What Can Nano-Chemistry Offer to the Paint Industry?

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Summary: Iron surface was modified by organic, self assembled nano-layer of 1,7-diphosphono heptane. The self-assembling film formation and the self-healing process of the injured layers was monitored by electrochemical methods. The morphological changes of paint and lacquer layers which was due to different pre-treatments were monitored by surface analyzing techniques.

Keywords: surface pre-treatment, self-assemble layer, phosphonic acid, paint, electrodimpedance spectroscopy, atomic force microscopy, scanning electronmicroscopy

Introduction

Researchers make significant efforts to develop environmentally acceptable chemicals for surface pre-treatment in the paint industry where many toxic and acidic additives are used for coating. For the paint industry among the new materials the so-called self-assembled nano-layers could replace other toxic materials. The self-assembled molecules form an adhesive layer between the metal surface and the paint layer.

The self-assembly of disulfides on gold discovered in 1983 [1], and, soon after, of alkanethiols opened new perspectives in surface science. This is a spontaneous process that takes place on an appropriate substrate by immersion into a solution of surfactant-like molecules. This process consists of adsorption/chemisorption and results in self-organized, highly ordered mono-layers of dense, oriented and stable structure. Self-assembled monolayers (SAMs) on metal surfaces form organic interfaces with properties mainly controlled by the end-groups of the molecules. SAMs are excellent systems for the study of interfacial processes, of molecular structure – layer property relationship and of technical importance in fabrication of sensors, transducers and protective layers.

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The chemical surface modification of metals by self-assembly is a new encouraging method of corrosion protection [2], too, which is able to replace the previously applied environmentally not acceptable surface treatments. Because of the high attractive interaction among the alkyl side chains, SAMs can exceed the corrosion protection effect of commonly used inhibitor molecules. First successful attempts to apply self-assembly of alkanethiols for corrosion protection were done on iron [3-5] and copper [6-8]. The stable hydrophobic film depressed significantly the metal dissolution. The chemisorption of n-alkanethiols takes place only on metallic-state iron [9], which substantially limits its practical application. Practically more promising are those molecules, which preferably form adsorption layers on oxide- or hydroxide-covered metal surfaces. Not only alkanethiols but alkane-mono- and diphosphonates have been successfully applied to form well-oriented self-assembled surface layers on iron [10-13], aluminum [14-15] and zinc [14]. The self-assembly process of phosphono-functionalized molecules takes preferably place at metal surfaces covered with thin hydroxide layer. The self-assembled layer formation consists usually of two separate adsorption kinetics; a fast adsorption step controlled by the adsorption of molecules on metal surface, and by slow organization/orientation step determined by the intermolecular van der Waals interaction between alkyl chains, that depends on the length of molecule. In corrosion protection one of the most important application of self-assembly process is a pre-treatment of metal surfaces beneath organic coatings [15]. The immobilized molecules are able to act as adhesion promoters and corrosion inhibitors. They can also be applied as a temporary corrosion protection of metals. The advantage of the molecular self-assembly lays mostly in the wide variety of functional groups and length of the alkyl chain. Beside its practical importance, the self-assembling phenomenon on metal surfaces provides an excellent model system for studies of adsorption of organic compounds at atomic scale.

The aim of this study was to elaborate new chemicals (of nano-scale at least in one dimension), and to elucidate the processes and mechanisms of protective layer formation on iron surface in order to get stable layer that not only has good anti-corrosion activity but renders the metal surface more proper for coating. Experiments in the presence of alkane-phosphonates were presented in our previous communication [10]. In this paper some selected results obtained on protective layer formation in the presence of diphosphonates will be presented. Because of the limited water solubility of molecules with long alkyl chain, only shorter molecules were studied in aqueous solutions (n=5-12). The kinetics of layer formation, the mechanism of inhibition, and the self-healing properties of phosphonates will be presented through the example of 1,7-diphosphono-heptane. The influence of self assembled molecules (SAM) on the morphological properties of paint and lacquer layers will be demonstrated by scanning electronmicroscope (SEM) and by atomic force microscope (AFM).

Experimental

The protective layer formation was studied in aerated aqueous solution of 0.001 $mol.dm^{-3}$ phosphonic acids (pH 7.0). Measuring electrodeimpedance spectroscopy (EIS) and open circuit potential (OCP) followed the layer formation of phosphonates. Electrochemical experiments were performed in a standard three-electrode cell of $500cm^3$ volume at room temperature. The working electrode was Armco iron embedded into epoxy resin. The counter electrode was platinum net, and the reference electrode was a saturated calomel electrode (SCE).

Electrochemical impedance measurements were carried out in Solartron 1286 Potentiostat and 1250 Frequency Response Analyzer. Impedance spectra were measured at the open circuit potential in the frequency range of 30 kHz to 1mHz with ten points per decade. A sine wave with 10mV amplitude was used to perturb the system. Polarization curves was detected with the rate of 10 mV/min.

The influence of surface pre-treatment on adhesion, on the morphological properties of lacquer and paint layers were visualized on air by atomic force microscopy (AFM) and by scanning electronmicroscopy (SEM).

Results and Discussion

Surface treatment of iron by diphosphonates

The protective layer formation was monitored in situ in the phosphonate containing solution using impedance spectroscopy and measurement of the open circuit potential of Armco iron as a function of time. Our previous result [13] proved that the presence of electrolyte (e.g. sodium perchlorate) affects the adsorption of phosphonate and, interrupting the protective layer formation, the growth kinetics of alkane-phosphonates layers in perchlorate-free solution was followed.

When Armco iron was immersed in the 1,7-diphosphonoheptane containing solution the change of OCP in the first hour of immersion is shown in Figure.1. Measuring the continuous shift of OCP towards the anodic direction followed the initial transitivity stage. The change of corrosion potential is relatively slow; the maximum value around -115 mV (vs. SCE) was reached after one day. This is the consequence of the adsorption of phosphono compounds that leads to the formation of a protective layer on the iron surface.

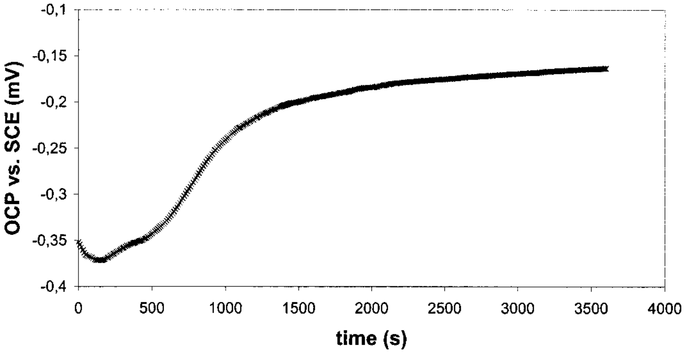


Figure 1. Change of OCP of Armco iron as a function of time in 10^{-3} M 1,7-diphosphono-heptane solution (pH 7.0)

The layer formation of diphosphonates on iron was monitored by impedance spectroscopy. After a 2-day-long immersion of iron in aqueous 1,7-diphosphono heptane solution the impedance spectrum shows the protective behavior of the adsorbed layer (Figure 2).

The effect of adsorption time on polarization resistance and corrosion potential of Armco iron in the 1,7-diphosphono-heptane solution is presented in Figure 3. With increasing immersion time the polarization resistance continuously increases. The polarization resistance is equivalent to the charge transfer resistance of iron dissolution that takes place at the uncovered metal surface, i.e. at pores and discontinuities within the film.

Therefore, the change of polarization resistance values gives direct information on the growth and quality of inhibitor layer.

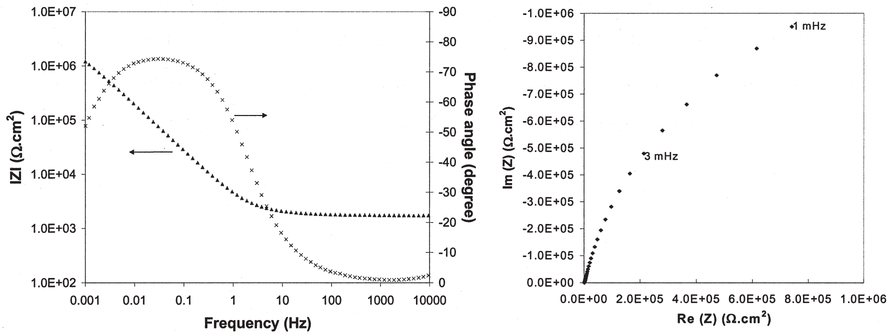


Figure 2. Typical impedance spectrum of Armco iron in phosphonate containing solutions

(a) Bode and (b) Nyquist plots of Armco iron in aqueous solution of 0.001 mol.dm^{-3} 1,7-diphosphono-heptane (pH=7) measured after 48 hours of immersion, and (c) Equivalent circuit modeling the impedance of modified iron. R_s: solution resistance, R_p: polarization resistance; Q_{dl}: CPE of the double layer

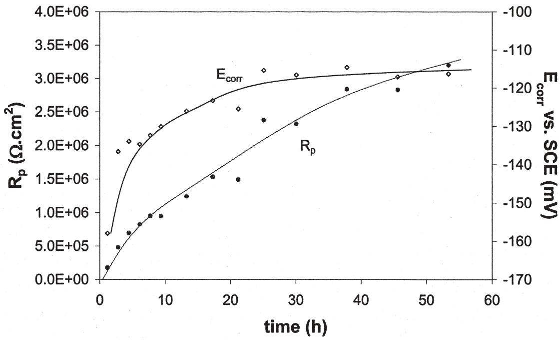


Figure 3. Time dependence of polarization resistance and open circuit potential of Armco iron in aqueous solutions of 0.001 mol.dm^{-3} 1,7-diphosphono-heptane (pH=7)

According to the results obtained by impedance studies, the iron dissolution is effectively hindered by the adsorbed phosphonate layer, which is supposed to have a continuous and dense structure. After few hours of immersion, significant protection could be achieved on bare iron. The fast adsorption of molecules is important in aqueous solution that can significantly decrease the disturbing iron dissolution process that runs parallel to the adsorption. Although, fast adsorption provides efficient protection of iron, a further increase in polarization resistance can be observed during a long immersion time. This observation refers to a time-dependent quality improvement of the film.

Due to the interaction of phosphono-groups with the solid surface, formation of a multi-molecular layer may also be considered. It was proved in our earlier SNIFTIRS studies [11] that thin multi-molecular adsorption layers of diphosphonic acids are formed on iron surface in aqueous solution. Although ordered structure and orientation of diphosphonates was observed in a certain degree, this was only qualitative information.

The composition of oxide layer influences the adsorption of phosphonates [16]. The adsorption of phosphonates takes place on aluminum surfaces, which is rich in OH-groups [17]. Presumably, the formation of thin iron oxide layer (that takes place at the first few minutes of immersion as shown in Figure 1 at the initial domain) ensures favored conditions for the protective layer formation of phosphonates.

All of the investigated diphosphonic acids inhibited the iron dissolution. The mechanism of inhibition was studied by polarization methods. Figure 4 shows anodic polarization curves of Armco iron in aqueous solution of 0.001 mol.dm^{-3} 1,7-diphosphono-heptane measured after different adsorption time (30min, 1h and 3h).

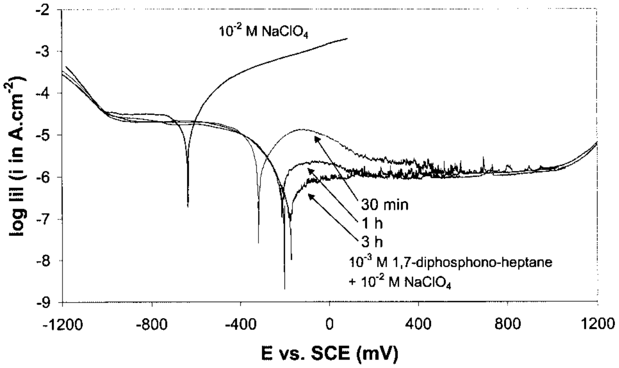


Figure 4. The effect of the adsorption time on the polarization curves of Armco iron in solution of 10^{-3} M 1,7-diphosphono-heptane + 10^{-2} M NaClO$_4$ (pH 7.0)

Significant decrease of anodic currents (which is related to the iron dissolution) in the active potential range was observed with increasing adsorption time, which suggests that the active iron dissolution was hindered by blocking of surface layer.

Film repairing properties of diphosphonates

A re-built protective layer formation can also be observed at defects of inhibitor film. This process is demonstrated on modified iron surface by using an artificial scratch by a sharp knife. Figure 5 shows the change of open circuit potential of modified iron electrode before and after an artificial scratch. Prior to scratching, a four-day-long surface modification was carried out by immersion of iron electrode into the aqueous solution of 1,7-diphosphono-heptane solution.

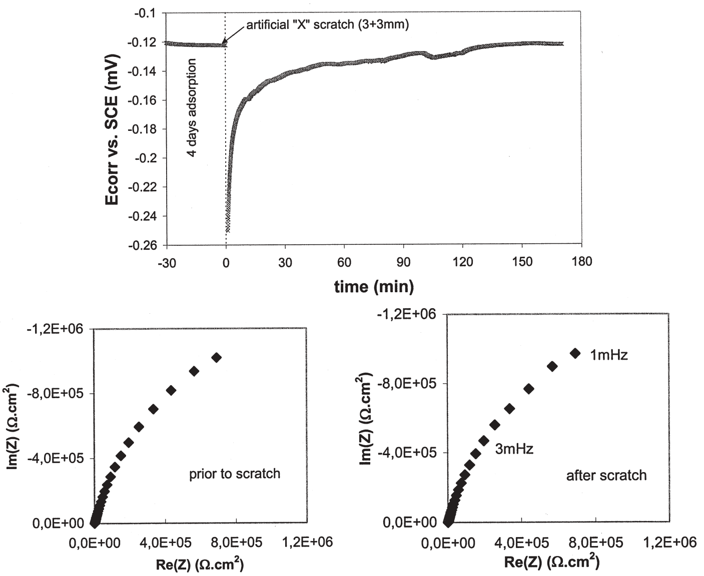
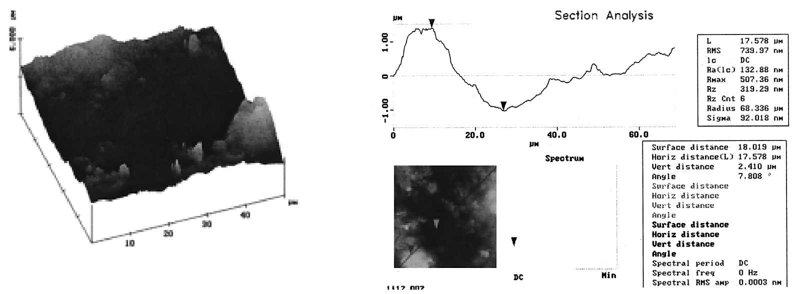


Figure 5. (a) Change of open circuit potential of Armco iron in 10^{-3} M 1,7-diphosphono-heptane before and after an artificial scratch; and impedance spectra measured (b) prior to, and (c) 3 hours after scratching

After replacing the scratched electrode into the solution of phosphonate, the open circuit potential first decreased which was the consequence of enhanced iron dissolution at the defect. But later, the open circuit potential increased showing the “healing” of the layer at the defect, which proved the repairing of the inhibitor film, the potential reached the initial value (–122 mV) within 3 hours. Impedance plots measured before (Figure 5b) and after the scratch (Figure 5c) shows actually the same electrochemical properties of modified iron.

Surface visualization by scanning microscopes

Assuming that the metal pre-treatment by self-assembling molecular layer can enhance the paint adhesion and improve the surface properties some measurements were done on lacquer and paint surface. The first question was how will be reflected the different coating treatment (e.g. heating) in the morphology of lacquer and paint surfaces. For the evaluation of surfaces atomic force microscope (AFM) and scanning electron microscope (SEM) were used. The influence of heating on the surface properties is demonstrated on Figure 6.



```
L         17.578 µm
RMS       739.97 nm
lc        DC
Ra(lc)    132.88 nm
Rmax      507.36 nm
Rz        319.29 nm
Rz Cnt    6
Radius    68.336 µm
Sigma     92.018 nm
```

```
Surface distance     18.019 µm
Horiz distance(L)    17.578 µm
Vert distance        2.410 µm
Angle                7.808 °
Surface distance
Horiz distance
Vert distance
Angle
Surface distance
Horiz distance
Vert distance
Angle
Spectral period      DC
Spectral freq        0 Hz
Spectral RMS amp     0.0003 nm
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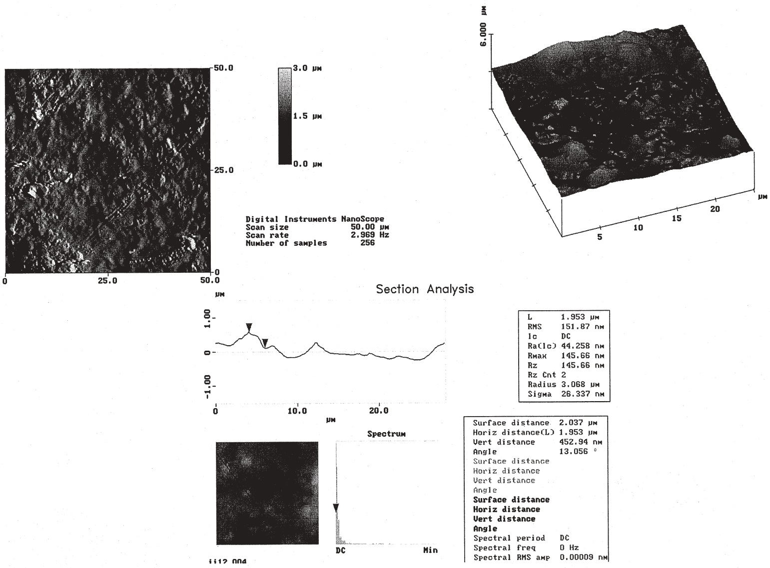
<u>RMS: 739,97nm</u>

Figure 6. AFM images and roughness factors of different paint and lacquer surfaces (continued next page)



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Digital Instruments NanoScope
Scan size              50.00 µm
Scan rate              2.969 Hz
Number of samples        256
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```
L       1.953 µm
RMS     151.87 nm
lc      DC
Ra(lc)  44.258 nm
Rmax    145.66 nm
Rz      145.66 nm
Rz Cnt  2
Radius  3.068 µm
Sigma   26.337 nm
```

```
Surface distance   2.037 µm
Horiz distance(L)  1.953 µm
Vert distance      452.94 nm
Angle              13.056 °
Surface distance
Horiz distance
Vert distance
Angle
Surface distance
Horiz distance
Vert distance
Angle
Spectral period    DC
Spectral freq      0 Hz
Spectral RMS amp   0.00009 nm
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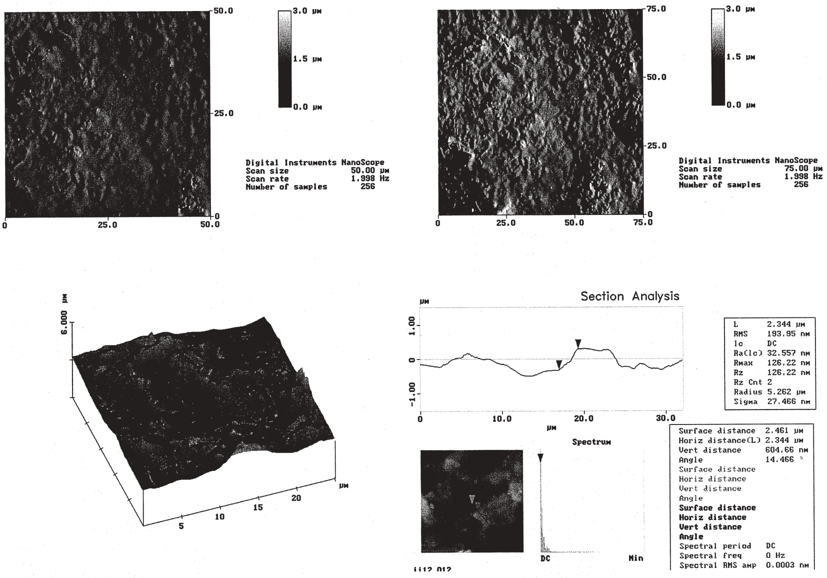
RMS: 152.87nm



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Digital Instruments NanoScope
Scan size              50.00 µm
Scan rate              1.998 Hz
Number of samples        256
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Digital Instruments NanoScope
Scan size              75.00 µm
Scan rate              1.998 Hz
Number of samples        256
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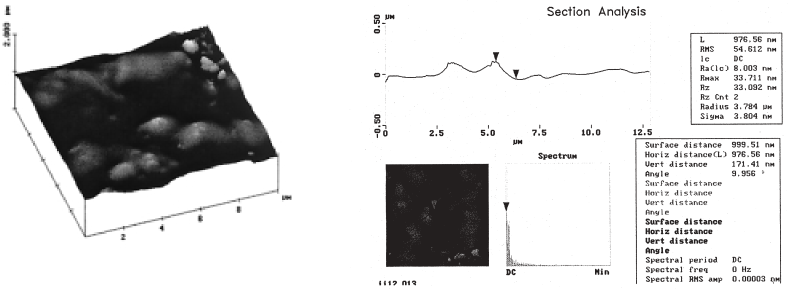
```
L       2.344 µm
RMS     193.95 nm
lc      DC
Ra(lc)  32.557 nm
Rmax    126.22 nm
Rz      126.22 nm
Rz Cnt  2
Radius  5.262 µm
Sigma   27.466 nm
```

```
Surface distance   2.461 µm
Horiz distance(L)  2.344 µm
Vert distance      604.66 nm
Angle              14.466 °
Surface distance
Horiz distance
Vert distance
Angle
Surface distance
Horiz distance
Vert distance
Angle
Spectral period    DC
Spectral freq      0 Hz
Spectral RMS amp   0.0003 nm
```

<u>RMS:193.95nm</u>



```
L        976.56 nм
RMS      54.612 nм
lc       DC
Ra(lc)   8.003 nм
Rmax     33.711 nм
Rz       33.092 nм
Rz Cnt   2
Radius   3.784 µм
Sigмa    3.804 nм

Surface distance    999.51 nм
Horiz distance(L)   976.56 nм
Uert distance       171.41 nм
Angle               9.956 °
Surface distance
Horiz distance
Uert distance
Angle
Surface distance
Horiz distance
Uert distance
Angle
Spectral period     DC
Spectral freq       0 Hz
Spectral RMS amp    0.00003 nм
```

<u>RMS: 54.61nm</u>

Figure 6 (contd.). AFM images and roughness factors of different paint and lacquer surfaces

Not only perceptible the difference is but the roughness factor (RMS), too, reflects the smoothing of the layer as a consequence of the treatment. In other set of experiments the usefulness of the SEM technique was proved in evaluation of surface properties (Figure 7).

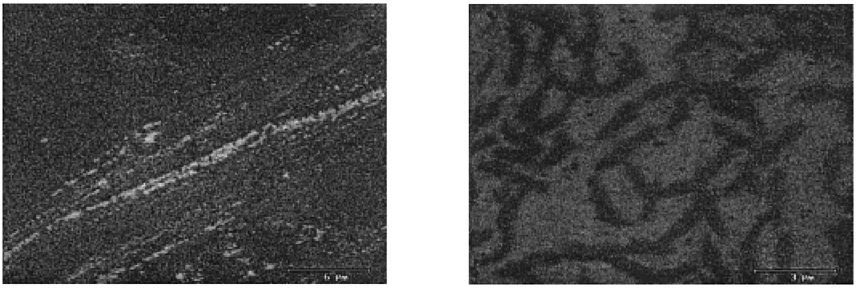

150°C 250°C

Figure 7. After heat treatment SEM images of paint surfaces

The influence of the self-assembled molecular layer on adhesion of paint and the surface roughness was visualized and measured by AFM. In accordance with electrochemical results the nano-structured surface layer improved the surface quality of coating.

Conclusion

Surface pre-treatment by 1,7-diphosphono heptane gave a self-organized, stable layer with ordered structure on oxidized iron surface. The pre-treatments of metal surfaces enhanced the smoothness and the adhesion of paints and lacquer layers.

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