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Surface Modification of Aluminium with Reactive Microgels

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Summary

The adsorption and organisation process of reactive microgels has been investigated on technical aluminium. The aim was to replace the present chromating procedure on reactive metals like aluminium because this process was been considered as an ecological problem. By means of a two-step emulsion polymerization with phosphate substituted monomer we have obtained polymeric nano-particles with phosphate groups on the surface. The core is synthesized by copolymerization from styrene (St) and butyl acrylate (BuA).
The results of several analytical methods like contact angle SEM or TEM measurements showed, that these microgels were able to adsorb spontaneously onto the substrate surface and subsequently a structured molecular order was formed. The properties of the adsorbed microgel layers were confirmed by industrial linked adhesion and corrosion tests.

Introduction

Aluminium has found a wide use in industrial and technical applications. In spite of its natural aluminium oxide, technical aluminium is not resistant against corrosion. Therefore, the aluminium surface has to be chromated after several staining processes, followed by coating.

The loss of adhesion of organic coatings is a direct result of electrochemical reactions which take place at the metal / lacquer interface resulting in filiform and pitting corrosion. This causes de-lamination of the coating and adhesive sites. A strong and intact bond between coating and metal can withstand electrochemical or chemical attacks from aggressive species found in the environment such as water, oxygen and pollutants.

With regard to former investigations we apply the self-assembly technique to reactive microgels [1-3]. 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 chemical bonds which inhibit any electrochemical reaction at the interface (see Fig. 1a) [4].

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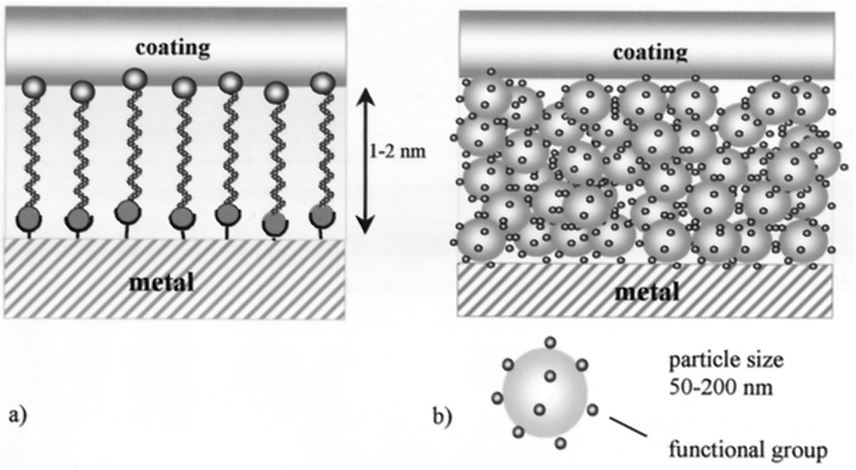

Fig. 1: Models of adsorbed layers of

a) bifunctional molecules and b) microgels with functional groups

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. By this way, useful systems for applications as reactive fillers and impact modifiers are available [5-7].

The core-shell morphology can be built up in a batch or semi-batch procedure (by adding two monomers at the same time or one after another) or by seed polymerization. For seed polymerization, the shell monomer is mixed with the pre-formed latex and polymerization of the second monomer is initiated by a free radical initiator [8-11].

In the first case, particle morphology is determined mainly by the copolymerization parameters of the two monomers; in the second case the polarity and the compatibility of the shell and core polymer, type of monomer addition, type of initiator and temperature could strongly influence particle morphology.

The morphology of latex particles can show a wide variety. A number of morphologies other than the core-shell have been reported [12, 13].

Polymeric nano-particles with phosphate groups and a core-shell-like structure were synthesized according to former publications of Funke [14] about functionalized microgels and our own results with self-assembling molecules based on phosphonate- and phosphate groups as reactive groups toward the aluminium surface. These particles can be used for corrosion inhibition of aluminium [15,16].

Synthesis and characterization of functionalized dispersions

According to Fig. 2, 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. The composite particles were obtained in this way.

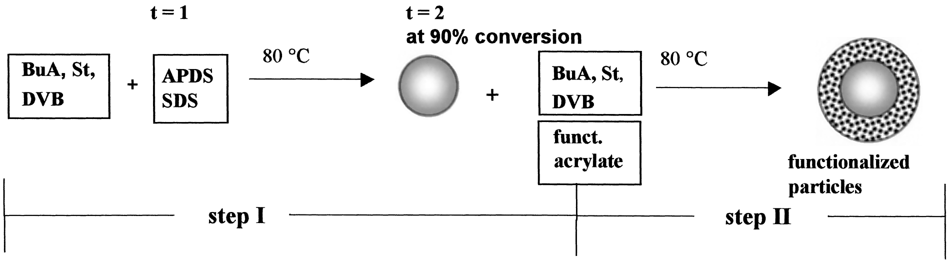

Fig. 2: Synthesis of functionalized composite particles

Especially, different P-functionalized acrylates (see Fig. 3) were used to incorporate the phosphoric acid group into the particle surface.

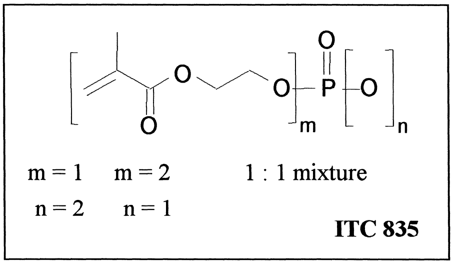

Fig. 3: P-containing acrylates used for functionalization of particles

Different reaction conditions were varied such as temperature, feed rate, and concentration of emulsifier.

The obtained dispersions were characterised by particle size measurements (DLS, F-FFF) and glass transition temperatures. The mean diameter of particles was in a range of 50 to 200 nm. By changing the reaction conditions, it was possible to control particle size and particle size distribution.

For phosphate-functionalized dispersions, it was possible to show the distribution of P-species around particles by an energy dispersive TEM picture. Fig. 4 shows two particles in the range of 160 nm in a P-sensitive TEM picture.

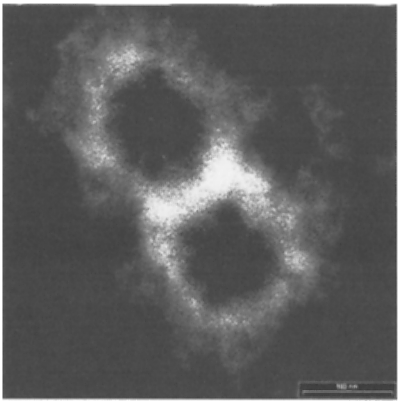

Fig. 4: P-sensitive TEM picture of two phosphate-functionalized particles

It was found that phosphate-functionalized dispersions are useful for corrosion protection of AlMg1 panels.

For application, AlMg1-pannels were dipped in phosphate-functionalized dispersions. Already after few seconds, particles were found on the AlMg1 surface. In Fig. 5 are shown an alkaline and acidic stained surface of technical aluminium alloy AlMg1 and such pre-treated surface after 30 sec exposure time in dispersion.

The stained Al surface of blanc AlMg1 is rough and contains a lot of pinholes and inclusions which initiate corrosion. After dipping particles are visible which protect the active sites on the surface. The rate of adsorption and the film formation depend on the particle size and content of phosphate groups.

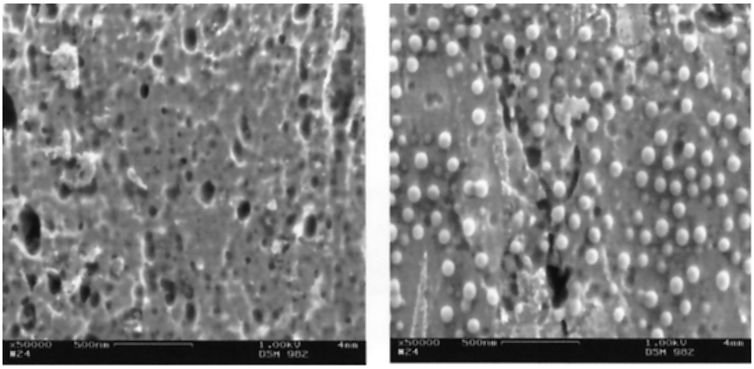

Fig. 5: SEM images of blanc AlMg1 (left) and an AlMg1 surface after dipping in a phosphate-functionalized dispersion (right)

Time-dependent SEM pictures are presented for 160 nm particles in Fig. 6 [16].

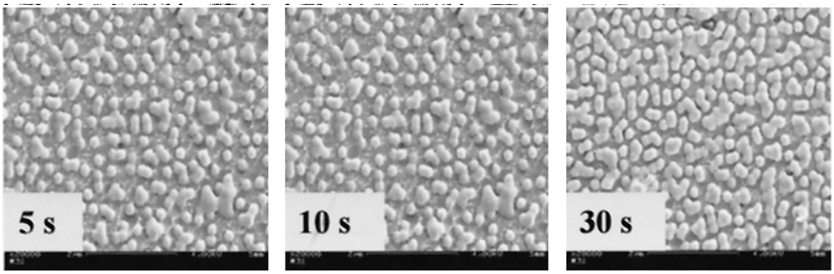

Fig. 6:SEM images of time-dependent SEM pictures for 160 nm particles

Fig. 7 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.

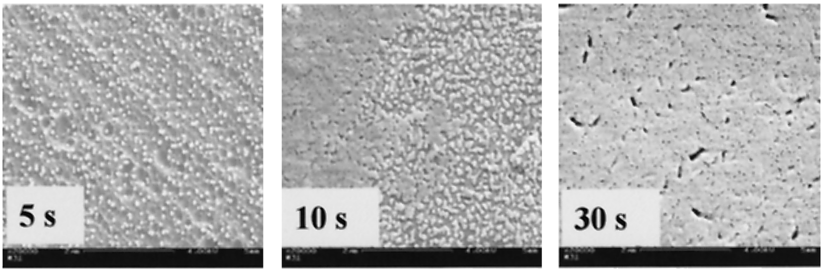

Fig. 7: SEM images of time-dependent SEM pictures for 60 nm particles

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

Therefore, the coated panels were tested according to DIN 65472 in a corrosion test. The panels were treated with unfunctionalized and phosphate-functionalized microgel dispersions of different average particle size and then coated with a commercial clear coating. The samples were scratched using a high-grade steel tip and exposed to an HCl-atmosphere for 1 h, followed by an exposure in a constant climate test chamber at 40°C and 80% humidity.

In Fig. 8 the panels are presented after 1200 h exposure time. In the case of the unfunctionalized dispersion the test panel showed filiform corrosion at the scratch. When phosphate-functionalized dispersions were used, no infiltration could be observed at the scratch.

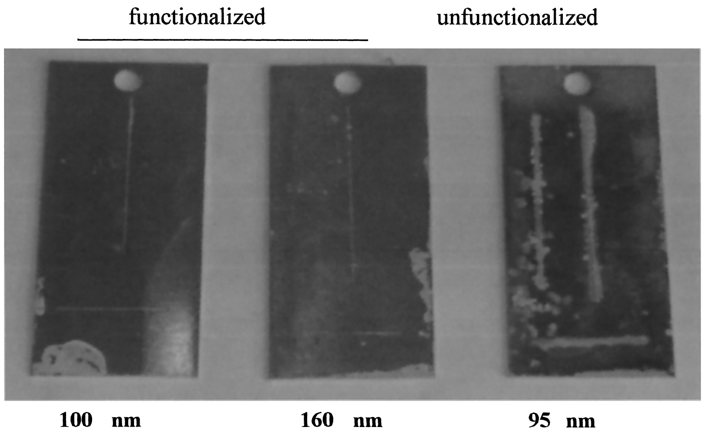

Fig. 8: Panels with un- and phosphate-functionalized particles after 1200 h exposure time in acetic acid salt spray chamber

The infiltration protection also depends on the particle size: smaller particles work better than bigger ones.

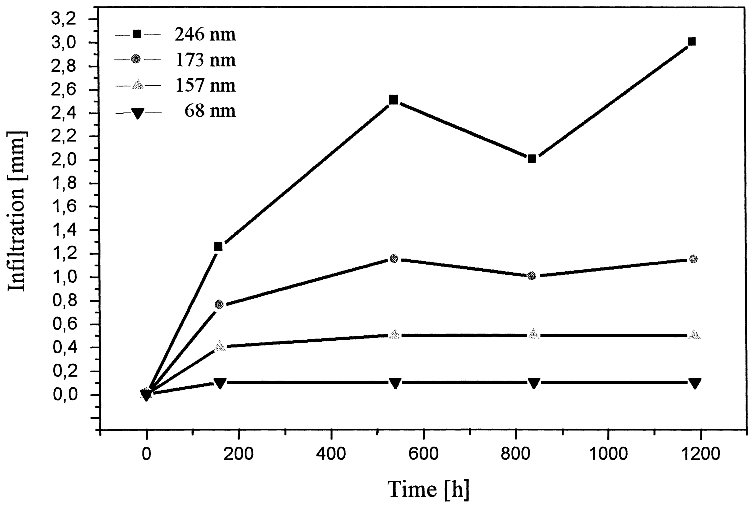

Fig. 9: Dependency of infiltration on the particle size and exposure time

In Fig. 9 the influence of particle size and exposure time on infiltration is shown:

The infiltration of the samples coated with small particles increases within the first 200 h of exposure, after that time it remains stable. The samples with big microgel particles show a growing infiltration all the time.

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.

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

compound	**ASS-Test** *DIN 50021* **infiltration [mm]**	**Filiform-test** *DIN 50024* **[mm]**
AlMg1 de-greased	8	5
AlMg1 alkaline/acidic stained	4	4
AlMg1 phosphated	3	<1
AlMg1 chromated	<1	<1
Molecular adhesion promoter	<1	<1
Microgels	<1	<1

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

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 microgel dispersion 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 microgel dispersions have an excellent corrosion inhibition effect on the aluminium surface.

Conclusion

The idea using reactive microgels containing phosphate groups as corrosion protection layers for reactive metal surfaces appears to be promising.

These nano-particles of different size adsorb spontaneously onto the aluminium surface from aqueous solution. The phosphate groups play the role of anchor-groups to the metal surface. They form well-packed layers, which have been proved by SEM measurements. The TEM-images show, that the phosphate groups are concentrated at the outer shell of the particle.

Industrial corrosion tests revealed the dependency of corrosion protection on particle size. Panels coated with phosphate-functionalized particles show clearly better results than the treatment with unfunctionalized particles.

The adsorbed particles have an excellent corrosion inhibition effect.

Acknowledgement

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