1). So, after 10 minutes of testing, the entire surface of aluminium is covered with a hydroxide (Al(OH)₃) layer. The presence of a more hydrophobic VS layer (two molecular layers thickness, applied from 0.03 M VS solution) on the surface results in a more than two-fold reduction in the weight gain of the aluminium sample after 12 minutes of testing (Figure 2, curve 2).

The resistometric study of the corrosion behavior of aluminium in chloride-containing electrolytes showed that instant metal dissolution rate was 0.315 and 2.68 mm per year in 0.01 M and 0.1 M sodium chloride solution, respectively (Table 4). The formation of a vinylsiloxane layer on the metal surface, with thickness 1-3 molecular layers (at concentration of deposition solution of VS equal 0.001 M) leads to a significant reduction in the corrosion rate of the aluminium foil (Table 4, Figure 13 a) and inhibition of thermally deposited aluminium dissolution (Figure 13, b). Increasing the layer thickness to 10 molecular layers reduces the inhibitory capacity of the nanolayer. Increasing the number of adsorbed molecules provides an increase in the layer thickness, but reduces its ordering and protective properties.

Thus, it was found that the presence of vinylsiloxane layer on the aluminium surface reduces the metal corrosion. Corrosion tests of aluminium foil samples carried out in a climatic chamber with periodic dipping in a 0.1 M NaCl solution and in a chloride-containing solution showed the inhibition of metal corrosion both in the atmosphere and in the solution (Figure 14, Table 4).

Scanner-refletoetnic study carried out on aluminium foil showed that the first corrosion products appear on the surface after 1 hour of exposure in a 0.1 M sodium chloride solution (Figure 15, curve 1). After 20 hours of testing, almost the entire surface is covered with corrosion products. The formation of a self-assembled vinylsiloxanenanolayer with a thickness of 3 molecular layers on the aluminium surface reduces the rate of uniform corrosion (Figure 15, curves 1, 2). Thus, the quantitative processing of reflectograms showed that in the presence of vinylsiloxanenanolayer for 50 hours there were practically no traces of uniform corrosion on the aluminium surface (Figure 15, curve 2) and only about 5% of the surface was occupied by corrosion products.

Thus, it was shown that surface organosilicon nanolayers reduce the rate of uniform aluminium corrosion. However, the presence of the organosilicon layer on the surface can reduce the rate of not only uniform, but also local aluminium dissolution.

Using resistonietricmethod allows us to estimate the change in the thickness of the metal conductor in the process of testing and makes it possible to divide the general and localized metal corrosion, although it is known that in chloride-containing media aluminium is susceptible to pitting corrosion. This is confirmed by visual inspection of samples after testing and corrosion rates (Table 4). In order to separate the contribution of uniform and localized aluminium corrosion and the influence of vinylsiloxanenanolayer on them, the initial stages of corrosion dissolution of thermally deposited aluminium in chloride-containing solution were studied using the method of quartz nano balance. Figure 16 shows the curves of changes in the mass of the freshly thermally deposited aluminium when the samples...
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| Table 4: Rates of uniform corrosion of aluminium foil in chloride-containing test solutions, determined resistometrically |
|---|---|---|
| NaCl concentration | System | 0.01 M | 0.1 M |
| Al foil | 0.315 | 2.689 |
| Al foil, modified in 0.001 M VS solution | 0.035 | 0.692 |
| Al foil, modified in 0.1 M VS solution | 0.293 | 2.43 |

Figure 12: Kinetics of water adsorption onto the “pure” (without organosilicon nanolayer) aluminium surface (1) and silicided aluminium surface coated with -1 siloxane monolayer deposited from the solution with the concentration of 5·10^-5 M (2) – VS. Gravimetry, quartz nano balance.

Figure 13: Samples of aluminum (foil, 100 mkm thick) after 30 days of testing in the climatic chamber RH 90%, t 660°C, periodic (once in 3 days) dipping samples in 0.1 m NaCl a. Aluminium without an organosilicon layer. b. Aluminium coated with a vinyl-containing layer (about 3 molecular layers thick (applied from 0.05 M solution).

Figure 14: Influence of vinylsiloxane nanolayer on aluminium corrosion in a chloride-containing electrolyte (NaCl) (pH 6.5) with the concentration of 0.01 M. 1. aluminium foil, 2. – aluminium coated with a vinyl-containing layer (about 3 molecular layers thick (applied from 0.05 M solution). Corrosion evaluation – resistometrically.

Figure 15: Kinetics of the uniform aluminium corrosion development in 0.1 M NaCl, pH 6.5. 1 – Al; 2 – Al+ vinylsiloxanenanolayer (3 molecular layers thick)

are kept in 0.001 NaCl solution. From Figure 16 it can be seen that in the interaction with water, i.e. when uniform corrosion occurs, the mass of the sample increases during the holding time in water, which may be due to the growth of an insoluble in water oxide-hydroxide layer on the metal. Above it is shown that the presence of vinylsiloxanenanolayer on the surface, one monolayer thick, leads to slowing uniform aluminium corrosion.

Introduction of chloride ions into water (Figure 16) causes local dissolution of the metal, which is expressed in the loss of mass due to the release of metal ions into the solution. During the first 5 minutes of testing on pure aluminum, the growth of the oxide-hydroxide film was observed. Further exposure to the solution led to a decrease in the mass of the sample, which was caused by a violation of passivity and local metal dissolution. It was found that for the first, at least, 150 minutes of testing, the loss of the sample mass is not recorded (Figure 16, curve 2). Apparently, vinylsiloxanenanolayer inhibits local corrosion at the initial stage. Thus, it was shown that the surface vinylsiloxanenanolayer is able to inhibit both uniform and local aluminum corrosion.

The study of the electrochemical behavior of aluminum also showed the inhibition of aluminum pitting by the surface vinylsiloxane layer (Figure 17). So, the critical potential of “purer” (without the organosilicon surface nanolayer) aluminum, determined by the fracture of the anodic polarization curve is -0.4 V. The presence of surface vinylsiloxane monolayer leads to Epitincrease, which indicates the inhibition of the pitting formation process. The reason for this may be a positive charge of the surface due to the amino group protonation at pH<9.5 (eq. 11) facilitating adsorption of chloride anions, responsible for the violation of passivity to the metal surface. As a result, on the one hand, the organosilicon nanolayer must inhibit the localized aluminum dissolution and, on the other hand, a positive charge of the surface must activate it. As a result, there was no noticeable influence on the potential of pitting formation (Figure 17 curves 1, 2) [28].

Scanner-reflectometric study conducted on aluminium foil showed (Figure 18) that the first corrosion defects (pittings) appear on the surface after 1 hour of exposure in 0.1 M sodium chloride solution. After 25 hours of testing the density of defects is about 40 units per cm² (Figure 18). Further exposure to aggressive electrolyte leads to an increase in the number and to the development of defects formed in the first 25 hours of testing. After 150 hours of testing pitting density was 253 pitting per cm on the surface of “pure” aluminium. It was noted that in the presence of the surface vinylsiloxane layer, pittings occur in the first 50 hours: further exposure of the sample in a chloride-containing solution (over 50 hours of testing) does not lead to the emergence of “new” pittings. The formation of self-assembled vinylsiloxanenanolayer 3 molecular layers thick on the aluminium surface reduces the rate of localized aluminum corrosion (Figure 18). Thus, after 150 hours of testing, the density of pitting on the silicicated surface is more than 4 times less than on the “pure” aluminium and is 53 pittings per 1 cm² (Figure 18, curve 2).

Quantitative processing of reflectograms showed that on the aluminium surface in the presence of vinylsiloxanenanolayer (Figure 18, curve 2), corrosion products occupy only 7% of the surface, while on “pure” aluminium after 50 hours of testing, corrosion products occupy the entire (100%) surface of the sample [30,31].

Electron microscopy of the samples of pure aluminum and aluminum with vinylsiloxanenanolayer of about 2 nm thick, applied from a solution with a concentration of 0.01 M VS, showed that after 10 days of preserving in a chloride-containing solution on the aluminum surface (both sprayed and foil), traces of corrosion products, occupying 18% and 29% of the surface for thermally deposited metal and foil, respectively were found. Corrosion products were also found on samples with siloxane nanolayer, but the proportion of the affected surface was about 2%. Localized corrosion defects (pits) with a diameter of 5 to 8 micrometers for the sprayed aluminum (Figure 19, a), from 7 to 17 µm for foil (Figure 19, b) were found on the pure aluminum. The presence of a vinylsiloxanenano layer on the surface leads to uniform corrosion (Figure 19, c). Nolocal defects were found after 10 days of testing, which also indicates inhibition of local corrosion.
Figure 16: Changes in the mass of thermally deposited aluminium during tests in 0.001 M NaCl: 1-Al, 2-Al + vinylsiloxanenanolayer (1 monolayer). Quartz crystal nano balance

Figure 17: Anodic polarization curves of aluminium in 0.1 M NaCl solution, pH 10:1 – Al – without treatment, 2 - Al+AS (3 molecular layers) 3 – Al+VS (3 molecular layers). Potential changing rate 0.1 mV/s

Figure 18: Kinetics of aluminium foil local corrosion in 0.1 M NaCl 1. Al, 2.Al with vinylsiloxanenanolayer (3 molecular layers thick). Evaluation of corrosion: "processing of scan-reflectometric images of the corroded surface. The images were obtained directly during testing when "in situ" observing surface changes during corrosion."
Figure 19: SEM images of the surface (a-c) and the spectrum of the RSMA (d) after 10 days of testing in 0.1 M NaCl solution. a. Thermally deposited aluminium. b. Aluminium foil. c, d. Aluminium foil coated with surface vinylsiloxanenanolayer.

XSMA spectra of aluminum coated with a vinylsiloxanenanolayer (Figure 19. d) showed that after conducting tests on the surface, quality elemental composition of the surface layer is almost not changed compared to the original spectra. Thus, in the regions damaged by corrosion, the presence of silicon and carbon bands was established and the intensity of Si and C bands was close to those obtained immediately after the application of the nanolayer. This confirms the conclusion about the strong interaction between the vinylsiloxanenanolayer and the metal corrosion.
and the surface groups of aluminium and also speaks about the stability of the nanolayer to the action of water and corrosion-active components.

**Summary and Conclusions**

1. It was shown that adsorbing silanes displace adsorbed water from the surface, occupying more than 2.5 adsorption places on the surface.

2. Aminosilan forms a densely packed layer vertically oriented to the surface at the initial stage of adsorption, the layer thickness is not less than 3 molecular layers at the solution concentration of 10-5 M.

3. It was found that in the case of vinylsilane there is a dissociative adsorption on the aluminium surface. The ethoxy silane molecule is hydrolyzed to form 1 silanol molecule and 3 ethyl alcohol molecules.

4. In the initial period of adsorption, VS molecules on the surface are horizontally oriented and do not interact with neighboring molecules in the region of fillings up to one monolayer.

5. Adsorption heats were calculated using different adsorption models. It was shown that the VS chemosorbes, forming a uniform, self-assembled, covalently bound with surface groups of metal vinylsiliconanerlayer on the aluminium surface, the thickness of the nanolayer can be controlled by changing the processing conditions, e.g., the concentration of the vinylsilane solution.

6. It was established that an ordered vinylsiliconanerlayer, up to 5 molecular layers tick effectively slows down uniform and localized corrosion of aluminium in chloride-containing electrolytes.

7. It was shown that after 10-day corrosion tests vinylsiliconanerlayer was preserved on the aluminium surface, indicating its resistance to water and corrosive components.

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