

10 The role of surfactants in phosphate conversion coatings

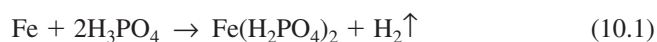
T. S. N. Sankara Narayanan

10.1 Introduction

Phosphating is defined as the treatment of a metal surface to give it a reasonably hard, electrically non-conducting surface coating of insoluble phosphate which is contiguous and highly adherent to the underlying metal and is considerably more absorptive than the metal [1]. The coating is formed as a result of a topochemical reaction, which causes the surface of the base metal to integrate itself as a part of the corrosion resistant film.

10.1.1 Chemistry of phosphating

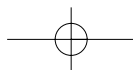
All conventional phosphating solutions are dilute phosphoric acid-based solutions of one or more alkali metal/heavy metal ions, which essentially contain free phosphoric acid and primary phosphates of the metal ions contained in the bath [1–7]. When a steel panel is introduced into the phosphating solution, a topochemical reaction takes place in which the iron dissolution is initiated at the microanodes present on the substrate by the free phosphoric acid present in the bath. Hydrogen evolution occurs at the microcathodic sites.



The formation of soluble primary ferrous phosphate leads to a concurrent local depletion of free acid concentration in the solution resulting in a rise in pH at the metal/solution interface. This change in pH alters the hydrolytic equilibrium which exists between the soluble primary phosphates and the insoluble tertiary phosphates of the heavy metal ions present in the phosphating solution, resulting in the rapid conversion and deposition of insoluble heavy metal tertiary phosphates [1–7]. In a zinc phosphating bath, these equilibria may be represented as



A certain amount of free phosphoric acid must be present to repress the hydrolysis and to keep the bath stable for effective deposition of phosphate at the microcathodic sites. Another factor affecting the shift in the primary to tertiary phosphate

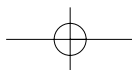


equilibria is the temperature of the bath. Higher temperatures favour easy precipitation of the tertiary phosphates in a shorter time. Hence a greater amount of phosphoric acid is needed for baths operating at higher temperatures. In contrast, in the case of phosphating baths operated at room temperature, the possibility of an increase in acidity during continuous operation is more likely [8] and is normally neutralised by the addition of the carbonate of the metal which forms the coating [$\text{Zn}(\text{CO}_3)_2$ in a zinc phosphating bath]. Hence, depending upon the working temperatures and the concentrations of the constituents in the bath, the free phosphoric acid content must be chosen to maintain the equilibrium condition. A higher concentration of phosphoric acid not only delays the formation of the phosphate coating, but also leads to excessive metal loss.

10.1.2 Applications

Phosphate coatings have been used in a wide variety of applications, e.g. the use of phosphate coatings for corrosion protection, as a base for paint, to provide wear resistance and as an aid in cold forming of steel [1–7,9,10]. Phosphate coatings provide an effective physical barrier to protect corrosion-prone metals against their environment. Owing to their insulating nature, phosphate coatings prevent the onset and spreading of corrosion. These coatings provide effective corrosion protection to both ferrous and non-ferrous metals. The extent to which these coatings provide corrosion resistance is dependent on the thickness and weight of the coating used. However, better corrosion protection can be achieved by finishing these coatings with paints, oils, etc. Phosphate coatings provide an effective base for the application of paints and this constitutes their most widespread application. They can be used as an excellent base for more recent methods of paint applications such as electrophoretic painting and powder coating [11,12] and have been shown to improve the corrosion resistance of steel coated subsequently with cadmium, zinc, nickel, etc., in both industrial and marine environments [13].

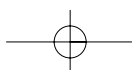
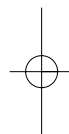
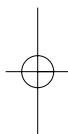
Phosphating is a widely used method of reducing wear on machine elements and moving parts [14]. Phosphate coatings function as lubricants and, in addition, their ability to retain oils and soaps further enhances this action. Heavy manganese phosphate coatings, supplemented with proper lubricants, are most commonly used for wear resistance applications [15]. The power used in deep drawing operations leads to a great amount of friction between the steel surface and the die, which decreases the speed of drawing operations and the service life of tools and dies [16,17]. Application of light to medium weight non-metallic zinc phosphate coatings to steel surfaces, which permit the distribution and retention of a uniform film of lubricant over the entire surface, prevents metal to metal contact and makes possible the cold forming and extrusion of more difficult shapes than is possible without the coating [18]. A combination of zinc phosphate and lubricant film prevents welding and scratching of steel in drawing operations and greatly decreases rejections. Further, phosphate has also been found to be useful in absorbent coatings for laser surface hardening [19] and thermal control coatings in satellite components [20].

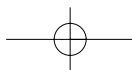


10.1.3 *Developments and implications*

Phosphating is the most widely used metal pretreatment process for the surface treatment and finishing of ferrous and non-ferrous metals. Owing to its economy, speed of operation and ability to afford excellent corrosion resistance, wear resistance and adhesion and lubricative properties, it plays a significant role in the automobile, process and appliance industries. Although the process was initially developed as a simple method of preventing corrosion [21,22], the changing end uses of phosphated articles have enforced modification of the existing processes and the development of innovative methods to substitute the conventional ones. To keep pace with the rapid changing needs of finishing systems, numerous modifications have been put forth in their development, both in the processing sequence and in the phosphating formulations. Prominent among these are (i) the use of low-temperature phosphating baths to overcome the energy crisis [23–25], (ii) the use of low-zinc technology [2,3], (iii) the use of special additives in the phosphating bath [26–34], (iv) the use of more than one heavy metal ion in existing compositions, particularly tri-cation phosphating [35], etc. New types of phosphate coatings such as tin, nickel and lead phosphate coatings have been introduced [36,37], together with the development of compositions for the simultaneous phosphating of multiple metal substrates [38–40]. There has been a growing use of substitutes for conventional Cr(VI) post-rinses to suit the regulations imposed by the pollution control authorities on the use of Cr(VI) compounds [41,42]. The common aim of these modifications is to obtain good, compact, fine-grained and adherent coatings having excellent corrosion resistance, in the most economical and environmentally viable method and to reduce the processing stages. However, the right choice of a processing sequence and a phosphating bath is critical and an important factor. Usually, in industry, the selection will be made based on the end use to which the phosphate coating is to be put to and the value and the worth of the material to be treated. Prominent among these factors, which dictate the ultimate selection of the process, are economy, factory floor space, ease of maintenance of the bath and treatment of effluents [43–45].

Economic considerations in the phosphating industry revolve around production costs, comprising both chemical and energy costs [46]. Fortunately, in pretreatment operations the chemical costs are lower than energy costs and the major factor contributing to the production costs incurred stems from the use of high-temperature cleaning and high-temperature phosphating baths which require electrical heating for their operation [47]. The present day energy crisis compounds the costs of heating of large volumes of solutions at the expense of valuable electrical energy. Although the cost incurred in the use of high-temperature cleaners is enormous, the cleaning step cannot be eliminated, as a clean surface is an essential prerequisite for the formation of a good phosphate coating [48]. Improper cleaning not only affects the bath life but also has an adverse effect on the service life of further finishes applied to phosphated articles [49]. It is therefore preferable to reduce the heating costs in order to make this step profitable without eliminating it. Several attempts have been made to overcome this problem through the formulation of low-temperature cleaners [47,50–55]. These





low-temperature cleaners invariably involve the use of surface-active agents [56]. They curtail evaporation losses, energy consumption and the associated costs but have the disadvantage that their choice in a processing sequence is difficult and the chemical costs associated with their use are greater as they require the use of surface-active agents, either alone or in combination [57].

Most phosphating baths reported in the literature require very high operating temperatures, ranging from 90 to 98 °C. Moreover, it has been recommended that the temperature of the bath is maintained at such a high temperature even when the process is not in operation, as this will avoid problems due to overheating of the bath [58]. The use and maintenance of heating coils under such conditions are extremely difficult owing to scale formation, which leads to improper heating of the bath solution and the need for frequent replacement. The life of the heating coil can be improved through the use of titanium heating coils [59], but cost factors do not make it a suitable alternative. The process can be further economized through the use of low-temperature phosphating baths. Although in use since the 1940s [60], low-temperature phosphating processes have become more significant today owing to escalating energy costs [61–64]. Through suitable formulation and optimization, coupled with the use of specific additives, these processes have been developed to perform as well as the high-temperature processes with other associated advantages, such as shorter start-up time, minimal evaporation losses, low sludge, lesser wear on equipment, better working environment and avoidance of the use of heating coils [61,65,66]. Their choice, however, is restricted by the fact that these processes involve greater consumption of chemicals and longer process times, and also limited process flexibility [61].

Limitations in factory floor space are often an important criterion in the choice and selection of techniques and processes in a phosphating sequence. Although spray, dip and combined spray–dip processes are available, the dip processes have been preferred as the compact arrangement of the immersion tanks affords better utilization of available floor space [63]. Proper utilization has been largely achieved through reductions in the number of operations/stages of the processing sequence. The need to economize the use of floor space has provided a major thrust to the development of combined degreasing and pickling and combined degreasing and phosphating formulations. These formulations are developed by the incorporation of certain surface-active agents or mixtures of surface-active agents and organic solvents, in conventional phosphating baths [43,67]. They provide service lives that approach those of the multi-step cleaner/phosphating compositions. Although the use of these combined processes has found widespread acceptance in terms of economy in floor space utilization, their use has been limited to processes involving lightly oiled surfaces and is less effective on heavily oiled surfaces [43].

It is evident that the modifications introduced in terms of economy, factory floor space and ease and maintenance of the bath warrant the addition of special additives to facilitate the process and to impart the desired characteristic properties to the resultant coating. The special additives that are commonly used in phosphating baths are compiled in Table 10.1 [68]. Each of these additives has been used to solve a

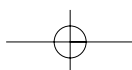
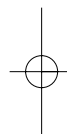
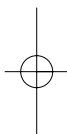


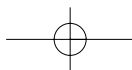
Table 10.1 Special additives used in phosphating baths

No.	Additive used	Purpose	Impact	References
1	α -Hydroxy carboxylic acids such as tartaric and citric acids; triphosphosphate; sodium potassium tartrate; nitrobenzene sulfonate	To reduce the coating weight	Improve bath life through lower consumption of chemicals	69–74
2	Chelants such as EDTA, NTA and DTPA Gluconic acids Polycarboxy- α -aminoacids	To increase the coating weight	Improved corrosion protection, shorter processing times.	75–80
3	Quaternary ammonium compounds; N and P compounds containing amido or amino group; calcium ions; formic acid esters; chelate of an acidic organic phosphate; glycerophosphate	Grain refinement	Better adhesion of subsequent finishes and better corrosion protection.	81–86
4	Nickel(II) ions	To improve surface texture	Better adhesion of subsequent finishes and better corrosion protection.	87
5	Lead compounds; tungstate ions; gaseous nitrogen peroxide; hydroxylamine sulfate; hexamine	To accelerate the phosphating process	Reduction in processing time	88–91
6	Persulfate; permonosulfuric acid	To prevent concentration of ferro-nitroso complex in nitrite-accelerated zinc phosphating bath	Better utilization of nitrite and reduction in the evolution of toxic vapours.	92
7	Cyclic trimetaphosphate	To improve salt spray resistance	Improved corrosion resistance	93
8	Lauric, palmitic and stearic acids with fatty amines and ethoxylated amines	To improve lubricant properties	Improved workability of the metal	94

(continued)

Table 10.1 (continued)

No.	Additive used	Purpose	Impact	References
9	Carbohydrates; dialkyltriamine pentakis(methylenephosphonic acid and its salts) Fluoroborate or fluorosilicate	To decrease scaling	Improved service life of heating coils and uniform heating of the bath	95–97
10	Phosphonic acid ester; magnesium or zinc nitrate	To prevent the build-up of sludge on tank walls	Improved service life of the equipment	98, 99
11	Five membered nitrogenous ring compounds	To improve tarnish resistance	Prevents luster of decorative finishes	100
12	Amines; tin(IV) ions; arsenic compounds; zinc salt of an organic N-compound	As inhibitors	Improves corrosion resistance	101, 102
13	Zinc carbonate	To reduce the acidity of the bath and to maintain equilibrium	Consistent performance of the bath	103
14	Thiourea	Stabilizer in non-aqueous phosphating solutions, as inhibitors	Improved stability of the bath	104
15	Methylphosphonic acid	To improve the hydrophobicity of the coating	Prevents corrosion due to transport of water and corrosive electrolytes, improved corrosion resistance	105



specific need in the phosphating industry, and among them surfactant additives have received considerable attention. The use of surfactants in the metal finishing industry is well established [106,107]. They have been widely used as pickling inhibitors in acid pickling baths [108,109] and as anti-pitting additives in plating baths [110,111] and they serve to prevent the embrittlement of the metal [112]. Their brightening action has been well utilized in electrometallurgy. They play a major role in electroplating baths because of their ability to change the polarization potentials at the cathode and to alter the smoothness of the plate, the grain size, rate of grain growth and adhesion of grains to the substrate and to each other [113]. The simple lowering of the surface tension of the bath by their addition can increase the economy of operation materially by lowering the dragout, which is why surface tension control is widely practiced in the metal finishing industries [114].

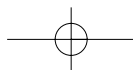
10.2 Surfactants in phosphating

Several phosphating baths have been developed with surfactants as one of the additives [115–117]. Being capable of reducing the surface tension and improving the wettability of the surface, the importance of the presence of such additives in phosphating baths is well realized. However, it should be remembered that surfactants are well known for their habit-modifying ability [118]. Their adsorption on a metal surface and on to the growing crystal faces could greatly influence the nucleation and growth of phosphate crystals and alter the kinetics of the phosphating process [119–121].

10.3 Effect of surfactants on phosphate film epitaxy

Neuhaus and Gebhardt [122] described the formation of a crystalline phosphate deposit on the metal surfaces as *epitaxial growth* and correlated the properties of the phosphate coating in terms of it. Since surfactant additives play a predominant role in phosphating formulations, it is of great interest to know how surfactants influence the epitaxial nature of phosphate film nucleation and growth [123].

Epitaxy is a nucleation and growth relationship between the guest phase that grows in a structure-dependent manner on a given host phase developing an interface, which is chemically and structurally inhomogeneous [124]. It is necessary that the phosphate crystal must grow in an epitaxial fashion so that it is possible to produce as many phosphate crystallites as possible, distributed over the α -iron surface uniformly and of about the same size and densely packed. Moreover, such a regularly repeated, epitaxially directed nuclei formation, growth and growth-retarding mechanisms ensure the transmittal of the substrate orientation to the primary phosphate layers and to all subsequent crystal deposits. Hence there results, at the same time for the layers, a properly adherent, fine-grained and about equally sized crystalline structure. To preclude perfect epitaxy in the phosphate film deposited on the metal surface, close attention has to be paid to the factors that decide the



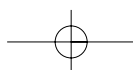
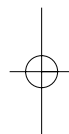
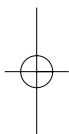
epitaxial nucleation and nucleus growth [125]. Epitaxial nucleation is a special case of heterogeneous nucleation and is greatly influenced by the contact angle, supersaturation and structural faults and contaminants, whereas the epitaxial nucleus growth is largely determined by coalescence phenomena.

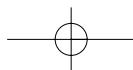
According to the laws of epitaxial nucleation [124], to favour epitaxial orientation over all other orientations, the contact angle should neither be too small nor too large, even though it is well realized that a low contact angle implies improved wetting. When considering phosphating formulations, the surface-active agents incorporated in them serve mainly to reduce the surface tension of the bath to about 35–40 dyne cm^{-2} , which is sufficient for producing a good phosphate coating following the increased wettability of the metal surface.

In general, the nucleation rate increases with increasing supersaturation. As the interfacial free energy of the host/guest should be smaller for the epitaxial orientation than for all other orientations, epitaxial nucleation becomes less and less favoured with increasing supersaturation [124]. If the free acid content of a phosphating bath is lower than is normally required, then there is the possibility of resultant high supersaturation with early consumption of the free phosphoric acid. Under such conditions, epitaxial nucleation will not be favoured and most of the tertiary phosphates are precipitated as sludge rather than nucleating on the metal substrate. However, the required low supersaturation, a favourable condition for the epitaxial nucleation, can be achieved with the addition of surface-active agents, the adsorption of which on the metal surface decreases the rate of consumption of the free phosphoric acid and helps to prevent excessive chemical loss, besides being beneficial for epitaxial nucleation.

The distributions of nuclei on a substrate surface are not usually regular; place having different surface consistencies and different nucleation conditions exists. These areas will then have different potentials and are termed active areas that increase the number of crystal nuclei. Several authors [126,127] have revealed the phenomena of favourable nucleation at the active surface areas. However, contamination of the substrate layer can result in an increase or decrease in the nucleation rate. According to Machu [126], if a very powerful pickling inhibitor is used in the pickling stage before phosphating, then the inhibitor is likely to prevent the formation of phosphate coating if the metal surface is not properly rinsed after pickling. The advantages claimed for the addition of small amount of Cu^{2+} , in terms of increased nucleation and growth, is due to the resultant heterogeneity of the surface [128]. Similarly, a titanium pre-dip creates a surface of heterogeneous consistency and favours the phosphating process [129]. In fact, the heterogeneities and potential differences are considered to be essential prerequisites for the formation of a large number of phosphate nuclei.

When iron or steel is manufactured, it is finally finished with an oil treatment. This is common in the case of a cold-rolled steel. Before phosphating, this oil or greasy matter should be removed otherwise, it will create a surface of homogeneous consistency without greater differences in the structure and in potentials and cause poor coating formation. The use of surface-active agents to ease the removal of such





oil or greasy matter has been extensively documented [130,131] and their addition to the phosphating bath helps to produce the required surface heterogeneity.

Several authors have studied the conditions of epitaxy during nucleus growth [132,133]. After the nucleation stages, the nuclei will sooner or later start to agglomerate, and this agglomeration will increase as islands are formed. At a later stage, the island chains join until only channels are left. Eventually, even these will disappear and a continuous film will be obtained; the surface irregularities will be smoothed out by further growth. The time taken for the coalescence of two islands is a function of the islands' size; the smaller the island, the more rapid is the diffusion process. Regarding the formation of phosphate coatings, the propagation of the crystalline phosphate deposit is nearly two-dimensional. After nucleation, the growth of the phosphate crystal tends to propagate laterally along the surface rather than out into the solution, because the pH is highest near the surface. It is generally believed that the growth is more lateral than vertical. However, when there are only a few nuclei, there is also pronounced vertical growth. The growth rate is controlled by diffusion or by the building-in of the particles on the crystal lattice. The addition of surface-active agents alters the rate of phosphate crystal growth by modifying one or both of these steps. Specific adsorption of the surface-active agents through coulombic and/or amphiphatic interactions causes contamination of the growing crystal faces. The adsorbed surface-active agents reduce the rate of transport of ions owing to their hydrophobic nature and reduce the area of the exposed crystal, thus causing a reduction in the interfacial tension and preventing Ostwald ripening [130,131]. Hence, with the addition of surface-active agents to the phosphating bath, it is possible to produce a larger number of crystals of smaller size.

It is evident that the addition of surfactants to phosphating baths is beneficial in obtaining the desired orientation of the phosphate crystal and the crystallites of the base metal, leading to improved adherence and excellent corrosion resistance of the resultant phosphate coating. Epitaxial nucleation, nucleus growth and its related phenomena of phosphate coating formation have not been adequately explored and the importance of this phenomenology is not yet fully realized. A systematic study of the influence of surfactants on epitaxial nucleation and growth will provide a better understanding on the use of surfactant additives in phosphating formulations.

To illustrate the influence of surfactants on the nucleation and growth of phosphate crystals, the kinetics of the phosphating process, the properties of the resultant coatings and their corrosion resistance, long-chain amines such as dodecylamine (DDA), tetradecylamine (TDA), hexadecylamine (HDA) and octadecylamine (ODA) were chosen as additives. Hot-rolled mild steel specimens (composition conforming to the IS 1079 specification) of dimensions $8 \times 6 \times 0.2$ cm were used as substrate materials. The chemical composition of the phosphating baths and their operating conditions are given in Table 10.2. The processing sequence involved various stages: degreasing, pickling, rinsing, phosphating, chromic acid sealing and drying. Phosphating was done by an immersion process at room temperature (27°C) for 30 min. The amounts of iron dissolved during phosphating and the phosphate coating formed were determined gravimetrically. To assess the kinetics of the phosphating

Table 10.2 Chemical composition of phosphating baths and their operating conditions

<i>Chemical composition</i>	
Bath used	Composition
Bath I	ZnO 5 gl ⁻¹ ; H ₃ PO ₄ 11.3 ml ⁻¹ ; NaNO ₂ 2 gl ⁻¹
Bath II	Bath I + 75 mg l ⁻¹ dodecylamine (DDA)
Bath III	Bath I + 75 mg l ⁻¹ tetradecylamine (TDA)
Bath IV	Bath I + 50 mg l ⁻¹ hexadecylamine (HDA)
Bath V	Bath I + 25 mg l ⁻¹ octadecylamine (ODA)
<i>Operating conditions</i>	
pH	2.70
Temperature	27 °C
Time	30 min

process, the amount of phosphate coating formed was determined every 5 min. Also, the open-circuit potential of the mild steel substrate was monitored for the entire duration of 30 min to judge the nature of the changes that occurred during phosphating. The zinc and iron contents of the phosphate coatings were determined by atomic absorption spectrometry (AAS). Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used to assess the surface morphology and the phase constituents of phosphate coatings. The corrosion resistance of phosphate coatings was evaluated by weight loss, polarization and electrochemical impedance studies.

10.4 Effect of long-chain amines on phosphate coating weight

Coating weight is the prime factor widely used in industry to assess the quality of a phosphating bath and is strongly recommended in many specifications [134,135]. Further, based on coating weight, phosphate coatings have been classified into different categories and recommended for different end uses.

The effect of variations in concentration of long-chain amines on phosphate coating weight is given in Table 10.3. The addition of these amines decreased the coating weight compared with a blank. Among the series (C₁₂–C₁₈), the coating weight increased with increase in chain length. The decrease in coating weight on inclusion of amines in the phosphating bath can be attributed to the adsorption of these amines on the metal surface [136], thereby preventing metal dissolution, which is an essential prerequisite for coating formation. It has been reported that these amines exist in their protonated form as onium cations (RNH₃⁺) in acidic media and are adsorbed on the metal surface [137]. Such an adsorption is supported by the reduction in the measured capacitance value of iron in acidic media in presence of these compounds [138]. Further, polarization studies indicate that in the presence of these amines the anodic branch of the polarization curve remains largely unchanged, thus confirming the ability of the onium cations to interact mostly with the cathodic half cell [138]. Hence the decrease in coating weight can be attributed to the adsorption of these amines as onium cations at the cathodic sites

Table 10.3 Effect of variation in concentration of long-chain amines on zinc phosphate coating weight

Concentration of long-chain amine (mg l^{-1})	Coating weight (gm^{-2}) ^{a,b}			
	DDA	TDA	HDA	ODA
0	9.92	9.92	9.92	9.92
10	5.33	6.11	6.40	7.14
25	5.84	6.68	7.21	8.36
50	6.46	7.24	8.10	8.06
75	7.43	7.94	8.06	7.82
100	6.88	7.40	7.97	7.64
125	6.42	7.12	7.64	7.40

^aAverage of five determinations.

^bDDA, dodecylamine; TDA, tetradecylamine; HDA, hexadecylamine; ODA, octadecylamine.

of the panel being coated. Such an adsorption increases the hydrogen overvoltage [139] and indirectly affects the metal dissolution, in addition to decreasing the available surface area for coating formation.

Comparison of coating weight values obtained for the amine homologous series (C_{12} – C_{18}) indicates that the extent of decrease in coating weight is large in the bath containing DDA and small with ODA as an additive (Table 10.3). The substantial inhibitory effect of DDA is presumably due to its minimum depolarizing efficiency, as the charge-transfer resistance for the process of metal dissolution is high in its presence [138].

Examination of variations in the coating weight with the additive concentrations (0–125 mg l^{-1}) for all the amines showed similar trends (Table 10.3). In each case the coating weight increased with increase in concentration of amine and, after reaching a maximum, it decreased with further increase in amine concentration. This trend can be explained on the basis of the surface-active nature of these amines. At low concentrations, these long-chain amines exist as free monomeric units [140] and become adsorbed at the steel/phosphating solution interface, owing to the electrostatic forces operating between the amine and the metal surface. Such an adsorption decreases the available cathodic sites for coating formation by acting as a barrier, thereby inhibiting the coating formation. Further increase in concentration of the amine additive in the bath results in an increase in coating weight up to a certain concentration. Since desorption would not occur under the experimental conditions used [136,137,139], the probable cause of the increase in coating weight is pre-micellar association of amine molecules [141]. However, beyond a certain concentration (specific to each amine additive), the coating weight decreased with increase in amine concentration. This is attributed to the aggregation of amine molecules to form micelles [140]. Micelles being large entities, they form a physical barrier [142] to the transport of tertiary zinc phosphate to the metal surface for deposition. The consequence of such an effect is a decrease in coating weight. Measurement of the amount of iron dissolved during phosphating with

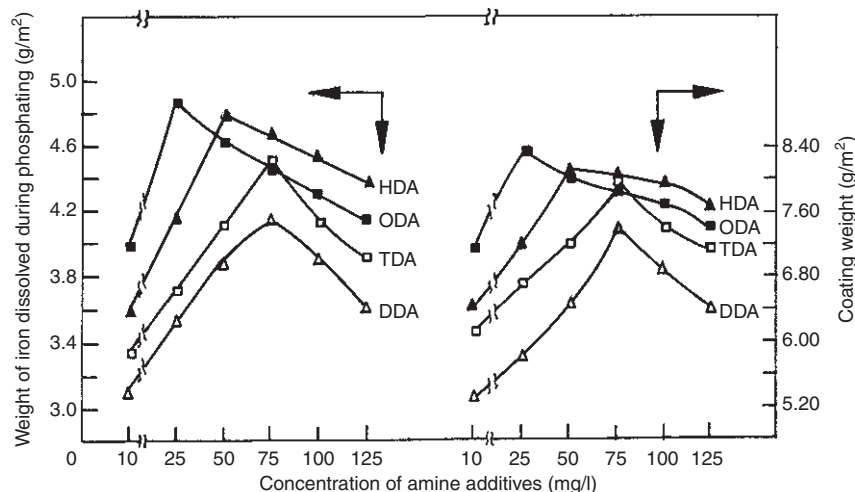


Figure 10.1 Comparison of the amount of iron dissolved during phosphating and the amount of coating formed as a function of concentration of long-chain amines.

long-chain amine concentrations (Figure 10.1) showed an identical trend (viz. an increase of coating weight with increase in metal dissolution) and strongly supports the above views. However, this attribute alone cannot account for the decrease in phosphate coating weight as these surfactant additives are also capable of adsorbing over the growing crystal faces and affecting the growth of the coating. In order to obtain a better insight into this phenomenon, the kinetics of the phosphating process were followed by studying the change in coating weight and open-circuit potential with time of deposition. Machu [126] described the use of potential–time measurements for monitoring phosphating process. Several researchers [143–151] have also adopted this technique to reveal the exact processes taking place in phosphate coating formation under different operating conditions.

The effect of time on coating weight for amine-containing baths in comparison with the standard bath is given in Figure 10.2. The decrease in coating weight in the initial period of processing (5 min) supports the view that these amines inhibit the process of metal dissolution and lengthen the induction period. This view is further supported by the rate of crystallization, which is calculated using the slope of the linear portion (first half of the crystallization period: 15 min) of each curve, and tabulated in Table 10.4 [152]. It is evident that DDA, having a greater number of adsorbable units compared with other long-chain amines, affects the rate of crystallization to a greater extent.

The potential–time behaviour recorded during phosphating for baths I–V at pH 2.70 is shown in Figure 10.3. The potential measured in the first min during coating formation in a phosphating bath having a considerable processing time (30 min in this case) is indicative of the nature of the metal surface undergoing corrosive attack

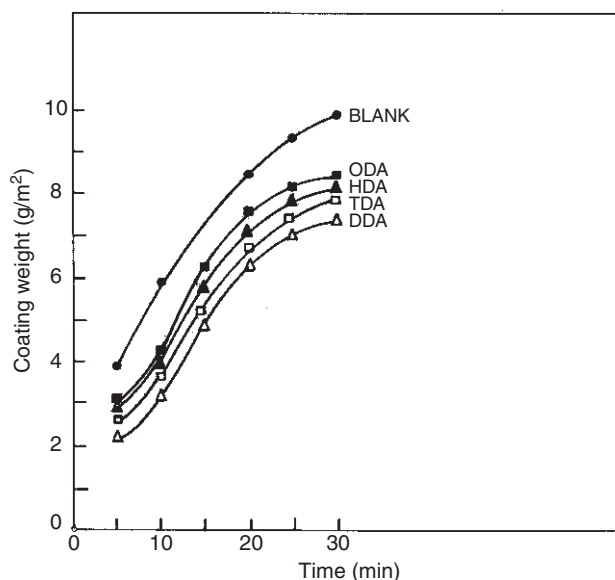


Figure 10.2 Effect of time on coating weight for baths I–V (source: *European Coatings Journal*, December 2001, pp. 39–44).

Table 10.4 Effect of long-chain amines on the rate of crystallization of zinc phosphate coating

Bath used	Rate of crystallization ($\text{gm}^{-2} \text{min}^{-1}$)	Ratio of rate of crystallization	Reduction in rate of crystallization (%)
Bath I	0.38	1.00	–
Bath II	0.25	0.66	34
Bath III	0.29	0.76	24
Bath IV	0.30	0.79	21
Bath V	0.33	0.87	13

by the free phosphoric acid present in the bath [145]. Addition of these long-chain amines was found to shift the measured potential in the first minute to a less negative value compared with the standard bath. The shift in potential towards less negative values is due to the adsorption of amines, which exist as onium cations in the bath solution, on the cathodic sites of the panel being coated.

The time at which saturation of metal dissolution occurs (the point at which ennobling of potential occurs) is a significant parameter in indicating the rate and the extent of coating formation in a phosphating bath [145]. Since in amine-containing baths part of the cathodic sites are covered by the adsorbed amine molecules, the number of available cathodic sites for hydrogen discharge is low. This leads to a decrease in the rate of metal dissolution, resulting in lengthening of the induction period and delayed attainment of the point of incipient precipitation (PIP)

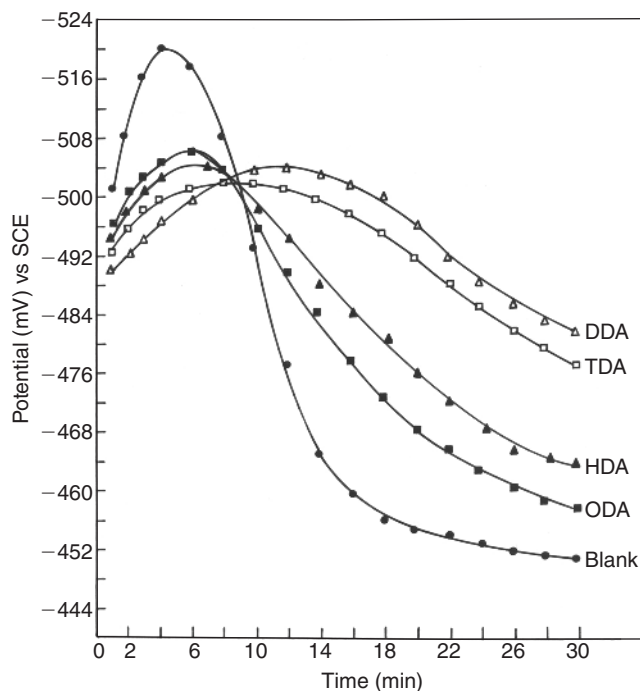


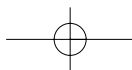
Figure 10.3 Potential–time curves recorded during phosphating for baths I–V at pH 2.70 (source: *European Coatings Journal*, December 2001, pp. 39–44).

in these baths compared with the standard bath. Among the homologous series of amines studied, the time of attainment of PIP decreased with increase in chain length. This is largely a consequence of the number of adsorbable units, which affects the metal dissolution and lengthens the induction period, which decreases with increase in chain length of these amines.

The potential near the coating completion time (30 min in this case) can qualitatively suggest the extent to which coating formation has occurred. When these long-chain amines are added to the phosphating bath, the potential measured at this stage is higher (more negative) than the blank, indicative of less coating formation [145] in the presence of amines. Among the series, the potential was found to be shift to more positive values with increase in chain length, which implies increased coating formation.

The difference in potential measured at the saturation of metal dissolution and that at the completion of coating (30 min in this case) usually gives a measure of the amount of coating formed. When amines are added to the phosphating bath, this change in potential decreased following the inhibiting action of these amines towards metal dissolution, thus leading to less coating formation under these conditions. Among the series, the extent of change in potential was maximum in the case of ODA.

The decrease in the initial potential, the increase in time of attainment of PIP, the decrease in final potential and the extent of change in potential strongly support the

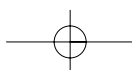
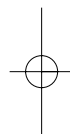
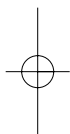


mechanism proposed to explain the role of long-chain amines in the phosphating bath and are in excellent agreement with the conclusions drawn from coating weight values.

The time lag that occurred during the initial periods of deposition (Figure 10.2) and for the ennoblement of the open-circuit potential (Figure 10.3) in the case of amine-containing baths indicates the influence of these additives on the nucleation of the phosphating process. The rate of crystallization is also affected by the presence of these amine additives (Table 10.4). Potential–time measurements also indicate that during coating formation the extent of change in potential (the difference in open-circuit potential measured at the point of ennoblement of potential and that measured at the 30th minute) is less in the case of amine-containing baths (Figure 10.3). If adsorption of surfactant additives on the metal surface and on the growing phosphate crystals is the only factor that is influencing the nucleation and growth of phosphate coating, then the curves obtained for long-chain amine-containing baths in Figures 10.2 and 10.3 should not vary much. However, although they look very similar in shape, they differ considerably among themselves. The inhibiting effect of long-chain amines on the metal dissolution reaction is mainly responsible for their behaviour during the nucleation stages. However, after the beginning of phosphate coating formation, it is believed that the surfactants mainly tend to alter the crystal habitus by virtue of their adsorption on the growing phosphate crystal faces. If this presumption is valid, then some other factor should also be responsible for the large decrease in the extent of change in potential observed in the case of amine-containing baths. In order to obtain a better insight into this phenomenon, the iron and zinc contents of phosphate coatings are determined after each 5 min of deposition for the entire duration of 30 min.

It is interesting that amine-containing baths fails to show a continuous increase in iron and zinc contents with deposition time rather a wavy pattern, contrary to the expectations (Figure 10.4a and 10.4b). Literature reports on the kinetics of phosphating reveal that such an occurrence is possible only under conditions where the phosphating process is extended beyond the coating completion time owing to the continuous dissolution and re-precipitation of the coating [1–7]. However, in amine-containing baths the variations in the iron and zinc contents occur much earlier than the coating completion time of 30 min. Decreases in zinc and iron contents during deposition might occur only due to the dissolution of the phosphate coating and such an occurrence is possible if the regenerated phosphoric acid is not consumed for further metal dissolution reaction. In amine-containing phosphating baths (baths II–V), desorption of adsorbed amine molecules is not expected to occur under the experimental conditions used. This might have necessitated the regenerated phosphoric acid to attack forcibly the phosphate coating that is already formed over the metal surface, since free metal sites are not available for reaction. Such a condition favours the continuous dissolution and re-precipitation of the phosphate coating and accounts for the observed variations in the iron and zinc contents of coatings obtained from baths II–V (Figure 10.4a and 10.4b).

It has already been established that the ratio between the formation and utilization of phosphoric acid regenerated during the phosphating reaction is very critical



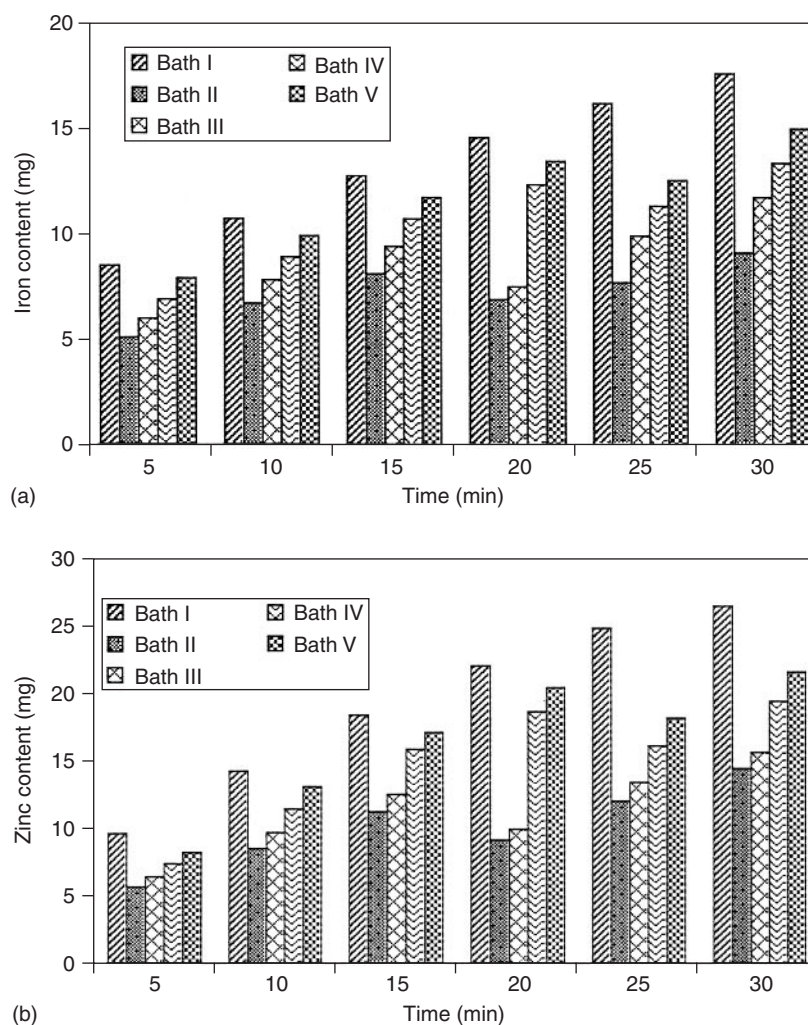
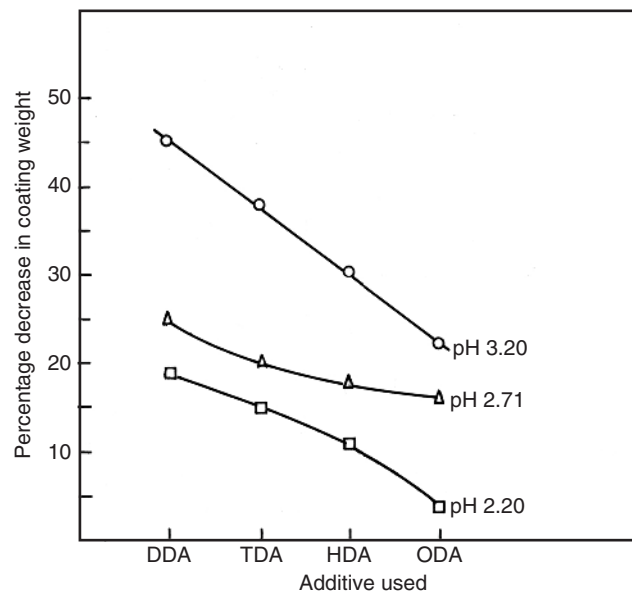


Figure 10.4 Variation of (a) iron and (b) zinc contents of phosphate coatings obtained from baths I–V with deposition time (source: *European Coatings Journal*, December 2001, pp. 39–44).

in phosphating baths that operate at low temperature (normally >1) [8]. Hence the observed variations in the iron and zinc contents caused by the regenerated phosphoric acid are understandable in the case of phosphate coatings obtained using baths II–V. To substantiate this view further, phosphating experiments were performed in which the pH of phosphating baths I–V (2.70) was altered to 2.20 and 3.20 with nitric acid and sodium hydroxide, respectively. The coating weight obtained from baths I–V at pH 2.20, 2.70 and 3.20 is given in Table 10.5. It is

Table 10.5 Effect of variation in pH of the phosphating bath on zinc phosphate coating weight

Bath used	Coating weight (gm^{-2})		
	pH 2.20	pH 2.70	pH 3.20
Bath I	8.50	9.92	14.68
Bath II	6.85	7.43	8.33
Bath III	7.26	7.94	9.78
Bath IV	7.60	8.10	10.12
Bath V	8.12	8.36	11.40

**Figure 10.5** Extent of decrease in phosphate coating weight obtained in the presence of long-chain amines as a function of pH of the phosphating bath (source: *European Coatings Journal*, December 2001, pp. 39–44).

evident that although the decrease in coating weight due to the presence of amine additives is prevalent at all pHs studied, the extent of the decrease in coating weight compared with bath I is higher in the case of panels phosphated at pH 3.20 (Figure 10.5). Similarly, the potential–time curves recorded during phosphating (Figures 10.3, 10.6 and 10.7) also exhibit a large decrease in the extent of metal dissolution and coating formation from baths II–V at pH 3.20. This cannot be attributed to the increased adsorption of surfactant additives with increase in pH, as the range of pH is too low. It is obvious that the rate of conversion of soluble primary phosphate to insoluble tertiary phosphate is relatively high at pH 3.20 compared with the rate of conversion at pH 2.70 and 2.20 [1–7]. This implies an increased availability of regenerated phosphoric acid at the metal solution interface at pH

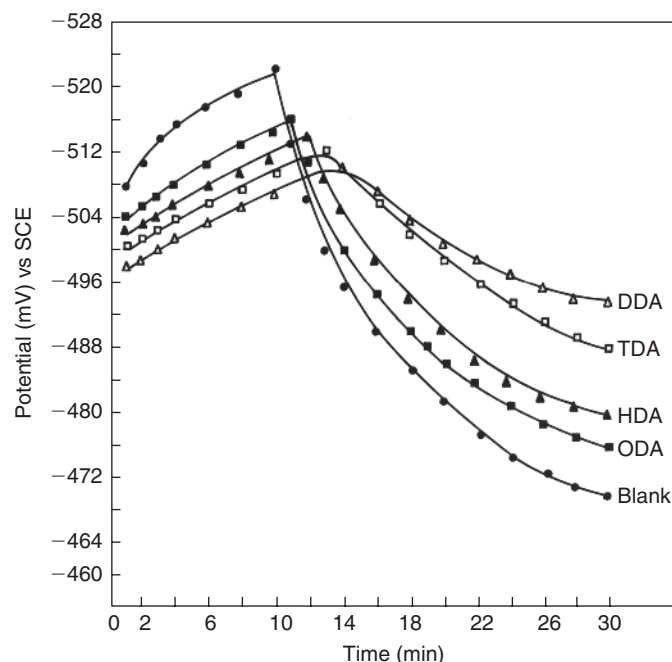


Figure 10.6 Potential–time curves recorded during phosphating for baths I–V at pH 2.20 (source: *European Coatings Journal*, December 2001, pp. 39–44).

3.20 and in the absence of available metal sites for reaction it implies a consequent attack on the phosphate coating that is already formed.

The possibility of an earlier attainment of the dissolution–re-precipitation stage in the case of amine-containing baths is likely to influence the surface morphology of the phosphate coating. Figure 10.8 shows the change in surface morphology of the phosphate coatings obtained from an additive-free bath and long-chain amine-containing baths. From the coating weight values, potential–time measurements and the kinetics of phosphating in the presence of long-chain amines, it is evident that these compounds have a major influence not only on the initial metal dissolution but also on the subsequent growth/deposition processes. The morphological changes that occur in presence of these compounds confirm such an influence on the initial nucleation and the subsequent growth stages. The additives adsorbed on the metal surface cause an initial decrease in potential, indicating an inhibition of metal dissolution, the basis of coating formation. Moreover, specific adsorption of these additives through coulombic and/or amphiphatic interactions causes contamination of the growing crystal faces. Such adsorption of the additives reduces the rate of transport of ions owing to their hydrophobic nature and the area of the exposed crystal. This causes a reduction in interfacial tension by these surface-active agents and prevents Ostwald ripening. The above phenomena will result in

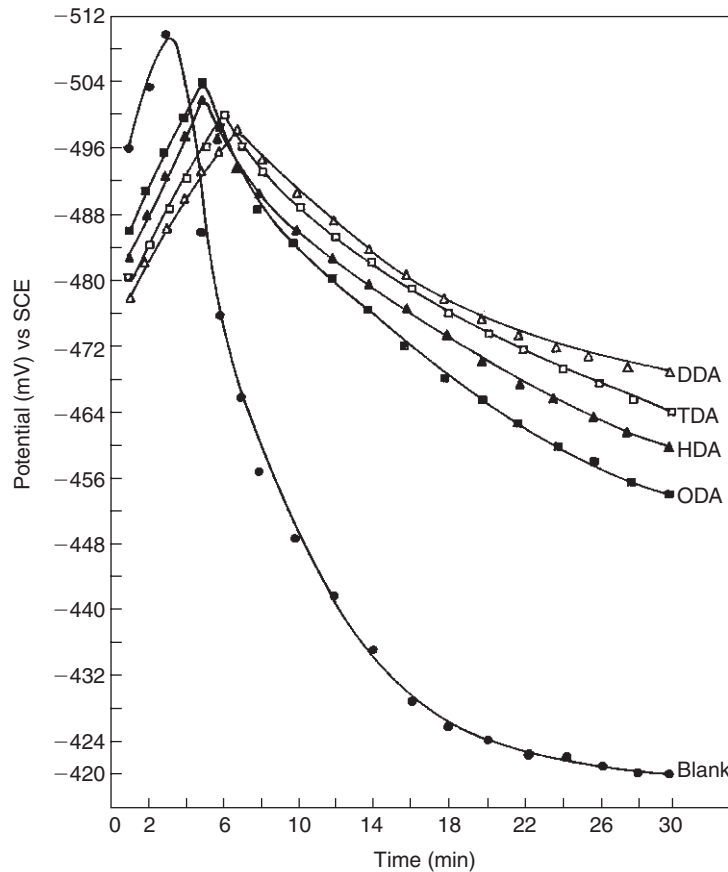


Figure 10.7 Potential-time curves recorded during phosphating for baths I-V at pH 3.20 (source: *European Coatings Journal*, December 2001, pp. 39-44).

the formation of a larger number of crystals of smaller size in the presence of these additives. The resultant surface morphologies confirm the above features. The refinement of phosphate crystals observed in the case of phosphate coatings obtained from surfactant modified baths (baths II-V) might have resulted either from the adsorption of surfactant additives on the growing crystal faces and/or the continuous dissolution and re-precipitation of the phosphate coating. To explain the role of surfactant additives on the kinetics of the phosphating process, a pictorial model is proposed (Figure 10.9).

Hence it is evident that surfactant additives play a crucial role in nucleation, growth, refinement of crystals and the continuous dissolution and re-precipitation of the phosphate coating. The influence of surfactant additives on the kinetics of the phosphating process indicates the need for a through understanding of the role of

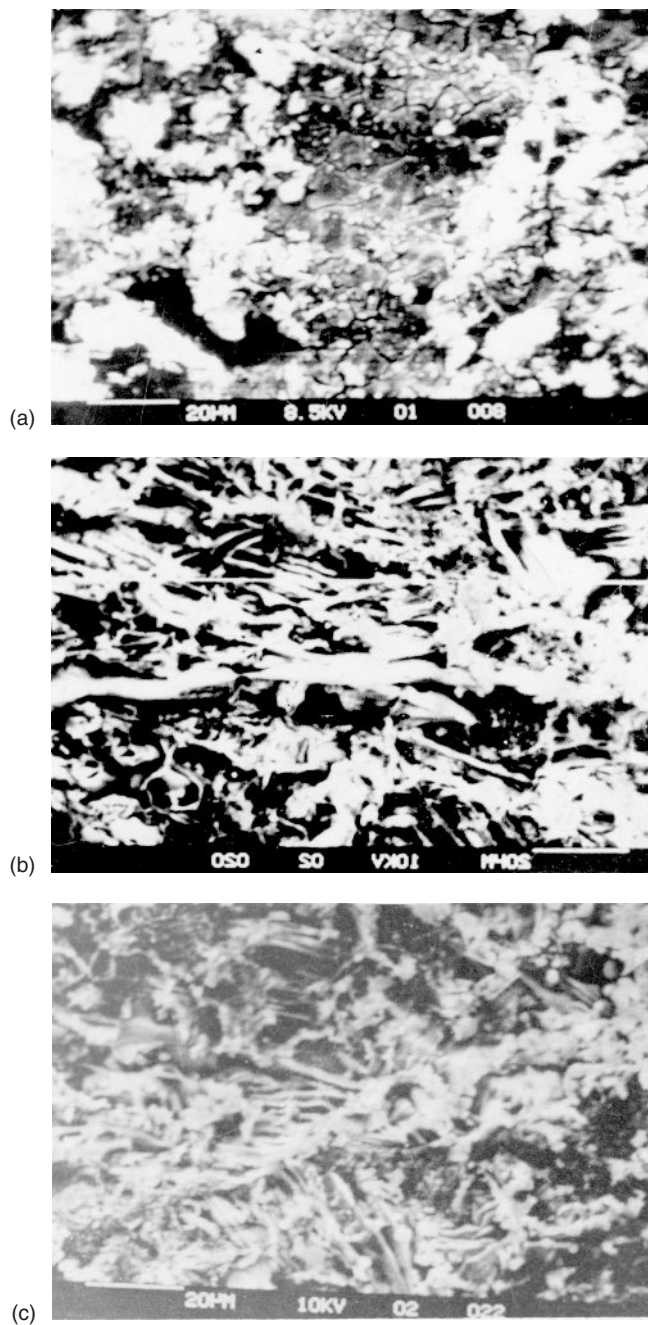
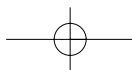
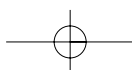
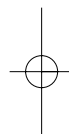
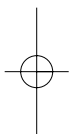


Figure 10.8 Surface morphology of the phosphate coatings obtained from baths (a) I, (b) II, (c) III, (d) IV and (e) V (reprinted with permission of Elsevier Science, Inc., New York).



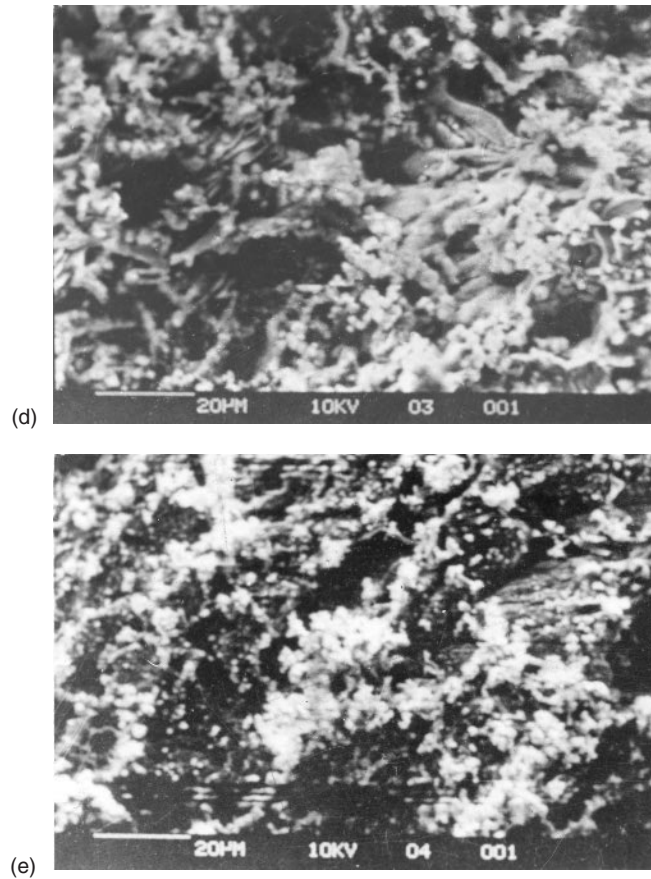
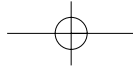


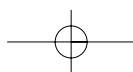
Figure 10.8 (continued)

surfactant additives often incorporated in phosphating baths so that the desirable qualities can be successfully built-in in the resultant phosphate coating.

In addition to their influence on nucleation, growth and crystal refinement, surfactant additives might also influence the properties and corrosion performance of the resultant phosphate coatings. To ascertain the nature of the influence of long-chain amines, the properties of the phosphate coatings, such as colour, appearance, uniformity, porosity, thermal and chemical stabilities, adhesion and corrosion performance, were evaluated.

10.5 Effect of long-chain amines on the properties of phosphate coatings

Zinc phosphate coatings obtained using an additive-free bath are grey, whereas the coatings obtained from long-chain amine-containing baths are greyish white.



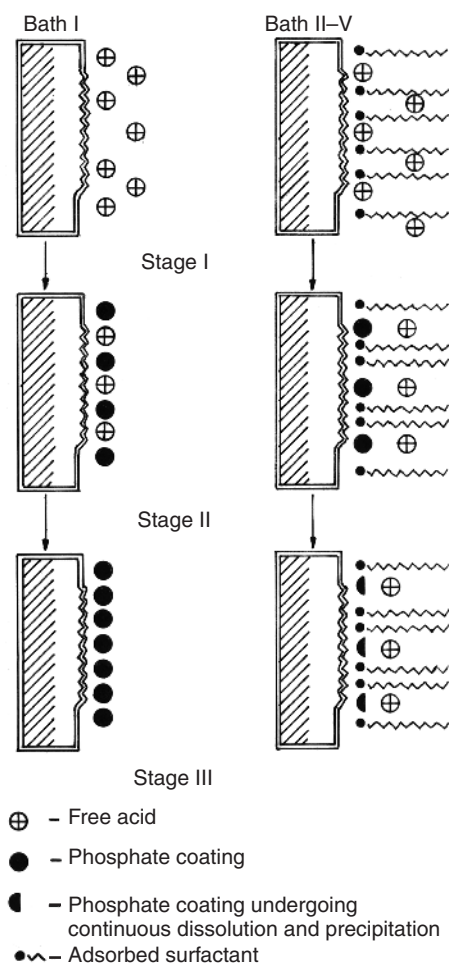


Figure 10.9 Pictorial model describing the influence of surfactant additives on the kinetics of the phosphating process (source: *European Coatings Journal*, December 2001, pp. 39–44).

However, the coatings are uniform irrespective of whether the bath contains surfactants or not. The porosity of the phosphate coatings assessed by the chemical method based on Prussian blue colour formation as a result of the interaction between the ferrous ions in the uncoated areas and the ferricyanide present in the test solution showed the appearance of not more than one blue spot per square centimetre in all cases (Table 10.6). However, the use of an electrochemical method, which measures the oxygen reduction current density (at -550 mV vs SCE) reveals that the panels coated using long-chain amines have a lower porosity value than those obtained from an additive-free bath (Figure 10.10).

Table 10.6 Effect of long-chain amines on the properties of zinc phosphate coatings

Bath used	Colour ^a	Uniformity ^a	Porosity ^b	<i>P</i> ratio ^c	Adhesion rating ^d
Bath I	Grey	Uniform	Slightly porous	0.48	3B
Bath II	Greyish white	Uniform	Relatively less porous	0.44	4B
Bath III	Greyish white	Uniform	Relatively less porous	0.45	4B
Bath IV	Greyish white	Uniform	Relatively less porous	0.46	4B
Bath V	Greyish white	Uniform	Relatively less porous	0.48	4B

^aBased on visual appearance.

^bBased on the oxygen reduction current density (current density at -550 mV vs SCE).

^cBased on the ration of intensities of the (100) plane of phosphophyllite and the (020) plane of hopeite.

^dAfter ASTM D 3359-87.

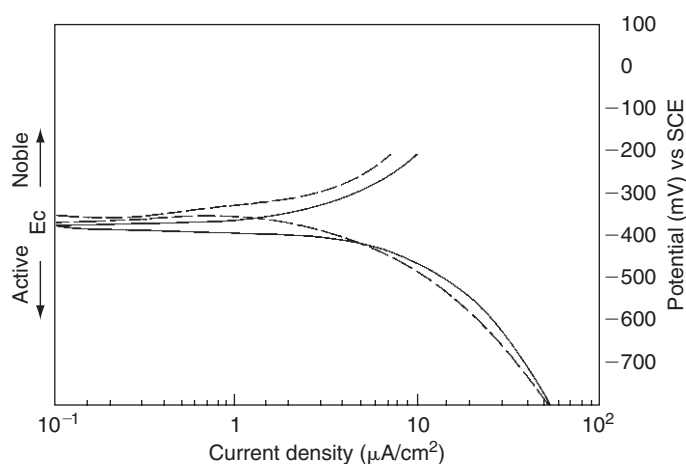


Figure 10.10 Cathodic polarization behaviour of panels phosphated using baths I and V in 0.01 N NaOH (reprinted with permission of Elsevier Science, Inc., New York).

The percentage weight loss obtained for panels coated using long-chain amines when subjected to heating at 120 and 180 °C for 30 min was found to be higher than those obtained for panels coated using an additive-free bath (Figure 10.11). The spontaneous decay of the open-circuit potential with time in borate buffer solution containing 0.01 M EDTA, which is a measure of the reactivation time of the coating, was found to be low for panels coated using long-chain amines (Figure 10.12). The percentage residual coating weight obtained after immersion treatments in solutions of varying pH in the acidic, neutral and alkaline ranges are relatively low for panels phosphated in the presence of long-chain amine additives (Figure 10.13). The percentage loss in weight obtained during thermal and chemical aggression suggests the formation of hopeite-rich coatings in the case of panels coated in the presence of long-chain amines, since the hopeite phase $[\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}]$ tends to lose four molecules of water of hydration when heated to 180 °C, whereas under

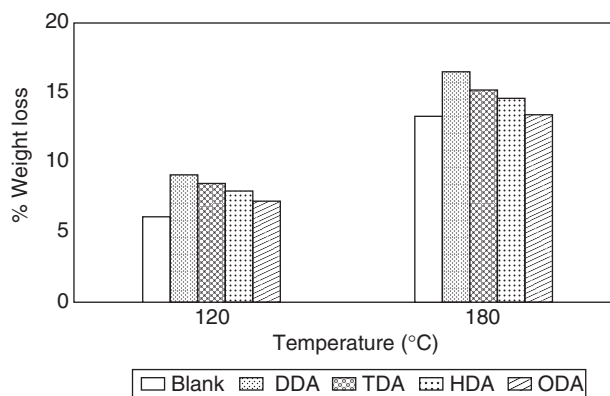
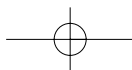


Figure 10.11 Thermal stability of panels phosphated using baths I–V when subjected to thermal treatment at 120 and 180 °C for 30 min (reprinted with permission of Elsevier Science, Inc., New York).

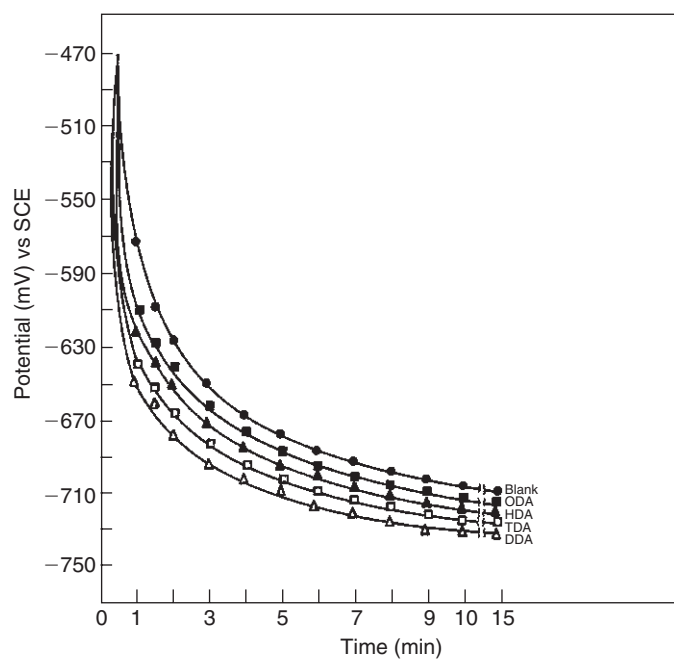
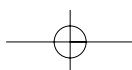


Figure 10.12 Spontaneous decay of open-circuit potential obtained for panels phosphated using baths I–V when subjected to immersion treatment in borate buffer solution containing 0.1 M EDTA.

similar conditions the phosphophyllite phase $[\text{Zn}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}]$ loses only two molecules of water of hydration and this phase possesses better alkaline stability than the hopeite phase [153]. The amount of iron dissolved during phosphating (Figure 10.1) strongly supports this view, whereas the lower values of the P ratio



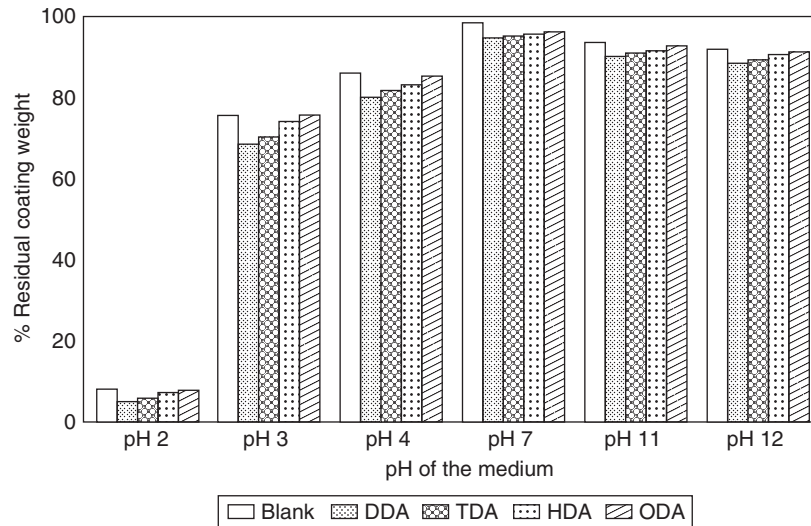


Figure 10.13 Chemical stability of panels phosphated using baths I–V when subjected to immersion treatment at various pHs for 30 min (reprinted with permission of Elsevier Science, Inc., New York).

(Table 10.6), which is the ratio of the intensity values of the (100) plane of phosphophyllite to that of the (020) plane of hopeite, confirms the formation of a hopeite-rich phase when the panels are coated in the presence of long-chain amines [154–156].

The absence of blister formation and the intactness of the coating with base metal resisting peel-off of the organic coating from a scribed region, after subjecting the phosphated and painted panels to immersion in deionized water at 45 °C for 240 h, indicates the lower permeability of water molecules due to the presence of the hydrophobic hydrocarbon chains in the long-chain amines (Table 10.6).

10.6 Effect of long-chain amines on the corrosion resistance of phosphate coatings

Visual observations made after 168 h of exposure at 100% relative humidity in a humidity chamber indicate that panels coated in presence of long-chain amines hardly exhibit any rust spots. This is due to the ability of these surfactant additives to prevent dragout and the presence of unwanted impurities after rinsing, which would otherwise promote corrosion when exposed to humid conditions.

The absence of rust spots on the panels and discoloration of the medium after 12 h of immersion in 3% sodium chloride solution indicate that panels coated in the presence of long-chain amines are more uniform and possess good corrosion-resistance property. The improvement in corrosion resistance is reflected in the weight loss values measured after 24 h of immersion (Table 10.7).

Table 10.7 Effect of long-chain amines on the corrosion resistance of zinc phosphate coatings

Bath used	Weight loss ^a (gm ⁻²)	Current density ^b (mAcm ⁻²)	E_{corr} (mV)	R_{ct} (Ω cm ²)	C_{dl} (Fcm ⁻²)
Bath I	13.12	1.5	-467	5000	2.02×10^{-7}
Bath II	12.35	1.2	-454	5200	1.93×10^{-7}
Bath III	12.09	1.1	-440	5400	1.86×10^{-7}
Bath IV	11.90	1.0	-426	5600	1.79×10^{-7}
Bath V	11.37	0.8	-412	5700	1.76×10^{-7}

^aLoss in weight after immersion in 3% NaCl solution for 24 h.

^bFrom polarization study using 0.6 M NH₄NO₃ solution.

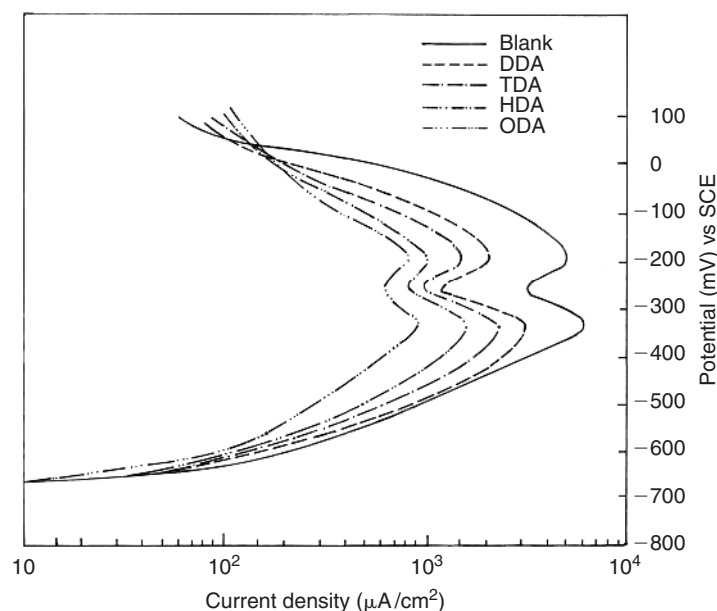


Figure 10.14 Anodic polarization behaviour of panels phosphated using baths I-V in 0.6 M NH₄NO₃ (reprinted with permission of Elsevier Science, Inc., New York).

The anodic polarization behaviour of phosphated steels in 0.6 M NH₄NO₃ solution presents an interesting feature of two current density maxima around -0.33 and -0.2 V vs SCE (Figure 10.14); the formation of a second current density maximum is specific to phosphated steel and is absent for unphosphated steel in the same environment [157]. Hence the current density values at the second maximum could be used to predict surface properties such as phosphate coating quality and crystal structure. The occurrence of two current density maxima is due to the competitive and potential-dependent adsorption of anions at the electrode surface. At potentials more negative than -0.33 V, phosphated steel undergoes active dissolution. Above -0.33 V, the first passive region occurs due to the adsorption of hydrox-

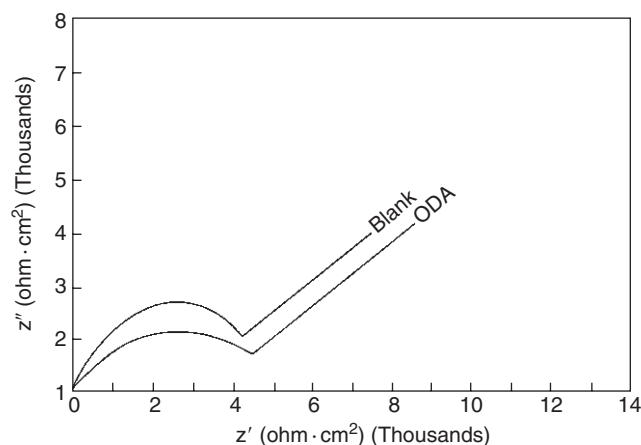


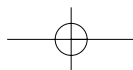
Figure 10.15 Nyquist plot of panels phosphated using baths I and V in 3% NaCl (reprinted with permission of Elsevier Science, Inc., New York).

ide ions at the electrode surface. The occurrence of a second active region is ascribed to the replacement of hydroxide ions by phosphate ions available at the electrode/solution interface. Replacement of these adsorbed phosphate ions by nitrate ions causes the occurrence of the second passive region. Although all these reactions occur in all the cases, the value of the second current density maximum differs in each case. Since its value depends on the availability of phosphate ions, which can accelerate the corrosion of steel over a particular potential range, the low value obtained for the panels coated using long-chain amine-containing baths implies a lower availability of phosphate ions and indicates better corrosion performance (Table 10.7) [158].

Figure 10.15 shows the Nyquist plots obtained for panels phosphated using the standard bath and a bath containing ODA in 3% sodium chloride solution at open-circuit potential. Both curves appear to be similar, with a semicircle in the high-frequency region followed by a linear portion in the low-frequency region; however, they differ in size. This indicates that the same fundamental process is occurring in both cases but over a different area [159–161]. The appearance of the linear portion in the low-frequency region suggests that the corrosion of phosphated steel is a diffusion-controlled process [162,163]. The values of the corrosion potential (E_{corr}), charge transfer resistance (R_{ct}) and double-layer capacitance (C_{dl}) obtained for panels coated with and without long-chain amines are given in Table 10.7, where it is evident that compared with the standard bath, panels coated in the presence of long-chain amines possess improved corrosion resistance.

10.7 Conclusion

Surface-active agents occupy a predominant role in the metal finishing industry. Being capable of reducing the surface tension and improving the wettability of the



surface, the importance of such additives is well realized and phosphating baths have been developed with surfactants as one of the additives. However, surfactant additives can influence the nucleation and growth of phosphate crystals and alter the kinetics of the phosphating process. The addition of surfactants to phosphating baths is beneficial in obtaining the desired orientation of the phosphate crystal and the crystallites of the base metal, leading to improved adherence and excellent corrosion resistance of the resultant phosphate coating. The influence of surfactant additives on the nucleation, growth and refinement of crystals and the continuous dissolution and re-precipitation of the phosphate coating calls for a thorough understanding of the role of surfactant additives often incorporated in phosphating baths so that the desirable qualities can be successfully built-in in the resultant phosphate coating.

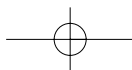
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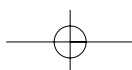
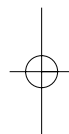
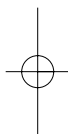
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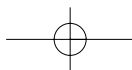
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