The Influence of Kinetic & Hydrodynamical Factors On the Structure & Properties of Conversion Coatings

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For each crystallization process, including the formation of conversion coatings, there must be a supersaturated solution, so that any steps taken to increase the number of nuclei will favor formation of fine-grained coatings. The greater the supersaturation, the greater the number of crystal nuclei and vice versa. Because the extent of such supersaturation is proportional to the concentration gradient of species, the thinner the diffusion layer, the larger the rate of spontaneous formation of new nuclei. This paper summarizes the results from a series of experiments that were aimed at decreasing the thickness of the diffusion layer by the combined application of pulsed cathodic polarization (up to 150 mV) on a rotating disk electrode and the addition of a hydrodynamically active (HDA) agent to the forming solution. The combination of these two factors results in accelerating the partial reactions of oxidation and reduction. By varying the pulse frequency of applied cathodic polarization, we can regulate and control both processes. The resulting leveling power dependence on pulse frequency helped define the optimal pulse frequency for the formation of conversion coatings with homogeneous and fine-grained structure. It coincides with the value of pulse frequency of the maximum leveling power.

The formation of conversion coatings (chromate, phosphate, oxide etc.) is an artificially induced and controlled process of electrochemical corrosion, as a result of which a layer is formed on the metal surface. This layer is firmly bonded to the base metal, and, as an integral part of the protected metal, most such coatings can serve as an appropriate base for paint, lacquers, plastics, oils and greases. Irrespective of the type of metal substrate or conversion coating, the formation of the layer is based on a common electrochemical mechanism involving two mutually linked reactions: anodic and cathodic.

The anodic process of metal oxidation and proton and electron release is related to the participation of precipitating anions (OH⁻, CrO₄, H_2PO_4):

The oxidizing agents depolarize at the microcathodes of the metal surface:

$$Ox_{(acc.)} + H^{\scriptscriptstyle +} + 2e^{\scriptscriptstyle -} = Red_{(acc.)} + H_2O$$

This paper examines the influence of kinetic and hydrodynamical factors on the rate of the above electrochemical reactions of oxidation and reduction. Knowledge of these influences ensures effective control of the structure and prop-



Fig. 1—Schematic representation of phosphating process.

erties of the conversion coatings. In addition, we can successfully define the optimal conditions for the formation of conversion coatings with homogeneous and fine-grained structure. The practical benefits from an application of the results obtained include:

- Improved adhesion of paints and powder coatings to the metal substrate.
- > Decreased friction and enhanced anti-seizing properties.

Electrochemical Aspects

Of the Phosphating Process

The formation of insoluble phosphate coatings is invariably linked with corrosion of the substrate metal in dilute aqueous solutions. In contrast to the non-coating processes, the dilute aqueous solutions for phosphating contain the main necessary constituents: phosphate anions and at least some of the metal cations.

The work of Machu¹ argues that phosphating should be considered an electrochemical process with discrete partial reactions at local anodes and cathodes. In the case of iron phosphating, a local anodic dissolution takes place during the preliminary etching step,

$$Fe \longrightarrow Fe^{+2} + 2e^{-} \tag{1}$$

while at the cathode, hydrogen evolution occurs:

$$2H^+ + 2e^- \longrightarrow H_2 \tag{2}$$

The greater part of the surface area behaves at first as an anode, whereas the cathodic regions are restricted to grain boundaries, residual oxides etc. The initially high corrosion currents are linked to the rapid formation of large amounts of the primary soluble iron(II) phosphate in the near-surface solution layer around the local anodic regions. Simultaneously, equivalent amounts of hydrogen ions are discharged at local cathodic areas. This causes reduction of the hydrogen ion concentration in the diffusion layer in the vicinity of the local cathodes. Diffusion from the bulk of fresh hydrogen ions is not fast enough to compensate for the depletion and soon the concentration of hydrogen ions falls below the level required for retaining the tertiary heavy-metal phosphate in the solution. As a result, this species is precipitated in the neighborhood of the local cathodes as the coatingforming species (Fig. 1).² This explanation is further supported by the following observation: The external cathodic polarization of the base metal encourages coating formation, whereas an anodic polarization has practically no influence on the deposition of crystallized metal phosphates, although it increases the concentration of dissolved metal ions.

In practice, the phosphating reaction tends to be slow, owing to polarization caused by the hydrogen involved in the cathodic part of the reaction. This process of discharge of hydrogen ions and, consequently, coating formation itself, can be favored by oxidizing agents (accelerators), which act as consumers of electrons and protons:

accelerator XO + $2H^+$ + $e^ \longrightarrow$ H_2O + reduction product of XO

Commonly used phosphating baths contain large amounts of accelerators, including nitrates, nitrites, chlorates, bromates, and per-compounds such as hydrogen peroxide and perborates. These oxidizing agents accelerate the etching process by preventing physical blocking of the metal surface by hydrogen bubbles and replace the heavily hindered hydrogen evolution reaction with alternative, faster processes:

 $\begin{array}{l} NO_3^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O \\ ClO_3^- + 6H^+ + 6e^- \longrightarrow Cl^- + 3H_2O \\ 2NO_2^- + 8H^+ + 6e^- \longrightarrow N_2 + 4H_2O \\ H_2O_2^- + 2H^+ + 2e^- \longrightarrow 2H_2O \end{array}$

The practice shows that the crystal shape and size of phosphate coatings depend on many factors, such as bath compo-



Fig. 2-Corrosion diagram and principle of cathodic protection.

sition, temperature and the method of surface preparation. Crystals may take on the form of plates, needles, or grains and their size can vary from a few μ m to tens of μ m. The coatings produced by slow phosphating baths are usually coarser than those from accelerated solutions. Particularly fine crystalline coatings are obtained from accelerated solutions containing modifying substances that promote the formation of large numbers of nuclei.³ For each crystallization process, including the formation of conversion coatings, there must be a supersaturated solution, so that any steps taken to increase the number of nuclei will favor the formation of fine-grained coatings (*e.g.*, coatings with properties that are particularly valuable from a technical standpoint). The greater the supersaturation, the greater the number of new crystal nuclei. Also, according to the electrochemical kinetics,

$$i = \frac{zFD}{\delta} (C_{b} - C_{e}),$$

at a given supersaturating ($C_b - C_e$), the rate of spontaneous formation of new nuclei is conversely proportional to the diffusion layer, δ . The thinner the diffusion layer, the greater the rate of conversion coating formation.

Therefore, we argue that acceleration of the crystallization process and the formation of fine-grained coatings can be achieved if the thickness of the diffusion layer is decreased. During phosphating, the metal is in contact with a large volume of the phosphating solution, so a ready exchange between species in the near-surface liquid diffusion layer and the bulk of solution can easily take place. The extent of such exchange is proportional to the concentration gradient of these species in the diffusion layer. In other words, the thinner the diffusion layer, the greater the rate of spontaneous formation of new nuclei.

Here we propose two ways to decrease the thickness of the diffusion layer, δ :

Through addition of hydrodynamically active agents in agitated phosphating solutions.

Hydrodynamically active agents are special substances (water-soluble polymers) that, added to plating baths, even in minuscule quantities, can reduce by several times the value of kinematic viscosity of the electrolyte and thus the thickness of the diffusion layer.



Fig. 3—Dependence of leveling power on pulse frequency of cathodic polarization.



Fig. 4—Electron micrographs of phosphate coatings formed in low-zinc phosphating solution not containing hydrodynamically active (HDA) additive: (a) without cathodic polarization; (b) at 3 Hz pulse frequency of cathodic polarization; (c) at 6 Hz pulse frequency of cathodic polarization.

> Through the potentiostatic application of cathodic pulses. In the immediate vicinity of the electrode surface, the concentration of reacting species pulsates with the frequency of the pulsating current; it decreases during the pulses and relaxes in the interval between them. Thus, a pulsating diffusion layer is formed in close proximity to the cathode. If the duration of the pulse is short, the diffusion layer does not have time to extend very far into the solution and it does not reach the region where convection takes over the mass transport.

According to Ibl, the thickness of the pulsating diffusion layer is defined by the equation:

$$\delta_{\rm p} = (2\mathrm{D}\mathrm{T_{op}})^{1/2} \tag{3}$$

It follows from Eq. (3) that the shorter the pulse length, T_{on} , the smaller the thickness of the pulsating diffusion layer, δ_{n} .

As can be seen from the schematic diagram of corroding metal (Fig. 2), the potentiostatic application of small cathodic pulses (up to 150 mV) results in a decrease of the rate of anodic reaction during the pulse time, T_{on} . If the potential of the metal is reduced from E_{corr} to C, the anodic current is reduced from I_{corr} to I_a . It can also be seen that if the potential is reduced to E. the anodic current will be zero and the external current will be represented by E₂D.⁴

Experimental Results The experimental part of this study is based on the combined application of the above possibilities to create a synergistic effect and, thus, effectively decrease the thickness of the diffusion layer. This is the reason that the experimental conditions for the application of phosphate coatings include rotation of the cathode (disk electrode), the application of pulsed cathodic polarization, and the addition of hydrodynamically active agents to the phosphating bath.

The presence of a finegrained structure is a mandatory, but not a sufficient, condition to obtain a phosphate coating with good functional properties. It is necessary, therefore, to find an objective criterion for the determination of those pulse conditions under which phosphate coatings

with the best properties are obtained.

formed in low-zinc phosphating solution containing

hydrodynamically active (HDA) additive: (a) without

cathodic polarization; (b) at 3 Hz pulse frequency of

cathodic polarization; (c) at 6 Hz pulse frequency of

cathodic polarization.

Our research suggests that microthrowing (leveling) power could be such a criterion. Those pulse parameters that enable a maximum value of leveling power, represent the conditions for formation of coatings with the best properties.

The microthrowing power can be qualitatively characterized as the ability to diminish the difference in heights between protrusion peaks and recesses in a surface microprofile. The greater this ability, the thinner the coating thickness required to achieve leveling. The following expression is used in order to define the leveling power (LP):

$$LP = \frac{(R_{a,o} - R_{a,c})}{R_{a,o}}$$
(4)

where $R_{a,o}$ is the roughness of the uncoated substrate, and

 $R_{a,c}$ is the roughness of the coated surface.⁵ The initial roughness, $R_{a,o}$, is obtained by grinding the disc electrode surface in one direction only with 280 grade emery paper. The phosphate coatings are applied on half the surface of the electrode of mild steel because the other half has been previously insulated with a thin film of photo-resist lacquer. After coating formation, this film is removed with the help of an organic solvent. In such a way, it is possible to determine the coating thickness directly from the profilogram.

The composition of the "low zinc" phosphating bath and its operating conditions are as follows:⁶

ZnO	2 g/L
H_3PO_4	13 mL/L
Accelerator NO_3^{-}/NO_2^{-}	3 g/L
Total acid value (TA)	16-20 points
Free acid value (FA)	1-3 points
Temperature	40 °C
Time	5 min

As can be seen from the leveling power dependence on pulse frequency of cathodic polarization (pulse duration is constant; $T_{on} = 20$ msec), the roughening tendency of phosphate coating occurs in the beginning of the frequency range (Fig. 3). The leveling power increases steeply above 3Hz and reaches its maximum value at 6Hz. Here the leveling power of phosphate coating is four to five times higher than in conventional phosphating without cathodic polarization. A further increase of pulse frequency leads to diminished LP%, and the coatings gradually get rougher.

The leveling performance of phosphate conversion coatings obtained can serve as a basis for the following considerations:

- There is complete cathodic protection in the time period of pulse duration, T_{on}, and spontaneous anodic metal dissolution during the interval between two pulses, T_{off}.
- > As the pulse frequency increases (T_{on} const.), T_{off} decreases (*i.e.*, the time for anodic dissolution (roughening) decreases progressively, whereas the cumulative time for the cathodic process of reduction of hydrogen ions shows a relative increase). This cathodic reduction results in alkalization of the layer adjacent to the electrode surface, which leads to precipitation (leveling) of insoluble heavy metal phosphates.
- The pulse frequency at which the leveling maximum occurs (6 Hz), results in the optimal coordination of both processes of anodic iron dissolution and of cathodic reduction and precipitation. In other words, this value of pulse frequency determines the formation regime of phosphate coatings with the best properties.

Actually, electron micrographs (Figs. 4 and 5) show the most uniform and very finely-crystalline phosphate coatings, formed in low-zinc phosphating solution at 6 Hz of pulsed cathodic polarization. The linear dimensions of crystals are about 2 to 3 μ m. The crystal grains are larger when formed at 3 Hz pulsed cathodic polarization. This frequency corresponds to the minimum value of leveling power. The largest are the crystals of phosphate coating, formed without any polarization and their linear dimensions are approximately 15-25 μ m.

Also, comparing two sets of pictures of phosphate coatings, formed in solutions with and without addition of a hydrodynamically active agent, it can be concluded that the influence of pulsed cathodic polarization on crystal shape and size for phosphate coatings is much greater than that of hydrodynamically active additives in a phosphating bath.

Conclusions

The results obtained offer further evidence for the possibility of regulation and control of every electrochemical process related to cathodic electrodeposition, conversion coating formation, or anodic oxidation by applying pulsed current or pulsed voltage.7 This possibility is based on the fact that the electrochemical processes above are influenced by the simultaneous action of binary sets of opposite factors: oxidation/reduction, acidic/basic, adsorption/desorption, and growth/dissolution. The characteristics of the process in every particular case are determined by the individual factor that prevails over the others. In the case of conversion coatings formation, application of pulsed cathodic polarization (up to 150 mV) can be used successfully to modify the structure of conversion coatings. By varying the pulse frequency of applied cathodic polarization, which suppresses the anodic process but stimulates the cathodic process, we were able to find the optimal coordination of both processes of dissolution and growth. Thus, from the leveling power dependence on pulse frequency obtained, we can define the pulse frequency corresponding to this optimum; it coincides exactly with the value of pulse frequency of the maximum leveling power. It is under these conditions that the formation of conversion coatings with homogeneous, fine-grained structure and best properties take place.

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