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Reactive Dispersions for Corrosion Inhibition

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Summary: Several concepts have been developed for the improvement of adhesion promotion and corrosion inhibition of reactive metal surfaces, like aluminum. The aim of these studies was to replace the present technical procedure for pretreatment of aluminum surfaces with chromium acid.

Therefore, the adsorption and organization process of mono- and bifunctional alkyl phosphonic acids and mono alkyl phosphoric acid esters has been investigated. The properties of the adsorbed SAM's were confirmed by industrial linked adhesion and corrosion tests. By functionalization of the terminal position with thiophene, molecules are prepared which can graft conducting polythiophene layers via surface polymerisation on silicon/metal substrates.

Also polymeric nano-particles with phosphoric acid groups form thin and smooth well-packed films on aluminum surfaces.

Stable core-shell polypyrrole (PPy) dispersions were prepared by using polystyrene (PST) or poly (styrene-co-butyl acrylate) (PST-co-BuA) as the core, and polypyrrole as the shell.

Keywords: SAM, microgel, adhesion promoter, corrosion inhibition

1 Introduction

Reactive metals like aluminum is one of the most used metallic materials in industry –from buildings over cars to aircrafts. Protecting reactive metals by covering their surface with organic coatings is a smart way to take advantage of mechanical properties of metals like aluminum while preventing them from corrosion and introducing requested surface properties in one step.

Mainly the treatment with chromic acid is applied to reduce the thickness of the natural oxide layer, to eliminate particles of other metals, which are present like iron, and to form a new layer of a mixed aluminum-chromium oxide inhibiting corrosion.

One topic of this work was the replacement of the chromating process on aluminum by thin organic adhesion promoter layers as an alternative pretreatment for the coating. Therefore, we used as reactive species self-assembly molecules. A strong and intact bond between coating

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and metal can withstand electrochemical or chemical attacks from aggressive species found in the environment such as water, oxygen and pollutants.

Self-assembly molecules (SAM's) with two reactive groups, one to the metal surface and the other to the lacquer connected by e.g. an aliphatic spacer form such bonds, which can stand up to the attack of water and simultaneously inhibit any electrochemical reaction at the interface [1-3] (see figures 1a and 2). Those very stable bonds between reactive organic monomers and metal surfaces can be achieved, if the reaction conditions are optimized for the given metal/coating system.

Especially, phosphonic and phosphoric acid groups showed a strong effect on the aluminum surface [4, 5]. The formed chemical bond to the substrate inhibits any electrochemical reaction at the interface (figures 1, 2)

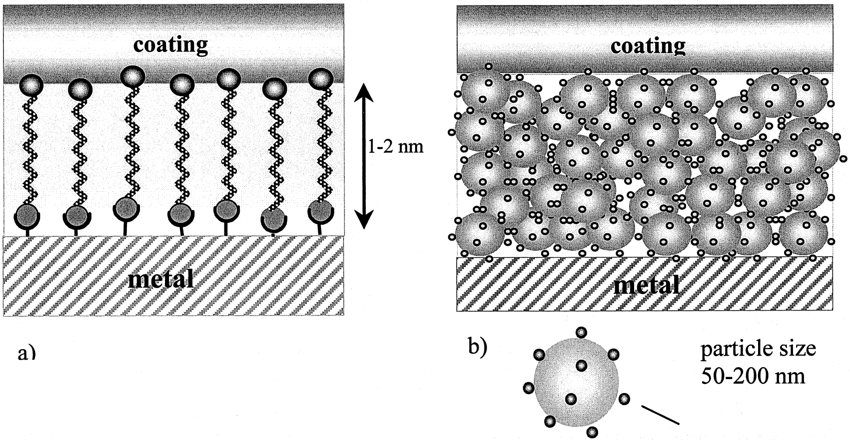


Figure 1: *Models of adsorbed layers of*

a) bifunctional molecules and *b) microgels with functional groups*

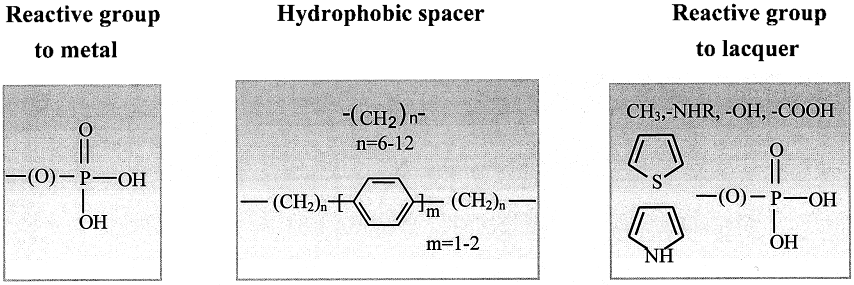


Figure 2: *Structural concept for adhesion promoters*

Microgels are the basic of the second concept (see figure 1b). Polymeric core-shell particles are combinations of different mostly incompatible polymers and offer the opportunity for introducing functional groups on the surface of the particles. They were functionalized with phosphorous containing groups according to former works [4-6] and were tested as links between aluminum and a final coating.

Based on these investigations microgels with a conductive shell have been developed. In order to improve the processability of e.g., polypyrrole, a lot of efforts have been made to obtain conducting polymer-coated composites where the "core" consists of a non-conducting particulate material [7-10]. Nanometer-sized polystyrene (PST) or poly (styrene-co-butyl acrylate) (PST-co-BuA) core particles were synthesized by using three different kinds of monomer/polymer as the surfactant which can produce particles with different charge.

The applied SAM's have a thickness of few nanometers and the microgel layers of 50 to 200 nm. The characterization of these very thin layers is not easy. Special surface sensitive methods were used to investigate the adsorbed monolayers. With the help of X-ray photoelectron spectroscopy and FT-IR spectroscopy it was shown that the density and structure of the films strongly depends on the surface roughness, the pre-treatment of the metal substrate, the structure and concentration of the surfactant, and the adsorption time. Surface plasmon resonance spectroscopy (SPR) was used to follow the kinetics of the adsorption process. The effect of core particles on the morphology and conductivity of PPy containing composites have also been investigated [11].

2 Results

2.1 Monofunctional self-assembly layers

The adsorption of alkyl-phosphonic and phosphoric acid monoalkyl esters on aluminum surfaces is an acid-base reaction. The driving force is the formation of a surface salt (see further explanation [4]).

Surface Plasmon Resonance Spectroscopy (SPR) was used to examine the kinetics of the adsorption process. In figure 4 one can see a typical SPR kinetics curve from the adsorption of octadecyl phosphonic acid on chromium. The advantage of SPR spectroscopy is that the kinetics of the adsorption process is directly visible without destroying the surface.

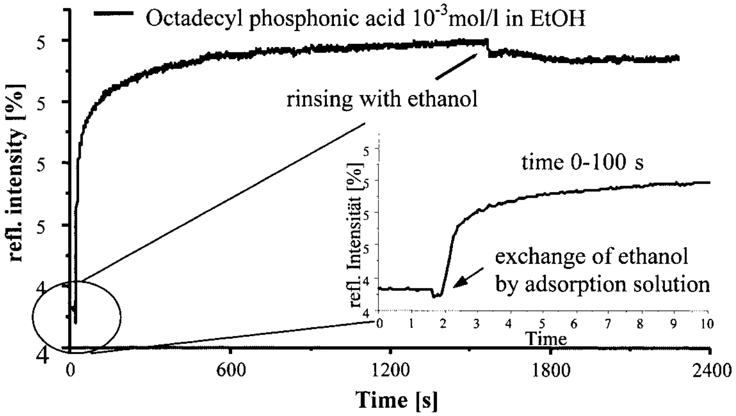


Figure 4: *Kinetically SPR measurement of the adsorption of octadecyl phosphonic acid on aluminum*

It is clearly seen from the curve that the adsorption process of phosphonic acids on aluminum starts very fast and reaches a plateau after some time (10 minutes to some hours). After rinsing with the used solvent some physisorbed species are removed and then the curve remains stable.

The organization and orientation processes of phosphonic acids also can be determined by angle-resolved X-ray photoelectron spectroscopy (ARXPS).

This method allows the quantitative detection of the element distribution on the substrate surface. These contributions change by varying the detector angles. Because of the limiting attenuation length of the electrons the depth information of XPS data is dependent on the varied angle α. A special region of the adsorbed layer can be seen at every detector angle. Though, at low angles (5-10°) the top of the adsorbed film is better detected than the deeper regions whereas at high angles (80-90°) one can get information from the substrate regions. Specific elements (marker elements) are watched at the different angles and from their distribution we have indications about the orientation and organization within the layer.

The thickness of the adsorbed layer was calculated from the experimental data and has a value of 2,21 nm. The theoretical C:P ratio is 12:1, but because of carbon contamination there could be detected an excess of C. Figure 8 shows the separation of adsorbed phosphonic (gray line) acid carbon and the carbon from the contamination (gray area). Now the layer thickness was about 1,1 nm.

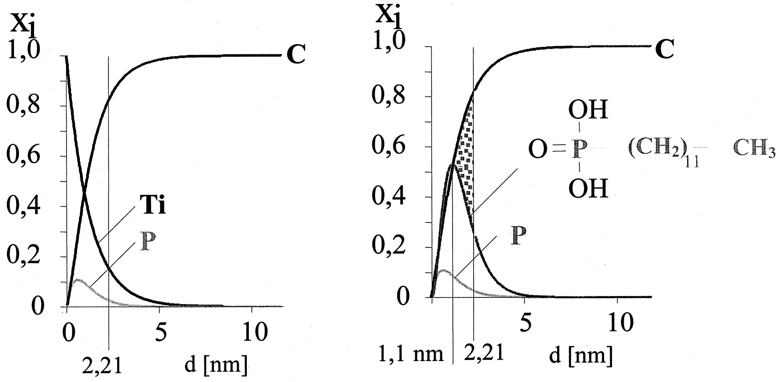


Figure 5: *Atomic contribution in dependence of layer thickness*

The calculated size of the dodecyl phosphonic acid molecule was 1,536 nm. From the ARXPS measurements we can conclude that the adsorbed dodecyl phosphonic acid molecules are tilted at 44° from the surface normale.

2.2 Bifunctional compounds

To form a chemical composition between metal and organic coating it is necessary to tailor self assembling molecules with two functions; one to chemisorb on the metal and another to react with the organic material of the top layer. A chain length of 10 to 12 carbons seems to be ideal for the preparation of α,ω-fuctionalized alkyl phosphonic acids. As second functional groups were chosen the amino group, hydroxyl group, phosphonic- or phosphate. The synthesis of these compounds is described elsewhere [4, 12].

The objective attention of the investigation was to find out whether and how the molecules were orientated after adsorption onto the chromium surface. Therefore, angle resolved X-ray photoelectron spectroscopy data were taken (see figure 6). The spectra with small α give the most information of the top layer. With increasing angle α more information of the substrate were obtained. The ARXPS spectra of an 50 h adsorbed AlMg1 sample were taken from 5° to 75° between the sample surface and the detector. The phosphorous 2s peak and the nitrogen 1s peak were used for analysis (marker peaks). The shape of the intensity ratios proved that the phosphonic acid group is attached to the substrate and the amino group is orientated off the surface.

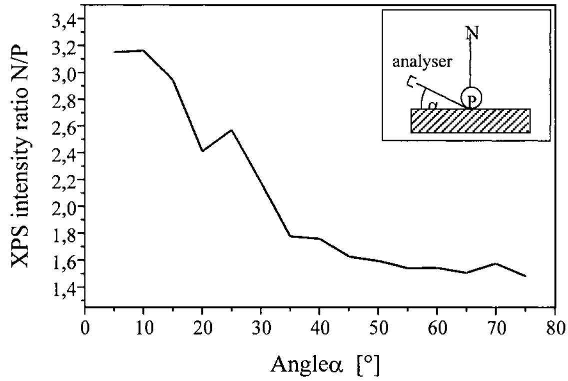
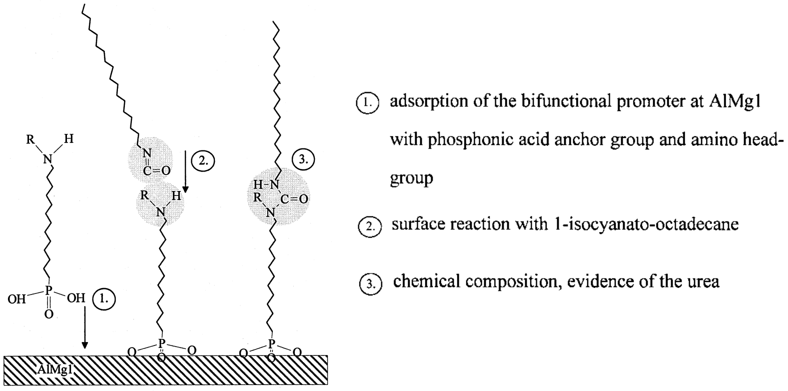


Figure 6: *ARXPS intensity ratio of P 2s and N 1s peaks of a 50 h adsorbed AlMg1 sample*

Model surface reactions were developed to give prove for the reactivity of the second reactive group. Aliphatic or aromatic isocyanates are cross-linking agents for many coating systems. Because the isocyanate-group is very reactive to hydroxyl and amino groups, we chose an alkyl-isocyanate for model reactions. The resulting urethanes and substituted ureas can be detected by their characteristic infrared bands [4].



① adsorption of the bifunctional promoter at AlMg1 with phosphonic acid anchor group and amino head-group

② surface reaction with 1-isocyanato-octadecane

③ chemical composition, evidence of the urea

Figure 7: *Model for surface reaction*

2.3 Surface reaction with thiophene-substituted phosphonic acids

Thiophene terminated self-assembly layers were synthesized as adhesion promoters to make polythiophene more compatible towards diverse metal substrates [13,14]. The surface polymerization can be undertaken either chemically or electrochemically. The principle of these reactions is shown in figure 8. $FeCl_3$ was used as an oxidative coupling reagent for the chemical polymerization, we used as. The terminal thiophene groups of the adhesion promoter take part in the polymerization process and a stable composite can be formed consisting of the conducting polymer, adhesion promoter and substrate.

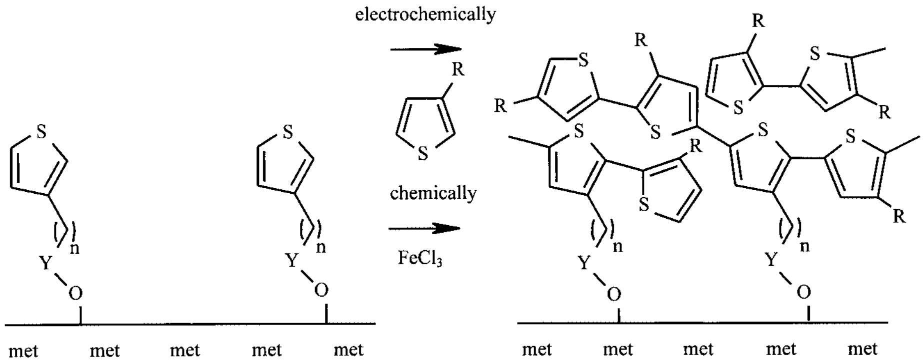


Figure 8: *Principle of surface polymerization via an adhesion promoter*

For electro-polymerization, the electrodes were coated with the adhesion promoter and polymerised at the corresponding oxidizing potential.

The polymer thickness could be adjusted between 3 and 250 nm depending on the reaction conditions. The AFM image of polythiophene grafted onto a Si-wafer is shown in figure 9. The layer has a relatively homogeneous and dense surface with a shell-like structure. A roughness analysis gave values of R_{ms} = 1,73 nm and R_a = 1,35 nm.

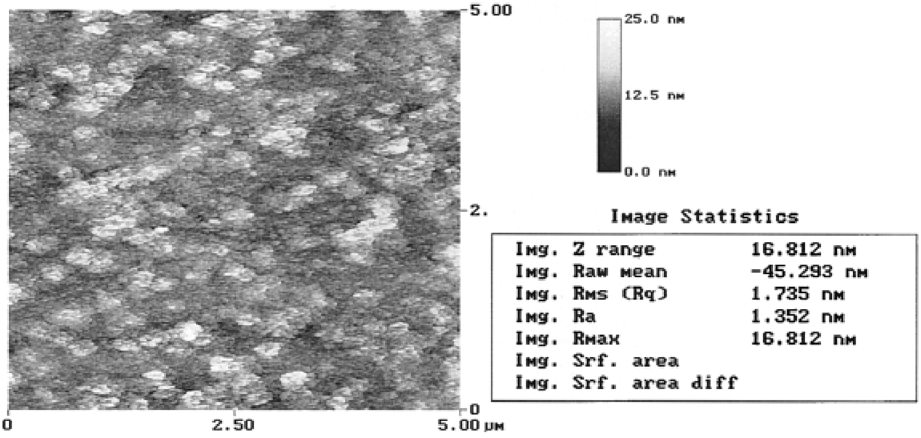


Image Statistics

Img. Z range	16.812 nm
Img. Raw mean	-45.293 nm
Img. Rms (Rq)	1.735 nm
Img. Ra	1.352 nm
Img. Rmax	16.812 nm
Img. Srf. area	
Img. Srf. area diff	

Figure 9: *AFM Image of polythiophene grafted onto SiO_2*

2.4 Functionalized microgels

Polymeric nano-particles with phosphate groups and a core-shell-like structure were synthesized according to former publications [6] about self-assembling molecules based on phosphonate- and phosphate groups as reactive groups toward the aluminum surface. These particles can be used for corrosion inhibition of aluminum [15, 16].

According to figure. 10, functionalized particles were synthesized in a two-step emulsion polymerization. Cross-linked BuA/St particles were formed in a first step. In a second step a mixture of functionalized acrylate and BuA/St was added to the system.

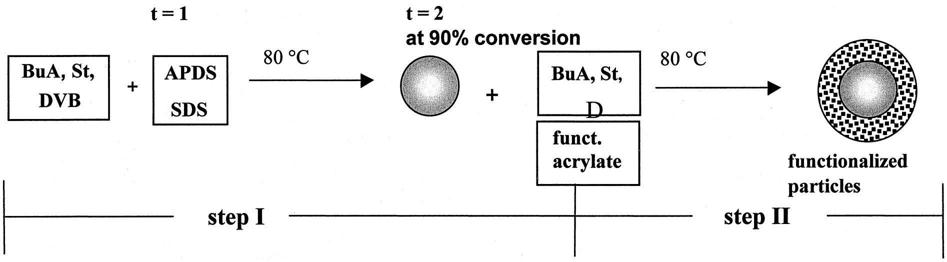


Figure: 10: *Synthesis of functionalized composite particles*

Special P-functionalized acrylates were used to incorporate the phosphoric acid group into the particle surface.

For application, AlMg1-panels were dipped in phosphate-functionalized dispersions. Already after few seconds, particles were found on the AlMg1 surface. Time-dependent SEM pictures are presented for 160 nm particles in figure 11 [16].

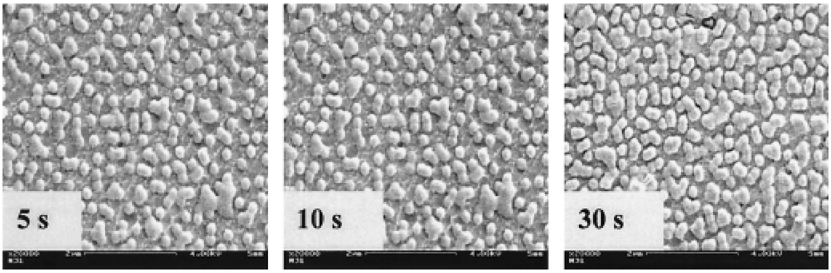


Figure 11: *SEM images of time-dependent SEM pictures for 160 nm particles*

Figure 12 shows that the film formation process begins within 10 s and is completed within 30 seconds in case of smaller particles. The transition of adsorbed microgel spheres to a closed film is clearly seen in the middle picture.

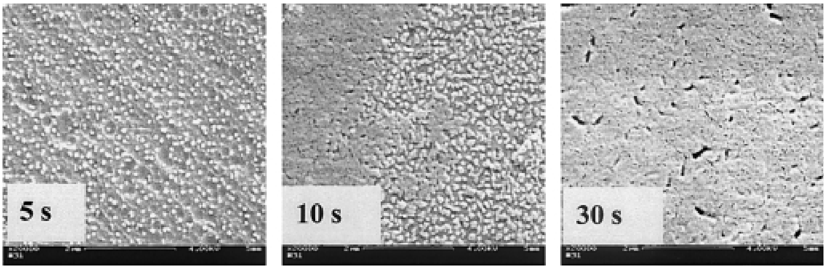


Figure 12: *SEM images of time-dependent SEM pictures for 60 nm particles*

Film formation of larger particles takes more time. The influence of particle size on film formation correlates with the results of corrosion tests.

For an application in corrosion protection, smaller particles (d~100 nm) seem to be more effective than bigger ones (d>150nm) due to better film formation properties during the adsorption process. This result correlates with the SEM pictures. Different testing methods exist controlling the corrosion protection of coatings on metal surfaces. For this work two usual methods were selected and performed by the CHEMETALL GmbH: the acetic acid salt spray-test (ASS-test, DIN 50021) and filiform test (DIN 50024). Therefore, the test panels were coated with SAM solution and a commercial clear coat, scratched and exposed to a mixture of NaCl-solution and acetic acid in a climate chamber for 1200h. The results were stated in mm infiltration. Infiltrations of < 1mm are the best values. The SAM treated samples have an excellent corrosion inhibition effect and better adhesion properties as the chromated surface.

The other industrial test results are summarized in table 1 with comparison with different coated samples.

Table 1: Industrial testing of coated AlMg1 panels with test panels

compound	**ASS-Test** ***DIN 50021*** **infiltration [mm]**	**Filiform-test** ***DIN 50024*** **[mm]**	**T-Bend-Test Exfoliated area LPV 75 [%]**
AlMg1	8	5	100
AlMg1 alkaline/acidic stained	4	4	85
AlMg1 phosphated	3	<1	10
AlMg1 chromated	<1	<1	25
Molecular adhesion promoter	<1	<1	<1
Microgels	<1	<1	<5

Polystyrene/Polypyrrole composites have been synthesized and characterized. Three different kinds of monomer/polymer, PM-MA, MEAK, and PEGMA have been used as the surfactant during the synthesis, which produce core particles with negative charge, positive charge and non-charge, respectively [11].

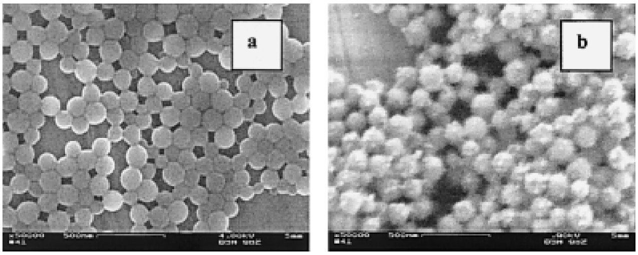


Fig. 13: *SEM images of (a) PST/MEAK core, (b) PST/MEAK/PPy composites Further details are published elsewhere* [11]

3 Discussion

Several methods have been developed to improve corrosion inhibition and adhesion promotion on reactive metals like aluminum.

The idea using self-assembly molecules as corrosion protection layers for chromium surfaces appears to be promising. The SAM's bearing a phosphonic acid head-group and polymer-reactive group were able to adsorb spontaneously onto the chromium surface. They formed orientated layers that could be proved by polarized external reflectance FT-IR measurements and X-ray photoelectron spectroscopy. Monofunctional phosphonic acids formed monolayers on the substrate. The chemical composition to organic coatings was realized with a second terminal functional group. This lacquer linking was confirmed by industrial adhesion- and corrosion tests. The effect of the bi-functional surfactants was equivalent to chromated panels due to corrosion inhibition and superiored due to adhesive strength.

Nanometer-sized composite PST/PPy particles with raspberry morphology were obtained when the core particles were stabilized by surfactant with charge, and with homogeneous morphology when non-charged surfactant was used. Stable polypyrrole dispersions can be prepared by using MEAK as the surfactant and Poly(ST-co-BuA) as the core, which give good ability of film formation. Conductivity of the composites was influenced strongly by the core material.

4 References

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