

## INVESTIGATION OF PHOSPHATE COATING FORMATION BY ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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In this investigation, an attempt has been made to use electrochemical impedance spectroscopy as a tool for monitoring the phosphate coating formation, especially the involvement of base metal in the coating formation. Results of the studies have been presented in the form of Nyquist plots of various immersion time which shows a depressed semicircle and the diameter and degree of depression increase with time. Charge transfer resistance and the interfacial capacitance of steel in phosphating solution are parameters of impedance study which helps in assessing and optimizing the conditions of phosphating. The results also show that presence of crystal refiner and/or accelerator accelerate the base metal dissolution at the initial stage of coating formation and the crystal refiner modifies the coating properties by lowering the porosity by redissolution and deposition.

**Keywords:** Impedance technique, phosphate coating, conversion coating steel.

### INTRODUCTION

Phosphating process has very early origin and it is widely used for all the engineering materials to improve paint adhesion, corrosion resistance, lubrication and to provide electrical insulation. In spite of its wide usage, search of literature reveals only very little information concerning the fundamental mechanism of phosphating while extensive reviews are available on various applications and theoretical aspects of phosphate coating [1-3].

Process proceeding during phosphating of metals involve substrate corrosion (dissolution) in the acidic bath [4-5] and this associates with an increase of interfacial pH which accelerates the precipitation of insoluble tertiary phosphate on the metal surface to form the so called phosphate coating. In order to achieve the process of the previous kind, it is essential that the phosphating bath should contain free phosphoric acid, a primary metal phosphate of type  $M^{II}H_2PO_4$  (where  $M^{II}$ ,  $Fe^{II}$ ,  $Zn^{II}$  or  $Mn^{II}$ ) with an accelerator typically an oxidant such as nitrate or chlorate. The general view is that the mechanism of phosphate coating formation is complex, and it depends on the following equilibrium



Rise of temperature and/or pH, shift the equilibrium to the right, favouring the precipitation of insoluble tertiary phosphate as coating on the metal surface.

The electrochemical nature of the process proceeding during coating formation has been used to follow the overall surface process. Thus, potential-time measurements have been used to monitor the completion of phosphate coating [4]. Though by this method, it is possible to follow as well as to identify various stages of phosphate coating formation, little information can be obtained on the involvement of base metal during the coating formation. One of the promising ways to get such information is by the use of sophisticated instrumentation such as electrochemical impedance spectroscopy (EIS). Such information is essential in engineering coatings for particular application and determining the precise role of additives present in the bath, i.e. accelerators.

In this investigation, attempt has been made to study the corrosion behaviour of steel in phosphating solution by EIS. Potential-time measurements have also been studied in support of the earlier study.

**TABLE I: Results of impedance study**

Bath type	Immersion time min	Polarization resistance $\Omega \text{ Cm}^2$	Corrosion current $\mu \text{ A/cm}^2$	Capacitance $\text{F/cm}^2$
2.5% $\text{H}_3\text{PO}_4$	---	60	216	$1.25 \times 10^{-4}$
Bath I	5	100	130	$6.10 \times 10^{-5}$
Bath I	10	520	25	$2.30 \times 10^{-5}$
Bath I	20	3200	4	$1.80 \times 10^{-6}$
Bath I	30	3600	3.6	$1.60 \times 10^{-6}$
Bath II	5	50	260	$4.20 \times 10^{-4}$
Bath II	10	3800	3.42	$1.76 \times 10^{-6}$
Bath II	20	4200	3.095	$1.62 \times 10^{-6}$
Bath II	30	4600	2.8	$1.48 \times 10^{-6}$
Bath III	5	60	216	$1.42 \times 10^{-4}$
Bath III	10	3950	3.29	$1.81 \times 10^{-6}$
Bath III	20	4600	2.83	$1.40 \times 10^{-6}$
Bath III	30	5000	2.5	$1.32 \times 10^{-6}$

### EXPERIMENTAL

Mild steel specimen of size 10 x 50 mm were mechanically polished, degreased with acetone. Before phosphating, the samples were immersed in 10% oxalic acid at room temperature for 10 minutes, followed by washing in distilled water. For impedance measurements the samples were lacquered so as to expose 1  $\text{cm}^2$  area. The phosphating bath used in this investigation has the composition as in Table I.

For potential-time measurements the samples were immersed in the bath with and without additive at room temperature. Potentials were monitored with respect to saturated calomel electrode (reference electrode) using a digital multimeter.

Impedance measurements during the coating formation were made with conventional three electrode cell arrangement which has mild steel as working electrode, platinum foil as counter electrode and saturated calomel electrode as reference electrode. Impedance measurements were made at corrosion potential by superimposing a sine wave of amplitude 10 mV in the frequency range of 10 kHz to 1 Hz. The results have been reported in the form of Nyquist plot.

### RESULTS AND DISCUSSION

Fig. 1 shows the potential-time behaviour of mild steel in phosphating bath. Initially the potential value has been found to shift cathodically (in the negative direction) and then rises progressively with time and attains a steady state potential value approximately after 25 minutes of immersion. In

phosphating bath with additives A and A+B, the potential behaviour is similar to that described previously but the time for attaining minimum value and steady state potential is much less when compared to that of additive free bath.

Potential-time behaviour of steel suggests that initial dissolution of steel is followed by the development of phosphate coating. Moreover, in presence of additive, both the dissolution of the base metal as well as coating formation rate have been accelerated. However, the extent of substrate corrosion or coating formation rate can not be predicted from this behaviour.

Typical impedance spectra measurement as obtained for steel in bath I as a function of time are presented in Fig. 2 which also includes that of steel in 2.5% phosphoric acid for comparison. The impedance diagrams obtained at the corrosion potential for steel in phosphating bath II, III are also similar. But a clear difference is observed between these diagrams obtained for different immersion times in the same bath.

The impedance diagram is characterised by a single capacitive loop. The value of charge transfer resistance  $R_{ct}$  obtained as a function of time for different baths are summarised in Table II. As the immersion time increases, the capacitive loop becomes more depressed, rather flattened loop. The degree of depression changes with immersion time. Such behaviour could be attributed to the increased micro-roughness caused by the deposition of the coating (chemical or structural heterogeneity) or by corrosion products.

The corrosion rate of the steel substrate from the  $R_{ct}$  value of the impedance expressed as current density can be calculated using the Stern-Geary relationship

$$I_{\text{corr}} = 0.013 / R_{ct}$$

where the value of 0.013 corresponds to the anodic and cathodic Tafel slope values of 0.04 and 0.12 V/dec respectively.

**TABLE II: Composition of the phosphating bath**

Ingredients	Bath I	Bath II	Bath III
	%	%	%
Phosphoric acid	2.0	2.0	2.0
Trisodium Phosphate	1.5	1.5	1.5
Zinc oxide	1	1	1
$\text{HNO}_3$	0.5	0.5	0.5
Additive A-Accelerator	-	0.05	0.05
Additive B-Crystal refiner	-	-	0.05

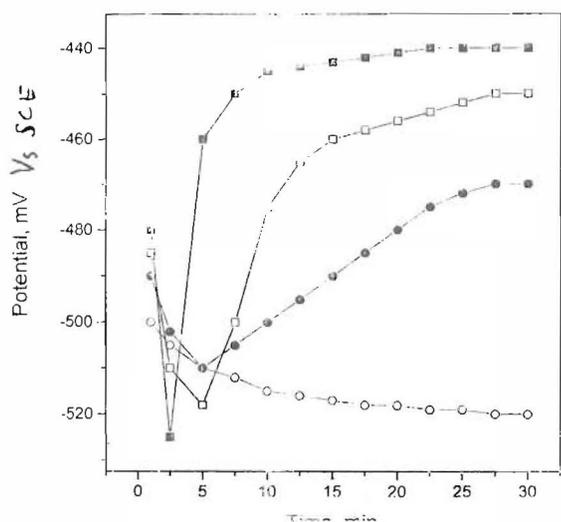


Fig. 1: Potential time behaviour of mild steel in phosphating solution  
 (○) Acid (●) Bath I (□) Bath II (■) Bath III

Thus calculated corrosion rate values are also given in Table I. The results reveal that the corrosion rate is higher initially, and decreases relatively rapidly, achieving a steady state value after immersion for 20 minutes. Presence of additive A and A + B accelerates the initial metal dissolution and the steady state is achieved in relatively lesser time and the magnitude of corrosion rate is much less indicating the less porous nature of the coating. The residual steady state current may be due to the dissolution of the substrate through pores of the coating.

Results of the studies by potential-time measurements, and EIS indicates that there are four distinct stages in phosphate coating formation viz i) the induction stage, ii) the commencement of film growth or nucleation stage, iii) the main exponential stage or film growth stage and iv) the steady state stage or crystal re-organisation stage.

Potvin and Ahali [4] have utilized the potential-time measurements not only to indicate the different stages of phosphating but also to locate when the effective phosphating has ceased. In the author's opinion, much information on the kinetics and mechanism of phosphating process can be inferred from the potential-time measurements. When following the potential-time measurements for all the baths chosen for the present study, though the nature of the curves appears to be different, the following points are of great importance in all the curves (Fig. 1) i) potential measured at the instant of immersion, ii) time taken for the potential maximum, iii) the time taken for the stabilised potential and

iv) extent of change in potential between the maximum and the stabilised potential.

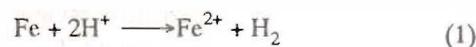
Hence it is possible to interpret the obtained data based on the above observations to reveal the kinetics and mechanism of phosphating which is difficult from the coating weight determination.

Together potential-time behaviour and impedance measurement provide much information than the potential-time behaviour alone. Moreover, assessing the resultant coating quality is not possible by the potential-time measurements.

The impedance spectroscopy employed in this study is capable of monitoring the in situ progress of the coating formation on steel. Importantly, the impedance behaviour of steel in phosphating bath allow insight to be gained into the solution chemistry and interfacial conditions during the course of phosphating process.

### Basic reactions in zinc phosphating of steel

The acidic zinc phosphating solution reacts with the metal surface. In a solution containing only acid and zinc ions, the reaction on an oxide free steel surface is



Immediately after the immersion, this dissolution of the base metal takes place which is indicated in the rise in potential-time measurements and low  $R_{ct}$  in the impedance measurements. Presence of additives increase the rate of the reaction by consuming the hydrogen at the metal surface. This enhanced dissolution is evident from low  $R_{ct}$ .

By the reaction (1), the pH value is increased in the metal/solution interface resulting to the deposition of the zinc phosphate of hopeite structure as indicated below:

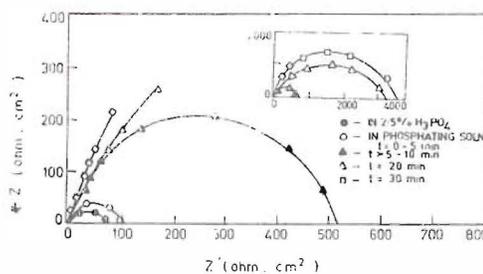
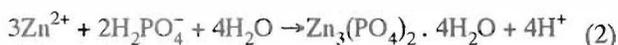
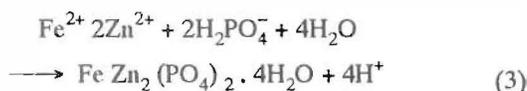


Fig. 2: Impedance behaviour of steel in phosphating solution as a function of time



On steel, phosphophyllite can be precipitated as



The most important reaction in the phosphating process is the nucleation of zinc phosphate crystals. The number of nuclei formed determines the property of the zinc phosphate coating. A large number of nuclei results in a fine-grained coating where as small number of nuclei results in a coarse coating that takes longer time to complete [6-8]. If nuclei are to be formed, the solution has to be supersaturated with zinc phosphate. Hence, if the hydrogen consuming reactions on steel surface can be speeded up by the additives, this results in a faster increase of pH and this results in a more supersaturated solution.

In addition to the enhancement of nucleation, the higher dissolution rate of the steel by the additives also result in a faster growth of the zinc phosphate crystals and thereby shortens the phosphating time. This can be seen in the impedance results which show large change immediately after immersion. The results correlate well with the observed changes in the potential-time behaviour. It also demonstrates clearly the effect of acceleration, which decreases by more than 50% the time taken to form the coating by accelerating the initial metal dissolution rate. Conversely, the marked difference in the stable  $R_{ct}$  value of coating from different baths (residual corrosion difference in physical properties of the films formed, for example, the degree of surface coverage or porosity and structural changes. Unlike potential monitoring, impedance studies provide an insight into the behaviour of coatings after its completion. Significant residual metal corrosion rates suggest a larger extent of porosity in the film or dissolution of the substrate in the bath through the pores.

Thus, by the addition of accelerators, highly corrosion resistant coatings are formed in shorter time by the acceleration of initial phase metal dissolution step. By this, the solution at the metal/solution interface becomes saturated with zinc phosphate crystals in shorter time and due to its

hydrogen consuming nature, the pH increases at the metal solution interface. Both these conditions favour the quick deposition of phosphate crystals on the surface. Moreover, due to its accelerating effect, more number of nuclei are formed which results in a compact (low porous) coating. In addition, this additive oxidises  $\text{Fe}^{2+}$  to ferricphosphate which decreases the diffusion of  $\text{Fe}^{2+}$  outwards and thus the higher concentration of  $\text{Fe}^{2+}$  necessary for the formation of phosphophyllite is achieved which is more corrosion resistant than hopeite form.

## CONCLUSION

Potential-time as well as impedance spectroscopy can be used to follow the phosphate coating formation and provide an indication of the completion of the process. Impedance measurement also indicates residual base metal corrosion after the completion of coating formation and it is due to the dissolution of the substrate metal through pores.

Presence of additive A alone or with additive B in the bath accelerate the rate of coating formation. In addition, it changes the porosity and composition of the resultant coating which makes then more corrosion resistant.

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