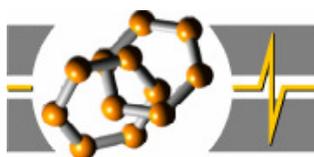


Ph. D. THESIS

**CHARACTERIZATION AND STUDY OF CORROSION
PROTECTIVE EFFECT OF
 α,ω -DIPHOSPHONO-ALKANE NANOLAYERS DEVELOPED ON
ZINC SURFACE**

Aranka Pilbáth

Supervisor: Prof. Dr. Erika Kálmán



HAS Chemical Research Center
Institute of Nanochemistry and Catalysis, Department of Surface Modification and
Nanostructures



Budapest University of Technology and Economics
Department of Chemical and Environmental Process Engineering

Budapest
2008

Introduction

Precedents

Corrosion is the continuous process of formation of detrimental surface reaction products on metals. Several procedures have been developed in order to avoid or reduce the corrosion damage thus prolonging the lifetime of metal goods. The most commonly used corrosion protective procedure is the application of inhibitors, since the presence of small quantities of inhibitors can significantly reduce the corrosion rate. One of the last decade's ambitions is the surface modification of metals by deposition or formation of surface layers from solutions preventing corrosion.

Zinc is one of the most commonly used metals all over the world, and one of the most important applications of zinc coatings is the cathodic type corrosion protection of iron and steel goods. The zinc overlayer on steel components is to be protected also. Traditionally, chromium compounds have been used as post treatment of the dip coated steel sheets and components to improve performance of the zinc coatings. According to the new European legislation the formerly used chromate conversion coating technique for temporary corrosion protection has to be substituted. Researchers all over the world are searching for environmental friendly alternative zinc treatments.

Literature background

Several novel passivation treatments have been proposed recently for galvanized steel and zinc surfaces: e.g. processes based on rare-earth metal salts; the formed films are reducing the metal corrosion, blocking the anodic and cathodic processes. Thin hybrid conversion films of zinc-phosphates, titanates and complexing organic compounds also reduce the zinc corrosion processes. Almeida and co-workers studied the behaviour of several zinc-conversion layers. Research has been done by silanes, polymer materials or chelation by organic substances which could form stable and hardly soluble organometallic compounds on the zinc surface.

One of the research directions is the application of functional organic substances in order to develop self-organized thin layers effective for corrosion protection. The

α, ω -diphosphono-alkane derivatives are molecules with functional groups, which are capable of binding to the surface of metals, metal oxide-hydroxides; but their mechanism of binding and protection is not fully clarified [1-3].

Results of our research groups proved that layers formed at room temperature by simple immersion into aqueous solution of phosphono-alkanes and diphosphono-alkanes are effective for corrosion protection of iron [3].

The bifunctional molecules can be used as adhesion promoters of paints for corrosion protection under-paint. As concerning the application of α, ω -diphosphono-alkane derivatives for zinc corrosion protection only few studies can be found in the literature. A single promising result showed that the layers formed at 40 °C from aqueous solutions of α, ω -diphosphono-alkanes showed corrosion protective effect for zinc surface [4, 5]. These studies are not detailed concerning the composition, chemical- and crystallographic structure of the formed layers and also about the processes occurring on the treated surface.

Aim of the work

Based on previous work, my research was focusing on the detailed study of the composition, structure and protective effect of α, ω -diphosphono-alkane layers developed on the zinc surface at 20 °C from aqueous solutions of α, ω -diphosphono-alkane derivatives. First, a series of α, ω -diphosphono-alkane were tested to choose which are layer forming. The detailed study of the interaction with the surface, the layer composition, chemical and crystallographic structure and also the processes occurring on the treated surface were in focus. Another interest was to test the corrosion protective effect of the developed layers on zinc surface. In order to test the possibility of application of layer formation from organic solvents, layer

-
1. M.P. Danahy, M.J. Avaltroni, K.S. Midwood, J.E. Schwarzbauer, J. Schwartz., *Langmuir* **20** (2004) 5333.
 2. W. Gao, L. Dickinson, Ch. Grozinger, F.G. Morin, L. Reven, *Langmuir* **12** (1996) 6429.
 3. I. Felhősi, E. Kálmán, *Corros. Sci.* **47** (2005) 695.
 4. R. Feser, T.H. Schmidt-Hansberg, *Symp. Eurocorr '97*, Trondheim, **2** (1997) 291.
 5. R. Feser, A. Friedrich, H.J. Adler, *14th International Corrosion Congress*, Cape Town, South Africa, Paper No. 380,0 (1999).

deposition from ethanol solution of α, ω -diphosphono-alkane derivatives were performed also.

Finally, taking into consideration the industrial needs, my aim was to find the shortest possible time for treatment, which, however, provides adequate protection for the investigated surface.

The fact that motivated me to draw up this research plan is to contribute to the efforts made all over the world to find an environmental friendly chromate replacing process.

Methods

Novel surface characterization techniques and electrochemical measurements were applied to study the reaction of α, ω -diphosphono-alkane with the zinc surface. The morphological changes of the treated surfaces were followed by *scanning electron microscopy (SEM)* and *in-situ atomic force microscopy (AFM)*. The *infrared reflection-absorption spectroscopy (IRRAS)* and *X-ray photoelectron spectroscopy (XPS)* was applied in order to study the chemical structure of the developed surface layers. The latter was used also to determine the composition of the layers. The wettability of the formed layers was followed by water *contact angle measurements (CA)*. The crystal structure of the developed layers and also of the synthesised model compounds were investigated by *X-ray diffraction (XRD)*. The *glow discharge optical emission spectroscopy (GD-OES)* was applied to show the in-depth elemental distribution of the total thickness of the developed layers. The corrosion behaviour of the layers was tested by *electrochemical impedance spectroscopy (EIS)*.

New scientific results

1. Series of α, ω -diphosphono-alkane [$\text{H}_2\text{O}_3\text{P}-(\text{CH}_2)_n-\text{PO}_3\text{H}_2$, $n = 5, 7, 8, 12$] were tested to develop layer on zinc surface. After 24 h of immersion into neutral 10^{-3} M aqueous solution of the α, ω -diphosphono-alkane solutions, continuous and dense layer was formed only using the shortest carbon-chain length molecules 1,5-diphosphono-pentane (DPP) and 1,7-diphosphono-heptane (DPH).

- Dynamic water contact angle measurement revealed formation of relatively more hydrophilic surfaces in comparison with the polished air exposed untreated surface (101°). Interestingly the two treatments resulted in different contact angle values: DPP – 77° , DPH - 42° [1].

- The layers developed on zinc surface from DPP and DPH aqueous solutions were of different thickness [1]. From the EDS results it was obvious that the phosphorus could be detected only on the surface treated with DPH. Only a small amount of phosphorus was noticed when DPP was applied. Based on visual observations, the layer developed from DFH solution resulted in the formation of white precipitated layer, while on the surface treated with DFP solution marked differences could not be observed compared to the untreated surface [2, 3]. The differences in thickness of the layers developed were obvious from the sputtering time needed for the determination of the elemental composition of the layers (GD-OES results) [1].

- XPS investigations showed that the untreated zinc was covered by a thin native oxide-hydroxide layer together with carbonaceous contaminations. XP spectra of deposited, well- defined $\text{Zn}(\text{OH})_2$ and its heat-treated alternative, ZnO were recorded for comparing these results with the native surface oxide-hydroxide. The O 1s spectra recorded on the untreated zinc could be decomposed with the same two component peaks what could perfectly fit the O 1s peak envelope of the $\text{Zn}(\text{OH})_2$ and that of the zinc-oxide prepared by heat treatment from that hydroxide [1].

• XRD results proved that on the zinc surface reacted with DPH a new crystalline phase was formed (Fig. 1). The new phase was similar with the compound synthesised by reaction of zinc-oxide and DPH at the same conditions as the surface treatment was done. The thinner layer developed from the DFP solution could not be studied with this technique (do not show diffraction pattern) [1]. Similarly, the stretching vibration bands of the phosphono group appearing in the IR spectra were identical for the synthesised material (zinc-oxide reacted with DPP) and for the protective layer developed from DPP aqueous solution. Due to the interaction with the surface, the characteristic bands are overlapped and widened (Fig. 2). XPS and GD-OES results evidenced the presence of high zinc content in the surface layer composition. The presence of zinc in the surface layer is shown in Fig. 3. Summarizing the previous results, it can be concluded that conversion type zinc-diphosphonate layers were developed on zinc surface [1].

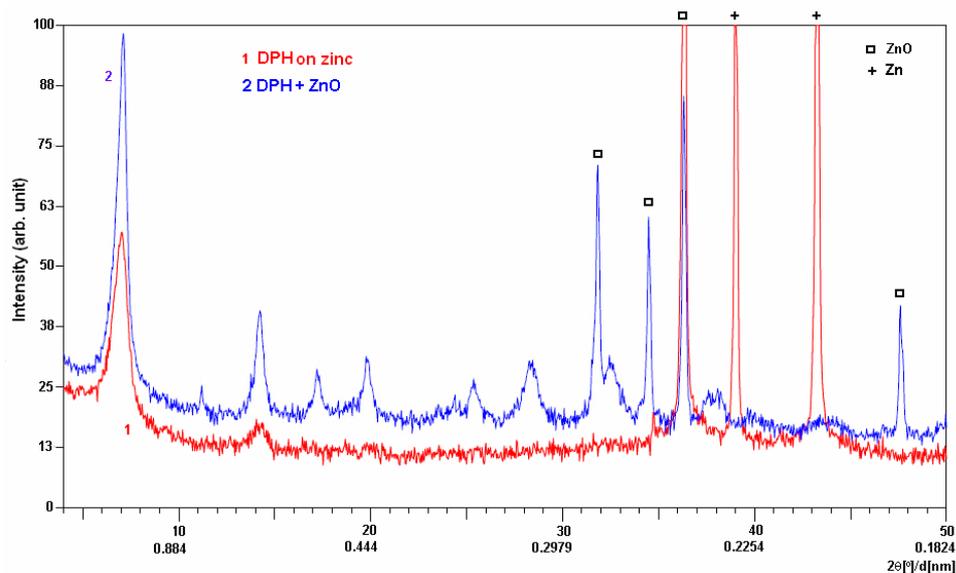


Fig. 1. XRD patterns of DPH treated zinc (1) and the precipitated zinc-phosphonate from zinc-oxide powder (2)

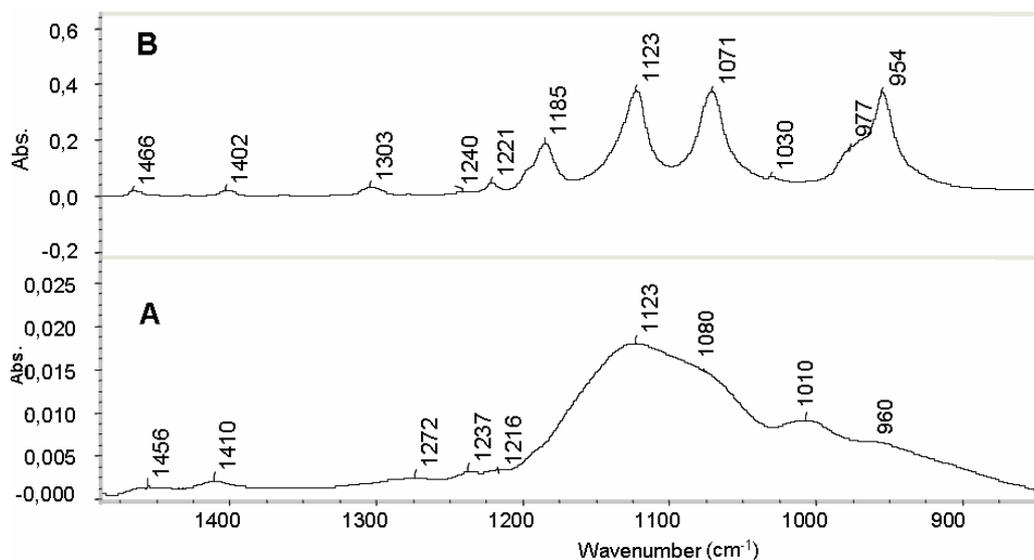


Fig. 2. Infrared spectra (phosphono-group stretching region) of zinc surface treated with DPP (24 h) (A) and the synthesized reaction product of zinc-oxide and DPP (B)

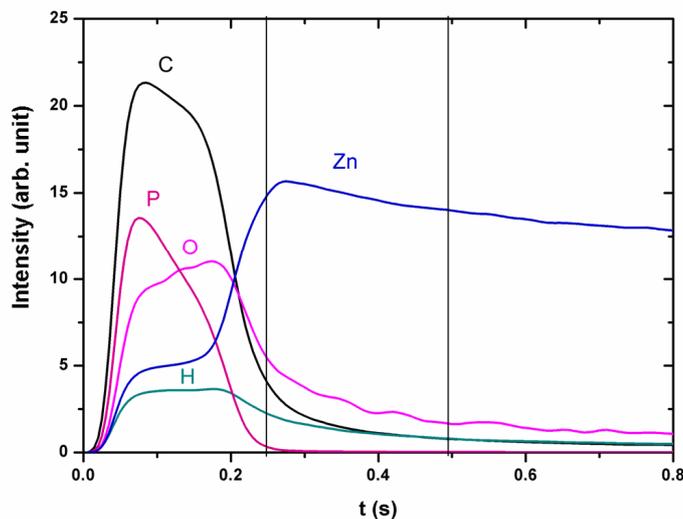


Fig. 3. Depth profile curve of zinc sample treated with DPP (24 h, 10^{-3} M, pH = 7)

- Quantitative XPS results give a closely 1:1 = P:Zn and P:O stoichiometry for samples treated with DPP and DPH. The same stoichiometry was found for the synthesized zinc-diphosphonates as well [1].

- Electrochemical impedance measurements proved that the layers developed from DPP and DPH treatment increase the zinc corrosion resistance in neutral 10^{-1} M Na_2SO_4 solution. The inhibition efficiency was determined to be $\sim 80\%$, albeit decreasing by time. The inhibition efficiency of the developed layers from DPP solutions was close to, but did not reach the inhibition efficiency obtained with DPP treatment. The applied DPP surface treatment significantly increases the charge-transfer resistance of the zinc dissolution, hindering the dissolution process. The hindrance of the zinc dissolution is due to the blocking effect of the formed zinc-diphosphonate layer on the zinc surface [1, 4].

2. The effect of the layers developed from ethanol solution (Et-OH) of a series of α, ω -diphosphono-alkane $[\text{H}_2\text{O}_3\text{P}-(\text{CH}_2)_n-\text{PO}_3\text{H}_2, n = 5, 7, 8, 12]$ derivatives do not show, based on visual observations, any change on the treated surface prior and after the treatment. Only the layers developed from DFP and DFH give protection to the zinc surface.

- The measured water contact angles revealed formation of hydrophilic surfaces: Et-OH-DPP – 70° ($n = 5$), Et-OH-DPH 72° ($n = 7$), Et-OH-DPO 79° ($n = 8$). When DPP was applied, the surface becomes more hydrophobic than the untreated one: Et-OH-DPD 130° ($n = 12$). In this case the molecules are lying down on the surface thus the effect of hydrophobic carbon-chain can be detected on the surface.

- The layer from ethanol-DPP solution was also successfully developed, but it proved to be thinner than the layer formed by aqueous DPP treatment. Comparing the Zn 3s and P 2p intensities, higher amount of phosphorus was present in the layer developed from aqueous DPP solution than from the ethanol solution. The differences in the layer thickness of the DPP layers developed from aqueous and ethanol solution were also proved by the Zn (LMM) spectra. The intensity of the oxide-hydroxide environment was prevailing at 986.3-986.7 eV *K.E.* (kinetic energy) in both cases, but on sample treated in ethanol solution a small intensity of metallic zinc at 992.5 eV *K.E.* was also present. This manifests the thinner layer developed from the ethanol

solution. The GD-OES results are well manifesting the same difference in layer thickness [4].

- Electrochemical impedance measurements proved that the layers developed from ethanol solution of DPP increase the zinc corrosion resistance in 10^{-1} M Na_2SO_4 solution. The applied DPP surface treatment significantly increases the charge-transfer resistance of the zinc dissolution, hindering the dissolution process [4].

3. The treatment in 1,5-diphosphono-pentane solution proved to be suitable for corrosion protection of zinc. The time dependence of the layer formation from aqueous DPP solution can be summarized as follows [5]:

- The DPP had remarkable effect on the studied surfaces; the obtained water contact angle values indicate the formation of films that are significantly more hydrophilic than the zinc surface before treatment. Decrease in the advancing contact angle values could be detected already after very short treatment time indicating the effect of the applied treatment. After 1 h treatment the contact angle seems to stabilize, the determined value of contact angle was 75° . Further significant change of the contact angle value could not be noticed ($\theta = 77^\circ$) even after 24 h treatment [5].

- *In-situ* AFM images showed that after 1 h aqueous DPP treatment the surface morphology had changed. A typically structured layer formation could be observed on the zinc surface. The growth in time of the grains could be followed and after 4 h treatment the surface was covered by a compact structured layer. A significant roughening was detected due to the applied surface treatment [5].

- The formed layer density increases by the applied treatment time. GD-OES showed unambiguously that the layer developed after 30 min DPP treatment was thin or incoherent as compared to layers developed at 4 h and 24 h DPP reaction [5]. XPS results are in accordance with the above mentioned differences between the developed layer thicknesses. The Zn (LMM) spectra are different from the short time treated sample and the two longer time treated samples. The Auger peak envelope justifies the presence of both metallic and oxidized zinc at 992.5 eV *K.E.* and

986.3 eV *K.E.* on the 30 min DPP treated sample. This manifests a very thin or incoherent layer developed on the short time (30 min) DPP treated sample. On samples treated for 4 and 24 hours, elemental zinc could not be detected; the formed layers are thicker than the layer developed after 30 min treatment. Based on the IRRAS measurement, the reaction of DPP with the zinc surface has been proved. The phosphono groups are in complete deprotonated form in the deposited films, which confirms again the reaction with zinc [5, 6].

- Electrochemical impedance measurements reveal differences between the short and long time treated samples. The results show that even a 30 min treatment with DPP had effect on the corrosion behaviour of the zinc samples, but a 4 h treatment proved to be necessary to obtain corrosion efficiency of ~80% [5].

4. To summarize the results from the point of view of practical applications, the DPP treatment increases substantially the corrosion resistance of zinc samples and thus DPP is a suitable candidate for industrial applications. In fact, based on the results obtained in the present thesis, a proposal has been made for development of a conversion bath using the DPP molecules as additives, in order to replace the chromating bath.

Theses

1. I have firstly managed to successfully develop layers on zinc surface from dilute α, ω -diphosphono-alkane aqueous solutions at 20°C. The layer thickness developed from 1,5-diphosphono-pentane (DPP) solution is increasing with the applied treatment time. A compact layer was developed on the zinc surface after 4 hours. Nanoscale investigations by using *in-situ* AFM proved that the DPP treated surface become rougher than the untreated sample [2, 3, 5].
2. I have found evidence of the formation of a new crystalline phase on the DPH treated surfaces. Data related to the structure of the new crystalline phase have not been found in literature [1].
3. I have established similarities between the X-ray powder diffraction patterns of the crystalline phase formed on zinc surface treated by DFH and the synthesized precipitated product developed from the DPH and zinc-oxide reaction [1]. Similarly, the vibration bands of the phosphono group appearing in the IR spectra are identical for the synthesised material (zinc-oxide reacted with DPP) and for the protective layer developed from DPP aqueous solution.
4. I have shown that in the full depth of the layers formed by DPP and DPH treatment, zinc is present in quantities comparable to that of phosphorous. I have proven by quantitative measurements that the new crystalline phases contain zinc and phosphorous in 1 to 1 atomic ratio, indicating that both functional groups of the diphosphonates are reacted [1]. In accordance, with this, IR measurements indicated that the phosphono groups of DPP were present in a deprotonated form [5, 6].
5. To summarise the results enlisted under 2 to 4, I established that as a result of DPP and DPH treatment, a zinc-phosphono conversion coating is formed [1, 5].
6. I have shown that the DPP and DPH layers inhibit zinc dissolution by reducing the rate of the zinc charge-transfer step. The layers are suitable for corrosion protection, and in 10^{-1} M Na_2SO_4 (pH = 7) solution an inhibitor efficiency of 80 % can be reached. The protective effect is a result of the developed zinc-

phosphonate layers [1-5]. On this basis, DPP appears to be promising for practical applications.

Possible applications

In cooperation with industrial partners, based on the results obtained in the thesis a chromate replacing composition have successfully been developed, which contains the 1,5-diphosphono-pentane compound as the main additive component. In the preliminary experiments the developed composition proved to be applicable for galvanized steel surface corrosion protection. The treatment time and temperature for surface treatment has been optimized. The treatment time used for chromating has been approached, for the effective chromate replacing bath this was 15-30 s. A half-industrial production technology has already been developed.

The developed bath can be used mainly in the factories working with the dipping-technology. Quality report has already been made from the treating bath developing conversion layers on galvanized steel surfaces.

The results of the thesis and the earned experience will be utilized for industrial application. Taking in consideration the hydrophilic properties of the treated surfaces, it is possible to develop a two-step corrosion protective technology, i.e. in automotive industry, for temporary protection of surfaces under paint.

Publications related to the thesis

1. A. Pilbáth, I. Bertóti, I. Sajó, L. Nyikos, E. Kálmán
Diphosphonate thin films on zinc: preparation, structure, characterization and corrosion protection effects, *Applied Surface Science* (2008) doi:10.1016/j.apsusc.2008.06.039.
IF (2007): 1,406.
2. A. Pilbáth, I. Felhósi, Gy. Tolnai, E. Kálmán
Application of self-assembly for replacing chromate in corrosion protection of zinc, *J. Solid State Electrochem.* **10** (2006) 721-729.
IF (2006): 1,542.
3. Pilbáth A., Felhósi I., Kármánné H. F., Telegdi J., Papp K., Kálmán E
Cink korrózió elleni védelme környezetbarát difoszfonsavval, *Korróziós Figyelő* **46** (5) (2006) 141-145.
4. A. Pilbáth, L. Nyikos, I. Bertóti, E. Kálmán
Zinc corrosion protection with 1,5-diphosphono-pentane, *Corrosion Science* (2008) doi:10.1016/j.corsci.2008.09.021.
IF (2007): 1,895.
Ann. Univ. Ferrara, N. S., Sez. V. Suppl. N., **12** (2) (2005) 859-872.
5. A. Pilbáth, I. Bertóti, É. Pfeifer, J. Mink, L. Nyikos, E. Kálmán
Formation and characterization of 1,5-diphosphono-pentane films on polycrystalline zinc substrates, *Surface and Coatings Technology* (2008) doi:10.1016/j.surfcoat.2008.10.016.
IF (2007):1,678.
6. A. Pilbáth, É. Pfeifer, F. H. Kármán, I. Felhósi, J. Mink, E. Kálmán
Environmentally acceptable pre-treatment of zinc with alkyl diphosphonates for corrosion protection, *Materials Science Forum* **589** (2008) 257-262.
7. A. Pilbáth, I. Felhósi, F. H. Kármán, E. Kálmán
Corrosion protection of zinc with diphosphonic acid, *Ann. Univ. Ferrara, N. S., Sez. V. Supp N.*, **12** (2) (2005) 859-872.

Other publications

8. I. Felhősi, Gy. Tolnai, F. Mavre, F. H. Kármán, J. Telegdi, A. Pilbáth, G. Hegedűs, Á. Kovács-Stahl, J. Bognár, P. M. Nagy, E. Kálmán
Ecologically friendly multifunctional coating systems with anticorrosive properties, *PITTURE VERNICI – Europeans Coatings*, **81** (2005) 7-15.
9. A. Pilbáth, F. H. Kármán, I. Felhősi, J. Telegdi, E. Kálmán
Chromate-free pre-treatment for zinc and galvanized steel
Bustruck, Combined Conference on Heavy Vehicles, XXXVI. Meeting of Bus and Coach Experts and Congress on Commercial Vehicles, Budapest
Conference proceeding, M-10 absztrakt, (2005) 76.
10. A. Pilbáth, F. H. Kármán, I. Felhősi, J. Telegdi, E. Kálmán
Surface Treatment of Zinc
5th International Conference: URB-CORR 2006, Study and Control of Corrosion in the Perspective of Sustainable Development of Urban Distribution Grids, Romania, Conference proceeding, (2006) 196-199.
11. A. Pilbáth, F. H. Kármán, I. Felhősi, J. Telegdi, L. Nyikos, E. Kálmán
Chromate-free surface treatment on zinc
EUROCORR 2007, European federation of corrosion, Event no. 289, Freiburg im Breisgau, Germany, Conference proceeding– (2007).
12. A. Paszternák, A. Pilbáth, Z. Keresztes, I. Felhősi, J. Telegdi, E. Kálmán
Atomic force microscopy studies of alkyl-phosphonate SAMs on Mica
Materials Science Forum **589** (2008) 257-262.

Oral presentations

- OP-1. A. Pilbáth, I. Felhősi, F. H. Kármán, E. Kálmán
Corrosion protection of zinc with diphosphonic acids
10th European Symp. Corros. Inhibitors (10SEIC), Ferrara, Italy (2005).

- OP-2. A. Pilbáth, F. H. Kármán, J. Telegdi, I. Felhősi, E. Kálmán
The role of self-assembling in zinc corrosion protection
5th Hungarian Conference and Exhibition on Materials Science Testing and Informatics, Abstract 0-II-22, 55, Balatonfüred, (2005).
- OP-3. A. Pilbáth, F. H. Kármán, I. Felhősi, J. Telegdi, L. Nyikos, E. Kálmán
Chromate-free surface treatment on zinc
EUROCORR 2007, European federation of corrosion, Event no. 289
Freiburg im Breisgau, Germany(2007).
- OP-4. A. Pilbáth, É. Pfeifer, F. H. Kármán, I. Felhősi, J. Mink, E. Kálmán
Environmentally acceptable pre-treatment of zinc with alkyl diphosphonates for corrosion protection
6th Hungarian Materials Science Conference, Siófok, (2007).

Posters

- P-1. A. Pilbáth, F. H. Kármán, I. Felhősi, J. Telegdi, E. Kálmán
Environmentally acceptable nanolayers against corrosion
The 57th Annual Meeting of the International Society of Electrochemistry (ISE) Edinburgh, UK (2006).
- P-2. A. Pilbáth, É. Pfeifer, F. H. Kármán, I. Felhősi, J. Mink, E. Kálmán
Environmentally acceptable pre-treatment of zinc with alkyl diphosphonates for corrosion protection
6th Hungarian Materials Science Conference, Siófok, (2007).
- P-3. A. Pilbáth, F. H. Kármán, I. Felhősi, J. Telegdi, E. Kálmán
Environmentally acceptable nanolayers against corrosion,
HUNN – Hungarian Network of Excellent Centres on Nanosciences
Budapest University of Technology and Economics (BME), (2007).