

Effect of surface organosilicon layers on corrosion and electrochemical behavior of metals

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Organic silanes are able to adsorb on metal oxide surface with formation thin organosilicon layers. These layers can be used to protect metal from corrosion. The objectives of the work is a study of the mechanism of silanes adsorption on aluminum and iron surface from a vapor phase and from aqueous and organic solutions, determination of effect and possibilities of inhibition of atmospheric corrosion of metals, processes of localized dissolution of metals in chloride containing electrolytes, and clarification of these layers influence on adhesion properties of polymeric coatings and underfilm corrosion of metals.

The study of ethoxysilanes $R_nSi(OC_2H_5)_{4-n}$ adsorption on aluminum and iron from vacuum, argon flow, aqueous, toluene and alcohol solutions have been carried out by quartz microbalance. The isotherms of adsorption of mono, triethoxysilanes, and bis-silanes have been obtained under different condition of deposition. We have calculated the magnitudes of the "landing sites" of silane molecules which allow to determine the orientation of molecules on the surface, and the energy of interaction of the adsorbate with aluminum surface was evaluated. The mechanism of silane chemisorption which includes hydrolysis to form silanol and the condensation with hydroxyl groups of the surface was determined. It has been established the conditions of formation of mono- and polymolecular siloxane layers with different chemical structure and adhesion to the metal surface. The anticorrosion properties of silane adsorbed layers on iron surfaces was studied by quartz microbalance, high sensitive resistometric technique, and by tests in climatic chambers. Corrosion tests in the flow of synthetic air with and water vapor introduction have shown both activation and inhibition of corrosion, depending on the siloxane synthesis technique, and orderliness and thickness of siloxane films. Thin crystallike films (10-12 monolayers) make the surface hydrophobic and inhibit iron corrosion. The increase of thickness up to 20-35 monolayers and decreasing orderliness result in an increase of superficial water concentration and the activation of corrosion. Corrosion tests of the modified iron and aluminum samples were carried out in climatic and salt fog chambers with "in situ" resistometric control of corrosion rate. The kinetics of iron corrosion modified by different organosilicon layers was obtained. The data indicate that silane chemisorbed monolayer can decrease by 2-5 times the atmospheric corrosion of the metals. The strongest effect was observed in triethoxysilanes and bis-silanes, which can form surface linear siloxane chains or bond the neighboring atoms of the surface. The mechanism

of organosilicon layers action on atmospheric corrosion of metals is proposed.

Corrosion of the modified iron, aluminum, and zinc samples in aqueous electrolytes was studied by quartz microbalance and resistometric technique. The obtained data indicate that silane chemisorbed monolayer can decrease by 1.5-4 times the interaction rate of the metal with water. Ion-exchange properties of metal oxide-hydroxide surface were reviewed. It was shown that modification of electric charge of a metal surface can lead to change the susceptibility of metal to localized dissolution of metals (Al, Mg, Fe). Chemisorbed monolayers were synthesized on an aluminum surface, the structure of which is similar to that of the Langmuir-Blodgett films with either negative (iminodiacetate and sulfate) or positive (ammonium and amino) ion radicals. A negative layer inhibits depassivation, and, hence, metal corrosion, whereas a positive layer promotes these processes. Charge density and potential in the plane of the ion-exchanging groups of the silane layer were calculated. Both values are associated with the pitting-corrosion potential and aluminum susceptibility to depassivation in chloride-containing environments. It has been shown that all the parameters (q , ψ' -potential, E_{pt} and depassivation susceptibility) depend on the ion-exchanger nature, acid dissociated degree, and ionic-chemical interaction with activating ions.

Effect of the silanes structure on the adhesion, water resistance and cathodic delamination of polymeric coatings was studied. Mechanism of formation of metal-polymer adhesive bonds in the presence of alkoxy silanes have been proposed. It was shown that organosilicon layers considerably improve adhesion and stability to the cathodic delamination action of coatings (siloxane-, epoxy-, ethylene-vinylacetate copolymer, and buty rubber polymers). The influence of modification of metal surface by silane coupling agents on the corrosion and electrochemical behavior of metals under polymeric coatings have been investigated. It was shown the inhibition of anodic dissolutions and of underfilm corrosion of metals in the presence of organosilicon layers at the metal-polymer interface, and mechanism of underfilm corrosion was proposed.