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ULTRATHIN ORGANIC LAYERS FOR CORROSION PROTECTION

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ABSTRACT

The adsorption and self-organisation process of alkyl-phosphonic acids and phosphoric acid monoalkyl esters on technical aluminium surfaces have been investigated by different surface sensible techniques: Grazing angle FT-IR- spectroscopy, angle dependent XPS and Auger- spectroscopy. The aim of these studies was to replace the present technical procedure for pretreatment of aluminum surfaces with chromate acid in order to improve the corrosion inhibition and the coating adhesion.

The ability for self-assembly is given by substances which have a surface reactive group and a long-aliphatic or aromatic spacer and a supramolecular order is built-up between these spacers. The results show that these molecules are able to adsorb spontaneously onto the aluminum surface and subsequently a structured molecular order is formed.

These effects were confirmed by industrial linked adhesion and corrosion tests.

Keywords: aluminium, self-assembly, adhesion promoter, corrosion inhibitor

1. INTRODUCTION

Aluminium has found a wide use in industrial and technical applications.

The aluminium oxide is performed in the presence of intermetallic inclusions, which are frequently responsible for corrosion problems of aluminium alloys. That´s why the aluminium surface has to be protected by coatings. Coatings also have an aesthetic function to colour and to improve the look of metal surfaces.

Mainly the treatment with chromium acid is applied to reduce the thickness of the oxide layer, to eliminate particles of other metals which are present like iron, and to form a defined layer of a mixed aluminium-chromium oxide.

This so called chromating process results in a layer protecting the aluminium surface against corrosion. The mechanism is not exactly understood. The chromating process is the common way for the pre-treatment of aluminium alloys.

Due to this, the chromating process will be increasingly considered as an ecological problem

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following the pollution by chromium and the content of this metal for the recycling of aluminium.

Alternative methods using zirconium salts, fluorides, phosphates and organic polymers are already industrial processes. These layers do not attain the quality of chromate pretreatment relating to adhesion and corrosion protection.

The loss of adhesion is a direct result of electrochemical reactions which take place at the metal / lacquer interface [1, 2].The bond between the coating and the metal substrate must be strong enough to withstand mechanical stress within the composite and must be stable enough to electrochemical or chemical attack 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.

Those very stable bonds between reactive organic monomers and metal surfaces can be achieved if the reaction conditions are optimised for the given metal / coating system.

This new class of composite materials can be prepared in three steps:

1. A reactive metal surface must be produced by cleaning and staining processes.
2. An ultrathin layer of tailored molecules is attached to the substrate.
3. The coating is then covalently bonded to these immobilised species.

This promising method of chemically modifying reactive metal surfaces with organic molecules was studied in previous works by Stratmann et. al. [3] at the mercaptan / iron system. Is there a possibility to apply the Stratmann concept to the reactive aluminium surface?

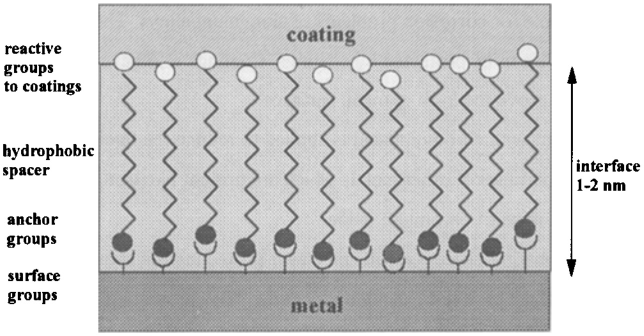


Fig. 1: Model of monomer promoters for metal/coating compositions

Figure 1 shows the model of the composition metal / adhesion promoter/lacquer. Molecules are needed, which are able to adsorb onto the aluminium surface, to form dense layers and to react with the lacquer completing the metal coating composition.

This aim requires the co-operation of scientists from a diversity of scientific disciplines such as electrochemistry, surface science, organic and polymer chemistries in order to optimise the structure of the organic monomers and to provide the best possible bonds to the metal and to the coating.

To solve these problems a project between industry, universities and the Ministry of Education and Science (BMBF) was created.

In cooperation with our industrial partners CHEMETALL GmbH, Frankfurt, who are responsible for the pretreatment and macroscopical examination of the Al surface, and BASF Lacke & Farben Münster, who in turn are responsible for the testing of the different coating systems, a composite system of adhesion promoter and coating which can replace the common chromating process was developed.The other participants of this project : Märkische Fachhochschule Iserlohn deals with the examination of the electrochemical surface conditions of the metal and metal/coating-composites and the Institute for Corrosion Science and Surface Technology Erlangen with the microscopical behavior of the metal (e.g. AES, XPS, Kelvin probe and Impedance measurments).

2. EXPERIMENTAL SECTION

All used reagents, solvents and substances were of reagent grade quality and were obtained from commercial sources. The synthesised compounds were identified by their melting points, FT-IR-, ^{13}C-NMR-, ^{31}P-NMR-measurements and elemental analysis.

2.1. Synthesis

2.1.1. n-Alkyl-phosphonic acids [4]:

Triethyl phosphite (0,11 mol) and bromododecane or bromooctadecane (0,1 mol) were heated for 4 h at 160-200°C with continuos distillation of ethyl bromide. The reaction mixture was refluxed with 40% HBr for 2 h or with 37% HCl for 8 h to receive the free phosphonic acid. After distillation of the mineral acid the product was purified by steam-distil-lation, dried and recrystallized with n-hexane. The dodecyl-and octadecyl-phosphonic acids were obtained in yields of 50%.

2.1.2. Aluminium salt of the dodecyl-phosphonic acid [5]:

Dodecyl-phosphonic acid was refluxed with an excess of $AlCl_3$ in a solution of ethanol / water (1:1). The product was filtered off, washed with water and dried in vacuum.

2.1.3. Phosphoric acid monoalkyl ester [6]:

Polyphosphoric acid (0,1 mol) was dispersed into di-isopropyl ether. Alkyl OH was dissolved in di-isopropyl ether and slowly dropped to the mixture under reflux. After 6 h the reaction was completed. 200 ml of distilled water were added to split the polyphosphoric ester to the monophosphat. The organic layer was separated and washed with water. After removal of the ether the product was recrystallized from ethyl acetate. The phosphoric acid monoalkyl ester was obtained in a 60 % yield.

2.1.4. [(Octadecyl-phosphonomethyl-amino)-methyl]-phosphonic acid [7]:

Octadecylamine (0,05 mol) and phosphoric acid (0,1 mol) were dissolved in aqueous HCl and heated under reflux. An aqueous solution of formaldehyde (0,2 mol) was then slowly added and heated to 70-80°C under stirring. After diluting with water the solid was withdrawn and washed several times with water. To remove by-products the solid was solved in diluted HCl, heated and filtrated. The obtained product was washed with water and dried. (Yield 78%, M_P >200°C)

2.1.5. α,ω- alkyl-diphosphonic acid [8]:

Triethyl phosphite (0,25 mol) and dibromoalkane (0,1 mol) were heated for 4 h at 160-200°C with continuos distillation of ethyl bromide under reduced pressure. The reaction mixture was refluxed with 40% HBr for 2 h or with 37% HCl for 8 h to obtain the free phosphonic acid. After distillation of the mineral acid the product was purified by steam-distillation, dried and washed with ethyl acetate. The α,ω- alkyl-diphosphonic acid was obtained in a 50% yield.

2.1.6. (12-Ethylamino-dodecyl)-phosphonic acid [9]:

Triethyl phosphite (0,1 mol) and 1,12-Dibromo-dodecane(0,4 mol) were heated for 4 h at 160-190°C with continuos distillation of ethyl bromide. The excess of 1,12-Dibromododecane was removed by extraction with n-hexane. The obtained (12-Bromo-dodecyl)-phosphonic acid ester [10] was refluxed with 40% HBr for 2 h. The purification of the phosphonic acid was accomplished as described above. Recrystallization of the product from n-hexane resulted in a yield of 60%. Refluxing the phosphonic acid with an excess of ethylamine (70% aq. soln.) for 16 h produces the expected product in 90% yield.

2.1.7. (4-Phosphonomethyl-benzyl)-phosphonic acid [11a,b]:

Triethyl phosphite (0,1 mol) and 1,4-Bis-chloromethyl-benzene (0,1 mol) were heated under continuos distillation of ethyl bromide until the theoretical amount of ethyl bromide is obtained. The reaction mixture was recrystallized from petrol ether to obtain the (4-phosphono-methyl-benzyl)-phosphonic acid tetraethylester (M_p 70-71°C). 20 g of the ester were refluxed with 37% HCl for 6 h. The excess of HCl was distilled off, the solid residue was washed with acetone and after recrystallization from water the free acid was obtained in a 80% yield.

2.2. Substrates

Aluminium powder (BET-surface 0,3 g/m ^{2}) was acquired from commercial sources.

Rolled Al-Plates (AlMg1) of technical grade were provided by Chemetall GmbH. The plates were cut into 15X15 mm pieces for contact angle measurements.

Substrates for IR-spectra were polished to obtain a reflected metal surface.

2.2.1. Pretreatment

Aluminium powder was used without further treatment for the flotation tests.
The technical Al-plates were cleaned and stained to get a standard metal surface without organic residues and with an uniform thickness of oxide layer.

General procedure: The cut Al-plates were ultrasonically cleaned in acetone for 3 min to remove organic residues. The plates were immersed in alkaline stain (1 vol% aqu. solution of BONDER®V338M from CHEMETALL) for 20 sec at 50°C, rinsed with distilled water and then dipped into the acid stain (aq. H_2SO_4 with additives) for another 30 sec at 50°C, rinsed with water and dried under a stream of nitrogen.

2.3. Adsorption of surfactants

Al-powder and cleaned and stained Al-plates, respectively, were exposed to a 10^{-3} M solution of the surfactant in water, ethanol, THF or mixtures of these solvents. The exposure time varied from 2 min to 24 h. The substrates were rinsed with the above solvents and dried in vacuum or under a stream of dry nitrogen.

2.4. Characterisation

2.4.1. Flotation tests:

For screening of active headgroups by flotation tests several monomolecular surface active compounds (C18) were adsorbed onto Aluminium powder (BET-surface 0,3 m^2/g).

General procedure:

a) Adsorption: 10 g Al-powder were shaken in 100 ml 10^{-3}M solution of the surfactant in THF/H_2O (9:1vol%) for 20 h. The powder was filtered off, washed twice with the solvent and dried in air and in a vacuum oven at 40 °C.

b) Flotation test: A small amount of the adsorbed Al-powder was shaken at room temperature in each of three solutions:
1. distilled water (pH=6-7), 2. diluted HCl (pH=2) 3. diluted NaOH (pH=12).
The behaviour of the Al-powder was documented after 24 h: Hydrophobized powder (adsorption took place) rises to the surface(it „swims„) non-hydrophobized (no adsorption) remains on the bottom.

2.4.2. Contact angle measurements

A K12 processor tensiometer from Krüss GmbH was used to measure the contact angles of the aluminium plates by the Wilhelmy method. Al-plates of known geometry were coated with the surfactant and measured by Wilhelmy method. Advancing and receding contact angels were calculated.

2.4.3. Constant humidity climate test

These tests were performed according to DIN 50017 by the CHEMETALL GmbH Frankfurt [12]. They were served to clarify the corrosion protection of pre-treated metal plates under influence of constant humidity at 40°C for 96 h.

2.4.4. FT-IR measurements

For detecting the infra-red spectra a Unicam RS 1000 FT-IR spectrometer was used. For acquising the bulk-spectra the sample was prepared by dispersing the substances into KBr-pellets.

Infra-red spectra of the adsorbed plates were measured using a MTC-detector and FT-80 unit from Spectra Tech Inc. All spectra consist of 500-1000 scans at 4 cm^{-1} resolution and were ratioed to stained and polished metal plates.

2.4.5. X-Ray Photoelectron Spectroscopy (XPS)

The analysis with XPS were measured on an ESCA 5700 system from Physical Electronics.

2.4.6. Auger Electron Spectroscopy (AES)

The AES data were detected using a SAM 670 xi system from Physical Electronics. This instrument is equipped with an CM analysator with a centred electron beam. The experiments were performed with 5 keV primary energy and 10 nA of current.

2.4.7. Industrial testing with lacquer coated aluminium panels

The aluminium panels were coated in two steps, first with a primer and second with a final polyester coil-coating from BASF L&F company. The primer and coating were dried for two hours and burned according to the application order of the producer. Different testing methods exist controlling adhesion and elasticity of lacquer films on metal surfaces. For this work two usual methods were selected and performed by the CHEMETALL GmbH [12]:

T-bend test:

Coated metal stripes were bended to 180°. Flexural cracking and/or flaking off lacquer were visually marked at the edge and given in per cent.

Cross-hatch:

The coating was cut down to the metal surface according to DIN ISO 2409. Then a hemisphere was pressed to the backside of the cross-hatch. This test was performed in accordance to DIN ISO 1520. The cross-hatches were judged by their appearances and marked with notes from 0 (not flaked off) to 5 (>65% flaked off).

For testing corrosion protection of the coating the acetic acid salt spray-test (ASS-test, DIN 50021) and filiform test (DIN 50024) were used. The results were stated in mm infiltration. Infiltrations of < 1mm are the best values.

3. RESULTS AND DISCUSSION

By screening a wide range of organic compounds some reactive groups surface could be found which are able to adsorb onto the Al.

The first test was the so-called flotation test. This gave an insight into the adsorption abilities of the substances and the wetting behavior of the coated Al powders.

Contact angle measurements gave information concerning the wettability of the coated plates - i.e. that they can hydrophobize the metal surface. The tests were carried out in dependance of adsorption time, concentration and /or different solvents.

Constant humidity climate tests were carried out by the Chemetall GmbH to study the corrosion inhibition capability of the surfactants.

3.1. Flotation tests

A number of different compounds of the type $C_{18}H_{37}$ - X were adsorbed on aluminium powder, where are X = Br, OH, SH, NH_2, COOH, SO_4Na, SO_3Na, $SiOMe(Me)_3$, $Si(OMe)_3$, $N(CH_2-PO(OH)_2)_2$, PR_3Br, $PO(OH)_2$ and $OPO(OH)_2$ groups. All substances expect the octadecyl-phosphonic acid, the phosphoric acid monooctadecyl ester and the [(octadecyl-phos-phono-methyl-amino)-methyl]-phosphonic acid were obtained from Aldrich and Fluka. The three phosphorous-compounds were synthesised as described above. The wetting characteristics of these coated powders were examined by pH-dependent flotation tests. Hence, the behaviour of coated aluminium powders was tested in water. If an adsorption of the surfactants took place, the aluminium powder was hydrophobized by the long alkylchains, and they try to separate and float to the water surface. This effect can be followed visually. Some surfactants hydrophobize the aluminium surface very well (e.g. phosphonic and phosporic acids), i.e. they float completely to the water surface; others show this effect partly or not (alkylbromide, alcohols, amines).

Trimethoxysilane, phosphonic and phosporic acids are the most effective groups giving a high hydrophobicity independent of the pH value.

3.2. Dynamic contact angle measurements

The above described surfactants were placed under equal adsorption conditions on pre-treated AlMg1-plates. Their effects on the wettability of the aluminium surfaces were studied by dynamic contact angle measurements.

Under ideal conditions advancing and receding angles are the same [13]. Actually, the advancing angle is higher than the receding angle. The difference is significant for the roughness and for the inhomogenity of the surface, but also for adsorption and desorption processes during the measurement. The used panels are technical products with non ideal surfaces. They are rough and particles of other metals and compounds are present. Therefore, plates were used from the same production to minimise errors of measurement. The given values in fig. 2 are average values resulting from three measured plates.

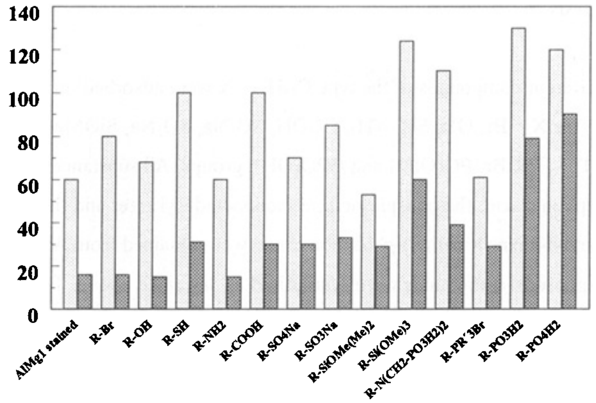


Fig. 2: Dynamic contact angles of coated Al-plates

The results confirm the conclusions from the flotation tests. Octadecyl-trimethoxysilan, octadecyl-phosphonic acid and phosphoric acid monooctadecyl ester show the highest hydrophobic effects. The phosphorous acids have the smallest differences between advancing and receding contact angle. This was an important result for the further investigations.

3.3. Constant humidity climate test

In a third test the corrosion inhibition capability of the surfactants was studied. Aluminium panels were coated as described above and exposed to condensation.

The tests were performed according to DIN 50017 with unlacquered samples to investigate the influence of the self-assembled films on the aluminium surface. The coated plates were exposed to a constant humidity climate for 96 h at 40°C to 100% of relative atmospheric humidity. The surface discolours from glossy to grey/black. After 96 h the attacked zone of the panels were visually marked in per cent of protected area. The two phosphorous acids were the best corrosion inhibitors with 90% of protected area (see fig. 3)[12].

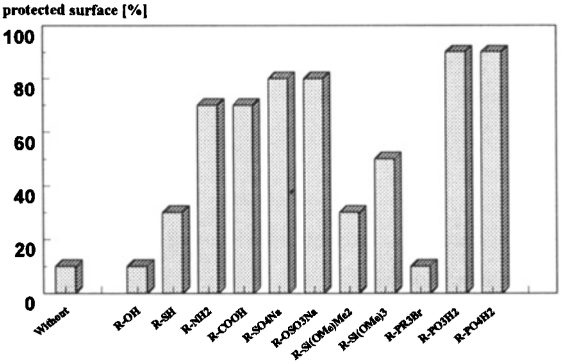


Fig. 3: Constant humidity climate test of coated Al-Plates

Because these compounds showed the best results for all three anchor group testings, they were chosen for further investigations.

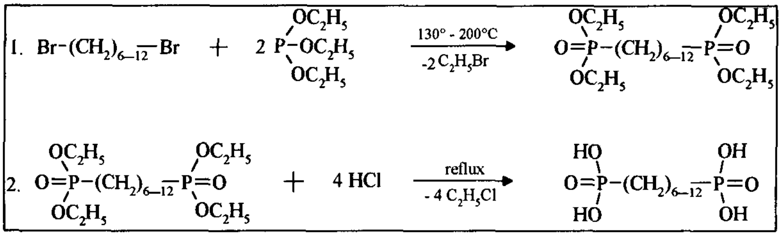
3.4. Synthesis of α,ω functionalised alkyl-phosphonic acids

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.

Long-chain molecules, particularly those with more than 12 carbon atoms, become more difficult to synthesise and purify because C-C coupling reactions are needed. Shorter chains are also more soluble than very long chains and allow a wider range of concentration and solvents.

A chain length of 10 to 12 carbons seems to be ideal for the preparation of α,ω-functionalised alkyl-phosphonic acids. 1,10-dibromodecane and 1,12-dibromododecane are marked parent compounds.

The preparation of ω-terminated alkyl-phosphonic acids with more than 6 carbons is rarely described in the literature. Mallouk who pioneered the zirconium diphosphonate multilayers has published a synthesis for long-chain alkyl-diphosphonic acids [8]. We chose the same principle way to produce diphosphonic acids via Michaelis-Arbuzov reaction:

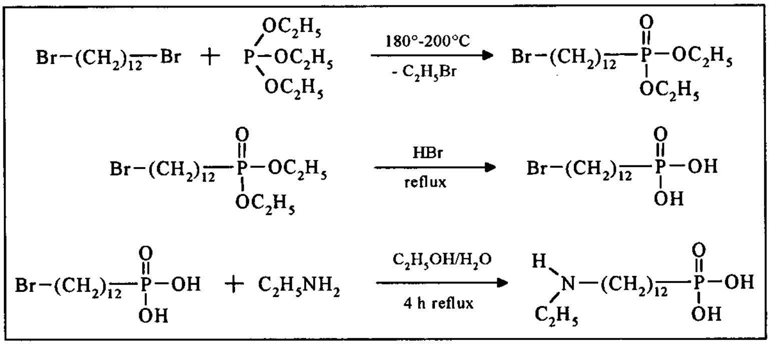


1. $Br-(CH_2)_{6-12}-Br + 2\,P(OC_2H_5)_3 \xrightarrow[-2\,C_2H_5Br]{130°-200°C} (C_2H_5O)_2P(=O)-(CH_2)_{6-12}-P(=O)(OC_2H_5)_2$

2. $(C_2H_5O)_2P(=O)-(CH_2)_{6-12}-P(=O)(OC_2H_5)_2 + 4\,HCl \xrightarrow[-4\,C_2H_5Cl]{reflux} (HO)_2P(=O)-(CH_2)_{6-12}-P(=O)(OH)_2$

Usually aryl phosphonic acids cannot be synthesised by the Michaelis-Arbusov-method. However, the analogous products can be obtained by using a catalyst [14]. The preparation of these compounds is in progress.

The synthesises of amino terminated decyl- or dodecyl-phosphonic acids have, as far as we know, not been previously described. The idea was to convert only one bromo of the dibromoalkane via Arbuzov reaction with triethyl phospite to the adequate bromoalkyl-phosphonic ester. This reaction was possible by using an excess of dibromoalkane, continuos distillation of the resulting ethylbromid and exact regulation of the temperature range (over 190°C the reaction mixture cross-links). The formation of by-products like diphosphonate and ethyl-phosphonic ester is unpreventable, but these compouds can be removed by following hydrolysis because of their different solubility behaviour. The amino-terminated phosphonic acid was obtained via nucleophilic substitution of bromoalkyl phosphonic acid with ethyl-amine.



3.5. *Adsorption and characterisation of alkyl-phosphonic acids on aluminium*

3.5.1. Monofunctional species

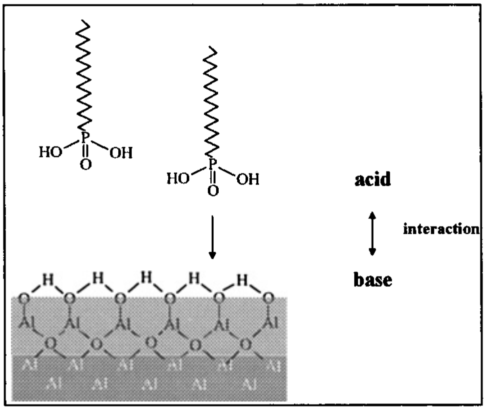


Fig.4: Model for acid-base interactions on the Al-surface

The adsorption of alkyl-phosphonic and phosphoric acid monoalkyl esters on aluminium surfaces is an acid-base reaction. The driving force is the formation of a surface salt. This fact is well known from the spontaneous adsorption of long-chain n-alkanoic acids ($C_nH_{2n+1}COOH$), which was studied in detail in the last few years [15]. In contrast to the alkanoic acids the phosphorous acids form insoluble salts with aluminium. A self-prepared aluminium salt of the dodecyl-phosphonic acid was practically insoluble in water. This may be one of the reasons for the high stability of these SAMs.

Compounds with the P-OH group have two broad bands in FT-IR spectra of weak-to-medium intensity at 2700-2500 cm^{-1} and 2300-2100 cm^{-1}, which are due to the O-H stretching vibrations. For phosphonic and phosphoric acids the band near 2700 cm^{-1} is stronger than those near 2300 cm^{-1}. Medium-to-strong bands at 1040-910 cm^{-1} arise from the P-O stretching vibrations. The band due to the stretching vibration of the P=O (associated) group is strong in the region of 1250-1150 cm^{-1}. Salts of the alkylphosphonic acids give characteristic stretching vibrations at 1125-970 cm^{-1} and 1000-960 cm $^{-1}$ [16]. Fig.5 shows the FT-IR spectrum of dodecyl-phosphonic acid (dotted line) and its aluminium salt (dashed line) in KBr. The vibrations have been adjusted. In fig. 7 the solid lined curve is a surface spectrum of dodecyl-phosphonic acid adsorbed on aluminium from a 10^{-4} M solution of ethanol. The intensities of the absorbances were multiplied by a constant of 250 to enable comparison with the KBr spectrum. The surface spectrum is similar to the KBr spectrum of the aluminium salt. The characteristic vibrations of the free phosphonic acids at 2700 and 2300 cm^{-1} are not present in the surface spectrum. The P-O stretching vibrations are shifted to higher wavenumbers. The absence of the P=O stretching vibration at 1225 cm^{-1} and the mentioned P-OH bands were interpreted as evidence for a tridentate bonding mode. Other authors came to the same conclusions [17, 18].

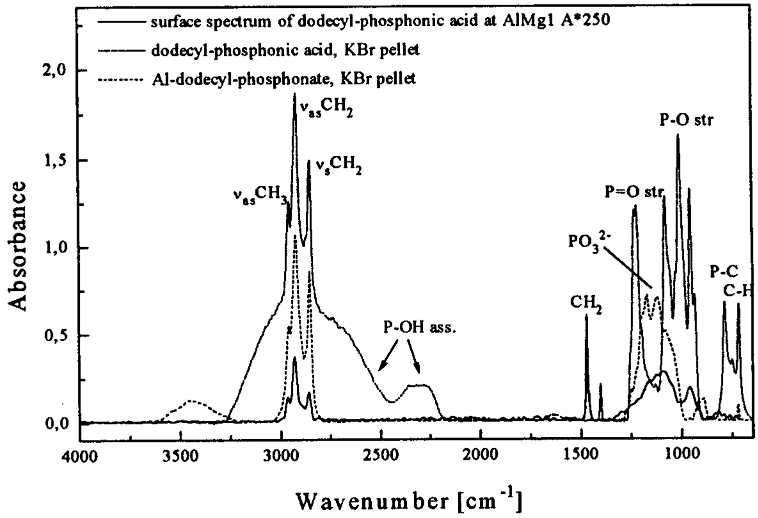


Fig. 5: FT-IR-spectra of dodecyl-phosphonic acid and its aluminium salt, KBr pellets and polarised external reflectance spectrum of dodecyl-phosphonic acid on AlMg1 for comparison

The timescale of the orientation of the molecules was examined by FT-IR to see whether the molecules can spontaneously organise on the defect rich surface. Fig. 6 shows the part of the spectrum with the asymmetric and symmetric vibrations of the CH_2 and CH_3 groups. There are large CH_2 and very small CH_3 bands because the molecule contains many CH_2 and just one CH_3 group. The time allowed for the molecules to adsorb onto the specimen surface was varied between 2 min and 4000 min. The spectra are shown for the two extreme exposition times. With increasing time of adsorption the CH_2 bands decrease while the CH_3 bands remain almost constant [19].

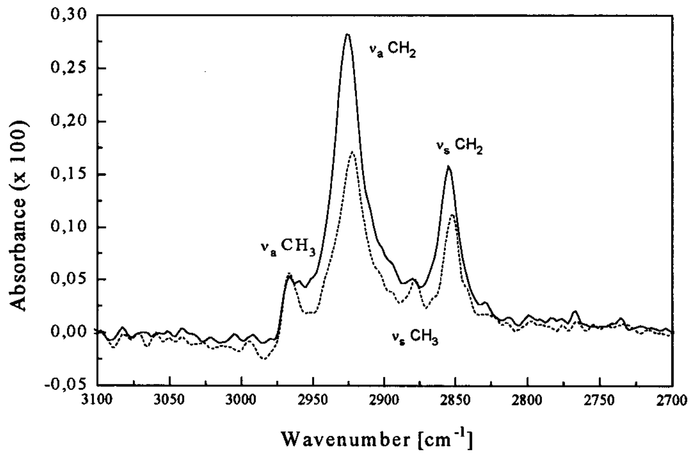


Fig. 6: External reflectance FT-IR spectra of the CH-bands at 2 min adsorption time (solid line) and after 4000 min (dashed line) on AlMg1

The organisation of the film improves with the time of adsorption and after 4000 min the organisation process approaches the reachable optimum.

3.5.2. Bifunctional compounds

The polar terminated phosphonic acids can be adsorbed from water, ethanol and their mixtures. The adsorption behaviour of bifunctional surfactants on AlMg1 substrate is shown in fig.7. In comparison to the simple alkyl-phosphonic acids the growing of the layer continues with adsorption time. Even after 24 h the process is not completed. The quality of the formed layer cannot be inferred from FT-IR spectra. Differencing between density or

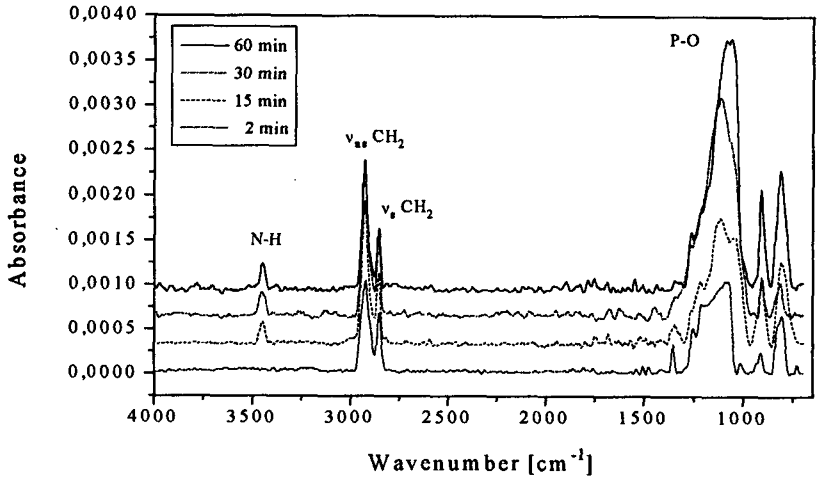


Fig. 7: Grazing Angle FT-IR spectra of (12-ethylamino-dodecyl)-phosphonic acid at AlMg1 adsorbed from a 10^{-3}M solution of ethanol/water (3:1 vol%) at different times

thickness of the layer is not possible. Apparently, no thick multilayers are formed because increasing of absorbances is minimal.

The closest attention of the investigation was to find out whether and how the molecules were orientated after adsorption onto the aluminium surface. Therefore, angle resolved X-ray photoelectron spectroscopy data were taken. Because of the limiting attenuation length of the electrons the depth information of XPS data is dependent on the varied angle α (fig. 8). 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 analyser. The phosphorous 2s peak and the nitrogen 1s peak were used for analysis. 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.

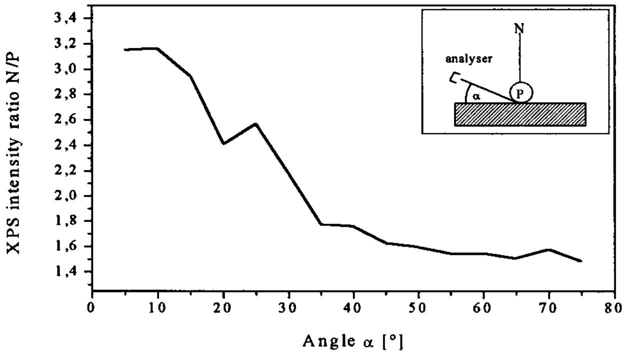


Fig. 8: ARXPS intensity ratio of P 2s and N 1s peaks of a 50 h adsorbed AlMg1 sample

3.6. *Model surface reactions*

It is impossible to establish SAMs after applying the lacquer by spectroscopic methods. Hence, model surface reactions were developed, which enabled evidence of the reaction capabilities to be obtained.

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 have characteristic infrared bands.

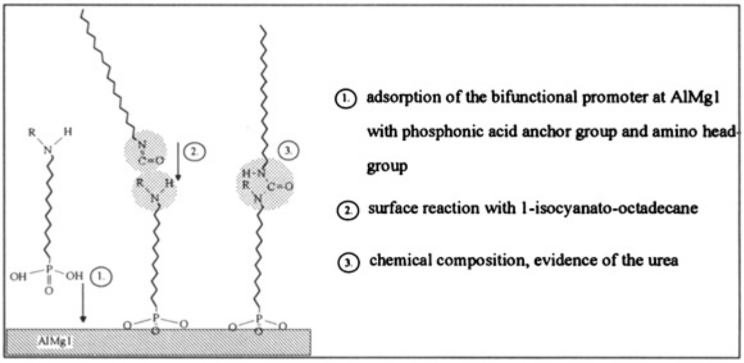


Fig. 9: Model for surface reaction

An ethylamino terminated dodecyl-phosphonic acid was adsorbed on polished AlMg1-plates (fig. 9). This coated plate was refluxed with a 10^{-3} M solution of 1-isocyanato-octadecane in acetone. After 1 h reaction time the plate was removed and rinsed twice with acetone. The resulting surface IR-spectrum is shown in fig. 10.

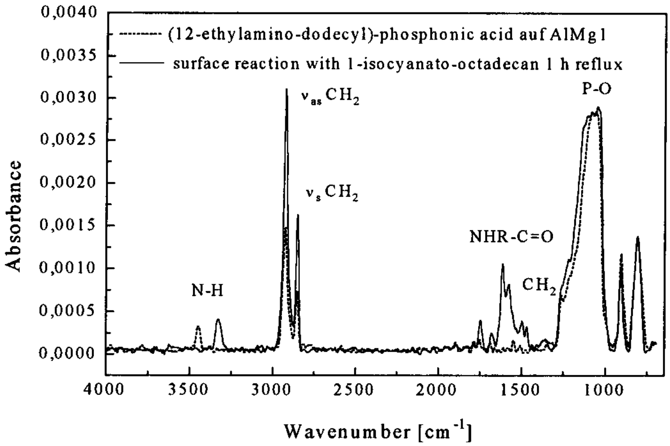


Fig. 10: Grazing Angle FT-IR spectra of (12-ethylamino-dodecyl)-phosphonic acid at AlMg1 before and after surface reaction with 1-isocyanato-octadecane

The peak area of the CH_2-valence bands at 2920 cm^{-1} and 2850 cm^{-1} had doubled following surface reaction. The newly formed N-H band at 3340 cm^{-1} as well as the urea-bands at 1615 cm^{-1} and 1575 cm^{-1} are clearly visible. The P-O absorptions from 1275 cm^{-1} to 1000 cm^{-1} are unchanged. This result shows a high degree of conversion, the stability of the SAM under the chose conditions and the orientation of the phosphonate group towards the metal surface.

3.7. Industrial testing with lacquer coated aluminium panels

In the following table the results which were obtained by measurements using bifunctional phosphonic acids as adhesion promoters are shown. The surfactants were adsorbed from a 10^{-3} M aqueous solution for 3 min at 40°C. The acetic acid salt spray-test (ASS) and filiform-test demonstrated that the thin layers guarantee a very good infiltration protection compared with the industrial pre-treated (phosphated, chromated) test panels. Only the chromated one showed a sufficient corrosion protection.

Tab. I: Industrial testing of SAM coated AlMg1-panels compared with test panels

Formula	**T-Bend-Test Exfoliated area LPV 75 [%]**	**ASS-Test DIN 50021 Infiltration [mm]**	**Cross-Hatch ISO 1520**	**Filiform-Test DIN 50024 [mm]**
$C_2H_5NH(CH_2)_{12}PO(OH)_2$	1	<1	0	not tested
$CH_2=CH(CH_2)_{10}COOH$	40	1	0	not tested
$NH_2(CH_2)_{10}COOH$	10	1	0	not tested
$HO(CH_2)_{11}COOH$	10	1	0	not tested
$(HO)_2POCH_2C_6H_4CH_2PO(OH)_2$	20	<1	not tested	<1
$(HO)_2PO(CH_2)_{12}PO(OH)_2$	0	<1	0	<1
AlMg1 (reference)	100	8	0	5
AlMg1 stained (alkaline/acid)	85	4	5	4
AlMg1 phosphated	10	3	1	<1
AlMg1 chromated	25	<1	2	<1

LPV- Labor-Prüf-Vorschrift - Chemetall

ASS- Acetic Acid Salt Spray-Test

T-bend- and cross-hatch tests of the bifunctional surfactants showed better adhesive strength to the coating than the industrial test panels.

4. CONCLUSIONS

The idea using self-assembly molecules as adhesion promoters for reactive metal surfaces appears to be promising.

The surfactants bearing a phosphonic acid head-group and polymer-reactive group were able to adsorb spontanously onto the aluminium surface. They formed orientated layers which could be proved by polarized external reflectance FT-IR measurements. The chemical composition to organic coatings was realised with a second terminal functional group. This lacquer linking was demonstrated by model reactions with isocyanates and confirmed by industrial adhesion- and corrosion tests.

The effect of the bifunctional surfactants were equivalent to chromated panels due to corrosion inhibition and superiored due to adhesive strength.

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