

# SURFACE PRETREATMENT BY PHOSPHATE CONVERSION COATINGS – A REVIEW

T.S.N. Sankara Narayanan

National Metallurgical Laboratory, Madras Centre CSIR, Complex, Taramani, Chennai-600 113, India

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**Abstract.** Phosphating is the most widely used metal pretreatment process for the surface treatment and finishing of ferrous and non-ferrous metals. Due to its economy, speed of operation and ability to afford excellent corrosion resistance, wear resistance, adhesion and lubricative properties, it plays a significant role in the automobile, process and appliance industries. Though the process was initially developed as a simple method of preventing corrosion, the changing end uses of phosphated articles have forced the modification of the existing processes and development of innovative methods to substitute the conventional ones. To keep pace with the rapid changing need of the finishing systems, numerous modifications have been put forth in their development - both in the processing sequence as well as in the phosphating formulations. This review addresses the various aspects of phosphating in detail. In spite of the numerous modifications put forth on the deposition technologies to achieve different types of coatings and desirable properties such as improved corrosion resistance, wear resistance, etc., phosphate conversion coating still plays a vital part in the automobile, process and appliance industries.

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Corresponding author: T.S.N. Sankara Narayanan, e-mail: [tsnsn@rediffmail.com](mailto:tsnsn@rediffmail.com)

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## 1. INTRODUCTION

Metals have been the backbone of civilization. Efforts have been spared to find alternatives and replacements for metals but these still play a major role in the manufacture and construction and are likely to do so for many more years. This is due to the combination of several useful properties like strength, workability, low-cost and ability to be recycled, that the metals possess. However, metals which are extracted from their ores by chemical or electrochemical means show a strong tendency to revert to their oxide form at the first available opportunity, i.e., they tend to corrode [1-4] and as a result they create a tremendous economic loss besides posing a serious threat to the national resources of a country.

The methods of corrosion prevention are many and varied. These methods may be generally classified [3] as:

- Modification of the metal by alloying and/or surface modification;
- Modification of the environment by the use of inhibitors; and
- Change of metal/environment potential by cathodic or anodic protection.

The most commonly used method of corrosion protection involves bulk alloying or surface modification. Surface modification is however, far more economical than bulk alloying and is more widely practiced. The methods generally used for surface modification involve the formation of a physical barrier to protect the metal against its corrosive environment [5]. This can be achieved by relatively more modern methods such as: (i) physical vapour deposition (PVD); (ii) chemical vapour deposition (CVD);

(iii) ion implantation; (iv) laser treatment; (v) deposition by thermal spray, plasma spray and arc methods; (vi) nitriding; (vii) carbiding; *etc.*, or through more conventional techniques such as: (i) painting; (ii) anodizing; and (iii) chemical conversion coatings. While the former methods are usually less economic as they involve the use of sophisticated application techniques and are meant for specialized applications, the latter methods are more cost-effective and have a wider spectrum of end applications.

## 2. CHEMICAL CONVERSION COATINGS

Chemical conversion coatings are adherent, insoluble, inorganic crystalline or amorphous surface films, formed as an integral part of the metal surface by means of a non-electrolytic chemical reaction between the metal surface and the dipped in solution [6]. In such coatings, a portion of the base metal is converted into one of the components of the resultant protective film, which is much less reactive to subsequent corrosion than the original metal surface. This film imparts an equal potential to the metal surface, neutralizing the potential of the local anodic and cathodic galvanic corrosion sites [7]. They also serve as absorptive bases for improving the adhesion to paints and other organic finishes. Chemical conversion coatings are preferred because of their adherent nature and high speed of coating formation besides being economical. Further these can be formed using simple equipment and without the application of any external potential. Chemical conversion coating processes are classified as phosphating, chromating and oxalating according to their essential constituents viz., phosphates, chromates, and oxalates respectively [8]. The present review focuses on phosphate conversion coatings with a special emphasize on zinc phosphate coatings on mild steel.

## 3. PHOSPHATING

Phosphating process can be defined as the treatment of a metal surface so as to give 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 [9]. 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.

**Table 1.** Historical development of the phosphating process.

Sl. No.	Year/ Period	Advancement made/process developed	References
1.	1906	Phosphating of iron and steel using phosphoric acid and iron filings	11
2.	1908	Treatment of phosphate coatings with oxidizing agents to reduce process time	12
3.	1909	Regeneration of the bath and formulation of zinc phosphate baths requiring high temperature – process time of one hour	13,14
4.	1911	Formulation of manganese phosphate bath requiring high temperature - process time of 2-2.5 hours	15
5.	1914	Parkerising process with maintenance of total acid to free acid ratio	16,17
6.	1928	Recognition of phosphate coating as paint base	18,19
7.	1929	Bonderizing process with the addition of Copper accelerator-coating time: 10 minutes to 1 hour	20
8.	1933	Use of oxidizing agents like nitrate for acceleration – coating time: 5 minutes	21
9.	1934	Use of phosphate coating for cold working operations for metals	22
10.	1937	Spray phosphating – phosphating time: 60-90 seconds	23
11.	1940	Development of non-coating phosphate process based on sodium or ammonium phosphates	24
12.	1940	Development of cold phosphating methods	25
13.	1941	Phosphating of aluminium surfaces using zinc phosphate and fluorides	26
14.	1943	Use of disodium phosphate containing titanium as pre-dip before phosphating	27
15.	1950's	Large scale application of manganese phosphate coatings as an oil retaining medium – for use on bearing or sliding surfaces etc.	28
16.	1960's	Use of special additives to control coating weight	29
17.	1960's	Spray process at operating temperature of 25-30 °C	18,19
18.	1970's	Improvement in coating quality, use of spray cleaners based on surfactant technology	18,19

### 3.1. History and development of the phosphating process

The use of phosphate coatings for protecting steel surfaces has been known since the turn of the century and during this period the greater part of the World's production of cars, refrigerators and furniture were treated this way. The first reliable record of phosphate coatings applied to prevent rusting of iron and steel is a British patent of 1869 granted to Ross [10]. In the method used by him, red hot iron articles were plunged into the phosphoric acid to prevent them from rusting. Since then numerous developments have taken place, of which the major developments are listed in Table 1.

During the last 30 years, work has been concentrated mainly on improvements in quality, particularly to keep in pace with the recent changing needs of the organic finishing systems. Prominent among these are: (i) use of low temperature phosphating baths to overcome the energy crisis [30-32]; (ii) use of low zinc technology [18,19]; (iii) use of special additives in the phosphating bath [33-42]; (iv) use of more than one heavy metal ions in existing composition-particularly tri-cation phosphating [43]; *etc.* New types of phosphate coatings such as tin, nickel and lead phosphate coatings have been introduced [44,45] besides the development of compositions for simultaneous phosphating of multiple metal substrates [46,47]. There has been a grow-

**Table 2.** Special additives used in phosphating baths.

Sl. No.	Additive used	Purpose	Impact	References
1.	$\alpha$ -hydroxy carboxylic acids like tartaric and citric acids, tripolyphosphate, sodium, potassium tartrate, nitrobenzene sulphonate	To reduce the coating weight	Improve bath life through lesser consumption of chemicals	49-54
2.	Chelants such as EDTA, NTA, DTPA gluconic acids and polycarboxy o-amino acids.	To increase the coating weight	Improved corrosion protection, shorter processing times.	42, 43 55-58
3.	Quaternary ammonium compounds, N and P compound containing amido or amino group. Calcium, Formic acid ester, chelate of an acidic organic phosphate	Grain refinement	Better adhesion of subsequent finishes; better corrosion protection.	59-63
4.	Nickel (II)	To improve surface texture	Better adhesion of subsequent finishes; better corrosion protection.	64, 65
5.	Lead compounds, tungstate ions, gaseous nitrogen peroxide, hydroxylamine sulphate, hexamine	To accelerate the phosphating process	Reduction in processing time	66-69
6.	Persulphate and permonosulphuric 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	70
7.	Cyclic trimetaphosphate	To reduce the operating temperature To increase the tolerance to dissolved iron	Thinner, smoother and improved corrosion resistant coating	71
8.	Lauric, Palmitic, and Stearic acids with fatty amines and ethoxylated amines	To improve lubricant properties	Improved workability of the metal	72
9.	Carbohydrates, dialkyl-triaminepentakis methylene phosphonic acid and its salts and fluoborate or fluosilicate	To decrease scaling	Improve the service life of heating coils and provide uniform heating of the bath	73-75
10.	Phosphonic acid ester, Magnesium or zinc nitrate	To prevent the build up of sludge on tank walls	Improved service life of the equipment	76, 77
11.	Amines, Tin (IV), Arsenic compounds, zinc salt of an organic N-compound	As inhibitors	Improves corrosion resistance	78, 79
12.	Zinc carbonate	To reduce the acidity of the bath and to maintain the equilibrium	Consistent performance of the bath	80

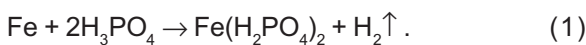
**Table 2.** Continued.

13.	Thiourea	Stabilizer in non-aqueous phosphating solutions, as inhibitors	Improved stability of the bath	81
14	Sodium lignosulphonate	To modify the physical form of sludge	Reduce the tendency to form a crust on heat transfer surfaces Improves process efficiency	82, 83
15	Methylaminoethoxysilane	To prevent rehydration of phosphate dihydrate	Impart hydrophobic and anti-corrosion properties	84
16	Hexametaphosphate	To decrease the surface roughness and increase the extent of absorption of sodium stearate	Enables deep drawing of tubes (~50% length) with reduction in wall thickness	85

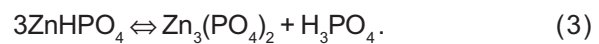
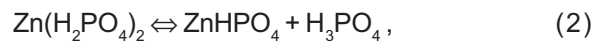
ing use of substitutes to conventional Cr(VI) post-rinses [48] to suit the regulations imposed by the pollution control authorities on the use of Cr(VI) compounds. The special additives used in phosphating baths is compiled in Table 2 and the alternatives to Cr(VI) post-rinse treatment is given in Table 3.

### 3.2. 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 [18,19,24,127,128]. 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 [18,19,24,127,128]. 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, more amount of phosphoric acid is needed for the baths operating at higher temperatures. In contrast, in the case of phosphating baths operated at room temperature, the possibility of the increase in acidity during continuous operation is more likely [129,130] and is normally neutralised by the addition of the carbonate of the metal which forms the coating ( $\text{Zn}(\text{CO}_3)_2$  in 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. Too much of phosphoric acid not only delays the formation of the coating, but also leads to excessive metal loss.

### 3.3. Acceleration of the phosphating process

In practice, phosphating reaction tends to be slow owing to the polarization caused by the hydrogen evolved in the cathodic reaction. In order to achieve coating formation in a practicable time, some mode of acceleration must be employed. The importance of the acceleration of the phosphating process was

**Table 3.** Alternatives to Cr(VI) post treatment.

Sl.No.	Type of compounds	Compound used	Reference
1.	Chromium containing substitutes	a. 0.001% Cr(III) as Cr- chromate complex	86, 87
		b. CrO <sub>3</sub> solution reduced by HCHO	88
		c. Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> as complex of divalent metal	89
		d. Chromate and colloidal silicic acid	90
		e. Aqueous solution of Aluminium chromate polymer	91, 92
		f. Trivalent chromium and ferricyanide	93
2.	Phosphonic acid derivatives	a. Alkane phosphonic acids	94, 95
		b. Alkene phosphonic acids	96, 97
		c. Polyvinyl phosphonic acids	98
3.	Ammonium phosphate derivatives	a. Dilute solution of ammonium primary phosphate and/or trietha nolamine ydrogen phosphate	99, 100
4.	Carboxylic acids	a. Citric, glutaric, maleic, succinic and phthalic acids	101
		b. Citrate in combination with nitrite	102, 103
5.	Oxidizing agents	a. Peroxides and persulphates	104
		b. Potassium permanganate	105
6.	Polymers	a. Modified hydroxystyrene	106
		b. Melamine-formaldehyde	107
7.	Tannins	a. Tannin + thiourea compound	108
		b. Tannin + melamine – formaldehyde	109
8.	Tin salts	Aqueous stannous salt solution containing Mn, Pb, Cd, Co and Ni	110-113
9.	Zirconium and Titanium compounds	a. Ti (III) in acid solution	114, 115
		b. Zr or Ti with an inositol phosphate ester	116
		c. Zr + myo-inositol phosphate and/or its salt	117
10.	Molybdenum type rinses	a. Dilute aqueous solution of MoO <sub>2</sub> in HNO <sub>3</sub>	118
11.	Hypophosphorus acid and hypophosphite	a. Hypophosphorus acid + Hydrofluorosilicic acid	119
		b. Sodium hypophosphite + Hydrofluorosilicic acid	
12.	Mixture of organo-phosphates or phosphonates and fluoride	a. Carboxyethylene phosphonic acid esters of butyl diglycidyl ether and bisphenol + fluorosilicic acid	120
13.	Mixture of Zr, V, F and phosphate ions	a. Hydrofluorozirconic acid + fluoroboric acid + Phosphoric acid + amm. metavanadate	121
14.	Mixture of Li, Cu and Ag ions	a. Nitrate (or) carboxylate (or) acetates of Li, Cu and Ag	122, 123
15.	Mixture of Ti, V, Mo, Ag, Sn, Sb + cathodic treatment at 0.1 to 10 A/dm <sup>2</sup>	a. As nitrates, sulphates (or) chloride	124
		b. Salt of hydroxycarboxylic acid	
16.	Tetravalent Ti (or) Divalent Mn, Co, Ni or Cu	a. Titanyl acetylacetonate	125
		b. Divalent manganese/cobalt/nickel/copper/ethanote	
		c. Divalent	
17.	Ni + Co + Sn + Pb	a. As acetates + Pb sheets + stannous chloride	126

felt way back in the 19th century and its development has gained a rapid momentum with the advent of the Bonderite process in 1929. Recently, Sankara Narayanan *et al.* [131] have made an overview on the acceleration of the phosphating process and justified its role on the hunting demand to reduce process time. The different means of accelerating the formation of phosphate coatings can be broadly classified as: (i) Chemical acceleration; (ii) Mechanical acceleration; and (iii) Electrochemical acceleration.

### 3.3.1. Chemical acceleration

Oxidizing substances [132,133] and metals more noble than iron such as, Cu, Ni, [19] etc., constitute the most important class of chemical accelerators. They accelerate the deposition process through different mechanisms. Oxidizing agents depolarize the cathode half-cell reaction by preventing the accumulation of hydrogen at the cathodic sites, whereas noble metal ions promote metal dissolution by providing low over-potential cathode sites by their deposition [134]. Since acceleration through depolarization is preferred to mere promotion of metal dissolution, oxidizing agents have found widespread use than metals. Moreover, they prevent the excessive build up of iron in the bath, which can be detrimental to good coating formation [25]. The most commonly employed oxidizing accelerators are nitrites, chlorates, nitrates, peroxides and organic nitro compounds either alone or in various combinations. Common combinations are nitrite-nitrate, nitrite-chlorate-nitrate and chlorate-nitrobenzene sulphonic acid. The characteristics of some of the commonly used oxidizing accelerators are given in Table 4. Some reducing agents such as alkali metal sulphites [135], hypophosphites [136], phosphites [137], formaldehyde, benzaldehyde, hydroxylamine [138], acetaldehyde oxime [139], Pyridine N-oxime [140], morpholine N-oxime [140], quinones [141], etc., have also been tried as accelerators but have not been as successful as oxidizing accelerators from the industrial point of view.

### 3.3.2. Mechanical acceleration

When a phosphating solution is sprayed forcibly on to a metal surface, coatings are formed more readily than would be by immersion in the same solution, since the former process eliminates the delay due to the diffusion of the constituents in the solution to the metal surface. The comparative kinetics of spray and dip phosphating was determined by Laukonis

[142]. The resultant coatings are thin, fine-crystalline and perfectly suitable as a paint base. Other means of physical acceleration are the action of brushes and rollers [143] on the surface during processing.

### 3.3.3. Electrochemical acceleration

Several electrochemical methods of acceleration, both anodic, cathodic and pulse method have been described in literature [144-161]. Coslett recognized acceleration of the phosphating process by cathodic treatment as early as 1909 by Coslett [144]. Subsequent studies reveal that anodic methods are more appropriate and advantageous than the cathodic methods, as they promote metal dissolution as well as passivity. Zantout and Gabe [148] claim to have achieved higher coating weights of low porosity in a shorter treatment time by the application of a small current. Ravichandran *et al.*, [157-159] established the utility of galvanic coupling of steel substrate with metals which are more noble than steel for accelerating phosphating processes. This methodology employs the galvanic corrosion principle for accelerating the metal dissolution reaction, which enables a quicker consumption of free phosphoric acid and an earlier attainment of the point of incipient precipitation, resulting in higher amount of phosphate coating formation. The application of a cathodic current to form phosphate coating on stainless steel using a calcium modified zinc phosphating bath was patented by Bjerrum *et al.* [160]. Sinha and Feser [161] have also studied the formation of phosphate coating on steel and stainless steel substrates by this method.

These three methods of acceleration described above are widely practiced in industries; but each of them has its own merits and demerits. Though chemical accelerators (Primarily those of the oxidizing type) accelerate the phosphating process by their mere addition, their concentration in the bath is very critical to yield the desired results. Acceleration by mechanical means is limited to spray processes, which are capable of providing fresh bath solution constantly. Electrochemical methods of acceleration though capable of yielding higher deposition rate, the practical difficulty in adding 'electrics' to the processing stage makes it less popular.

**Table 4.** Different types of accelerators used in phosphating.

Type of accelerator	Example	Effective concentration	Advantages	Disadvantages
$\text{NO}_3^-$	$\text{NaNO}_3$ $\text{Zn}(\text{NO}_3)_2$ $\text{Ni}(\text{NO}_3)_2$	1-3%	Lower sludge	Reduction of $\text{FePO}_4$ increases the iron content of the coating
$\text{NO}_2^-$	$\text{NaNO}_2$	0.1-0.2 g/l	Affords rapid processing even at low temperatures	Corrosive fumes. Highly unstable at high bath temperatures. Frequent addition is required.
$\text{ClO}_3^-$	$\text{Zn}(\text{ClO}_3)_2$	0.5 - 1%	Stable in liquid concentrates. Can be used for bath make-up and replenishment. Overcomes the white staining problem.	Corrosive nature of chlorate and its reduction products. High concentrations poison the bath. Removal of gelatinous precipitate from the resultant phosphate coatings is difficult.
$\text{H}_2\text{O}_2$	$\text{H}_2\text{O}_2$	0.05 g/l (liquid)	Low coating weight. No harmful products. Free from staining	Bath control tends to be critical. Heavy sludge formation. Limited stability. Continuous addition is required.
Perborate	Sodium perborate	–	No separate neutraliser is required. Good corrosion resistance	Continuous addition is required. Voluminous sludge.
Nitroguanidine	Nitroguanidine	–	Neither the accelerator nor its reduction products are corrosive.	Slightly soluble. No control for build-up of ferrous iron in the bath. Highly expensive.
Oxime	Acetaldehyde oxime	1-5 g/l	Stable in acidic environment Environmentally acceptable	–
Organic N-oxide	Pyridine N-oxide Morpholine N-oxide	0.3-2 g/l	–	Need to use highly concentrated activating solution before phosphating
Hydroxylamine	Hydroxylamine Hydroxylamine sulphate	0.5-5 g/l	Spherical and/or columnar phosphate crystal Does not decompose on its own	Decomposes in presence of Cu or $\text{H}_2\text{O}_2$ in the bath
Quinones	Benzoquinone Chloranil	–	Solubility of Quinone	High concentration causes a wavy pattern. Lower concentration not effective in acceleration
Amido sulphonic acid and their N-substituted derivatives	Benzoicacid sulphamide Benzenesulphoanilide N-cyclohexyl sulphamic acid	0.1-6 g/l	Immediate operation of the bath Fine grained coating Improved lacquer adhesion and corrosion resistance. Sludge formation is suppressed	Effectiveness is impaired in presence of Ca ions in the bath
Alkali metal bromate + Aromatic	Sodium bromate + nitrocompound m-nitro benzene-sulphonate	0.8-1.1 + 0.25-0.5 g/l	Fine grained coating Improved adhesion and corrosion resistance	–



### 3.4. Kinetics of the phosphating process

Kinetics of the phosphating process reveals the steps involved in the course of phosphating and their rates. Three different methods have been used so far for investigating the kinetics of formation of phosphate coatings namely: (i) the gravimetric method, by the quantitative determination of the quantity of phosphate deposited per unit time; (ii) the electrochemical method based on the determination of free, reactive uncoated areas through electrochemical passivation; and (iii) the radiographic method based on the determination of the intensity of the characteristic X-ray of the resulting compound.

All the three methods gave a similar picture of the phosphating process that showed the coating formation did not take place in a linear fashion, rather it was initially very fast, after which the rate slowly decreased with time.

Studies on the kinetics of phosphating indicate that there are four distinct stages in coating formation (Fig. 1), namely, the induction stage ( $\alpha$ ), the commencement of film growth ( $\beta$ ), the main exponential growth stage ( $\gamma$ ) and the stage of linear increase in film growth ( $\delta$ ). During the induction period, the oxide film remaining on the surface even after cleaning is removed. When film growth commences, the first nuclei are formed and the rate of nucleation increases rapidly with time. This, however, depends considerably on the conditions of the surface, the pretreatment procedures adopted and the oxidizing agents present in the phosphating bath. Growth occurs in the main exponential growth stage. Addition of accelerators reduces the induction period and extends the stage of linear growth.

In the opinion of Gebhardt [162], the rate of phosphating depends on the rate of diffusion of  $\text{Fe}^{2+}$  ions from the structural lattice to the coating/solution interface through the coating formed. Machu [25] has found that the rate of the phosphating reaction is a function of microanodes on the surface.

$$-dF_A/dt = K \cdot F_A \cdot dt$$

where  $dt$  – change in time;  $F_A$  – surface area of anodes in microcells; and  $K$  – reaction rate constant.

The rate of formation of the phosphate coating depends primarily upon the metal viz., the ratio of anode surface which was initially present,  $F_{A0}$ , to the anode surface at any given moment,  $F_A$ . The influence of various other factors controlling the rate of reaction, e.g., temperature, surface condition etc., is reflected in the value of the rate constant  $K$ , which is different for different processes.

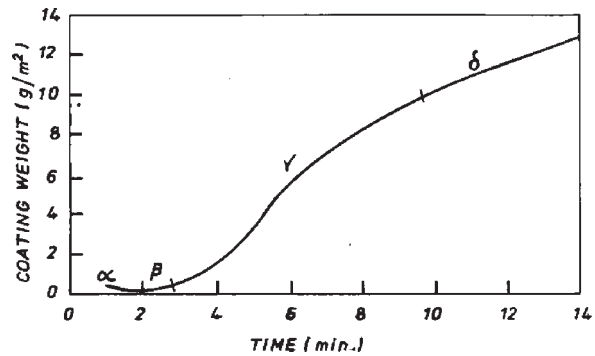


Fig. 1. The various stages in the growth of phosphate coating (in presence of accelerator).

The overall coating growth process can be followed by potential-time curves (Fig. 2), which indicate the different stages of coating besides indicating when the effective phosphating has ceased. Correlation of potential-time relationships with film properties leads to the conclusion that coating formation proceeds through the following stages:

- electrochemical attack of steel;
- amorphous precipitation;
- dissolution of the base metal;
- crystallization and growth; and
- crystal reorganization.

But, in actual practice, it is difficult to identify the 'b' and 'c' stages, and the curve mainly exhibits the process of metal dissolution, coating formation and coating completion. The use of potential-time measurements for monitoring the phosphating process was first described by Machu [25]. It has also been used by several workers to reveal the nature of the

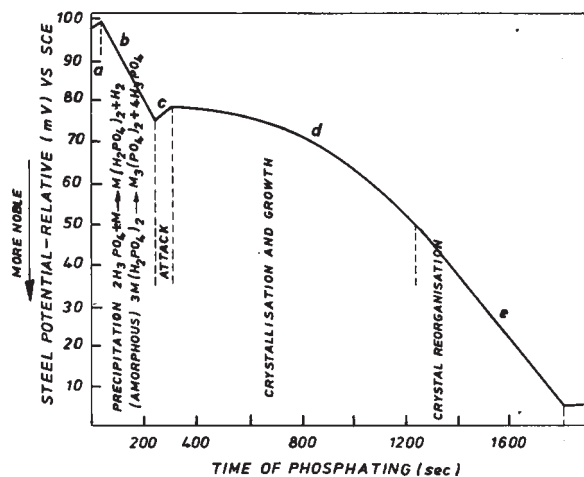


Fig. 2. Potential-time curve showing the various steps of phosphating.

process taking place during phosphating [145] and the properties of the coating formed [163]. Sankara Narayanan *et al.* [164,165] have discussed the usefulness of the potential-time curves in predicting the kinetics of the phosphating process. The utility of potential-time measurement for effective on-line monitoring of the phosphating process is also established [166,167]. The correlation between coating weight and potential time measurements is established by Sankara Narayanan [168-170], which enables calculation of crystallization kinetics from potential time measurement.

### 3.5. Process details

In general, phosphating sequence comprises of seven operations, as indicated in the flow chart. However, depending upon the surface conditions of the base metal, some of these operations may be omitted or additional operations may be incorporated into the system. A typical seven-stage sequence of phosphate pretreatment process is given in Fig. 3.

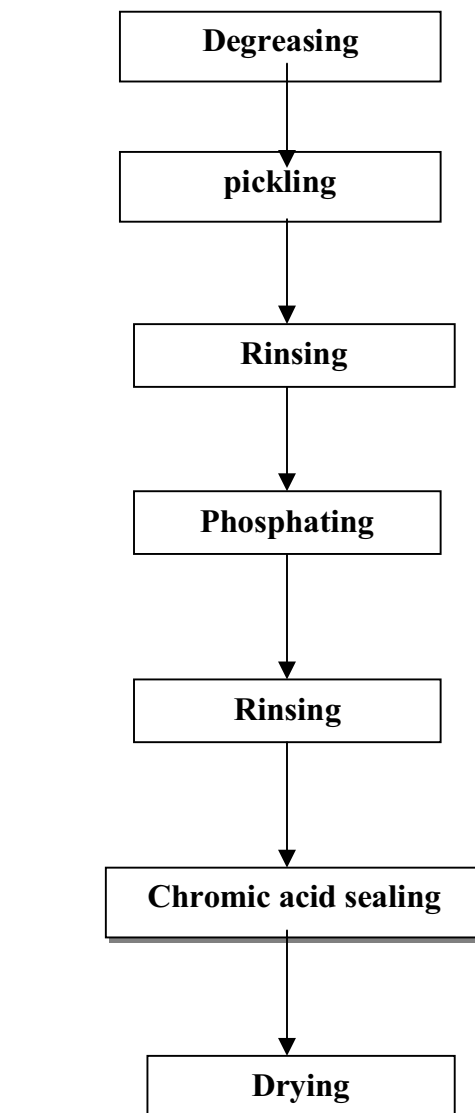
#### 3.5.1. Cleaning

Perhaps, the most important requisite for proper coating formation is a clean substrate, free from contaminants such as oils, greases, waxes, corrosion products and other soils. Many coating failures can be attributed to the poor metal surface preparation [171]. An ideal cleaning agent is the one, which is capable of removing all the contaminants from the metal surface, and prevents their re-deposition or the formation of other detrimental reaction products [172]. A variety of methods such as sand blasting, solvent degreasing, vapour degreasing, alkaline cleaning and pickling have been used to achieve this end.

Sand blasting is an effective method of mechanical cleaning. However, it is highly expensive and its use is justified as a field procedure where chemical treatments cannot be used and it is necessary to remove the loosened mill scale as well as paint [173].

Organic solvents are widely used to remove organic contaminants from the metal substrates. But they are of toxic and flammable nature and need to be used in large quantities, which is uneconomical. This has led to its replacement by the vapour degreasing technique. The unique advantage of the latter technique over solvent degreasing is that, continuous cleaning with small quantities of solvent is possible [174].

Alkaline cleaning provides an economical and effective alternative to the use of organic solvents to



**Fig. 3.** Flow chart depicting the operating sequence involved in phosphating process.

remove greases, oils and waxes. They are also used in conjunction with surface active (wetting) agents and emulsified hydrocarbon solvents [174]. Alkaline cleaners are particularly efficient when used hot (approx. 79 °C). While alkaline cleaning is free from the fire and toxicity hazards associated with organic solvent cleaning (unless emulsified solvents have been incorporated), the corrosive effects of alkaline materials on the skin and on ordinary clothing must be guarded against. Caustic soda in particular can cause serious burns to the skin and eyes and is extremely irritating to the nasal and bronchial membranes if inhaled.

Acid cleaning or pickling using acids such as HCl, H<sub>2</sub>SO<sub>4</sub>, and H<sub>3</sub>PO<sub>4</sub> is a very effective method

for the removal of rust and mill scale [175]. Dilute solutions (5-10% by weight) of  $H_2SO_4$  and  $HCl$  are used in presence of inhibitors to remove the inorganic contaminants by converting them into their ferrous salts. Pickling in  $H_2SO_4$  is usually performed at high temperatures (about 60 °C).  $H_3PO_4$  is an excellent time-tested cleaning agent which not only removes organic and inorganic solids present on the metal but also causes chemical etching of the surface by reacting with it to produce a mechanically and chemically receptive surface for subsequent coating formation [176].

Electrolytic pickling is an alternative to chemical pickling, which provides better and rapid cleaning through an increased hydrogen evolution, resulting in greater agitation and blasting action [174].

### 3.5.2. Rinsing

The rinsing step followed by cleaning plays a vital role in the phosphating sequence [172]. Rinsing prevents the dragout of chemicals used in the earlier cleaning that may contaminate the subsequent stages.

### 3.5.3. Phosphating

Suitably cleaned surfaces are next subjected to phosphating, which causes the formation of an insoluble, corrosion resistant phosphate layer on the substrate surface. A wide variety of phosphating compositions are available. However, the right choice of the components and the operating conditions of the phosphating bath are made based on the nature of the material to be treated and its end use. All the phosphating compositions are essentially dilute phosphoric acid based solutions containing alkali metal/heavy metal ions in them besides suitable accelerators [18,19,24,127,128]. Based on the nature of the metal ion constituting the major component of the phosphating solution, these compositions are classified as zinc, manganese and iron phosphating baths. The characteristics of the coatings obtained using these baths are presented in Table 5.

Phosphating can be effectively performed on both ferrous and non-ferrous metals. Among the ferrous metals, mild steels are most frequently used although maraging steels, galvanized steels and stainless steels can also be coated [177-180]. Non-ferrous metals that can be phosphated include zinc, aluminium, magnesium and cadmium [181-183]. Physical properties like hardness, tensile strength and workability of the original metal are retained af-

ter phosphating [21]. The dimensional change caused by phosphate coatings on the metal surface is of the order of  $10^{-3}$  mm.

Phosphate deposition can be achieved through the use of both spray and immersion processes and the choice of the appropriate method depends upon the size and shape of the substrate to be coated and based on the end use for which the coating is made. Spray process is preferred where shorter processing times are required. This method, however, requires more factory floor space and special equipment for their application. Immersion process though slower, produce uniform coatings and they require less factory floor space as the process tanks can be arranged in a compact manner. The benefits of phosphating by total immersion were considered by Wyvill [184]. But, immersion processes are more susceptible to contamination during continuous operation than are spray processes. Smaller parts can be effectively and economically phosphated by immersion process whereas spray process is more suitable for larger work pieces. Nowadays, a combination of both spray and immersion process has been successfully used particularly in automobile industries [185].

Phosphating may be carried out at temperatures ranging from 30-99 °C and processing time can be varied from a few seconds to several minutes. Suitable choice of these parameters is determined by factors such as nature of the metal to be coated, thickness and weight of the coating required and bath composition. The process of phosphating involves a consistent depletion of bath constituents and in order to obtain a satisfactory phosphate coating, the bath parameters such as: (i) the free acid value (*FA*) which refers to the free  $H^+$  ions present in the phosphating solution; (ii) total acid value (*TA*) which represents the total phosphate content of the phosphating solution; (iii) the ratio of *FA* to *TA*, expressed as the acid coefficient; (iv) accelerator content; (v) iron content; and (vi) other metallic and non-metallic constituents present, have to be strictly controlled within the optimum limits.

### 3.5.4. Rinsing after phosphating

The surface that has been subjected to phosphating should be thoroughly rinsed with deionized water to remove any acid residue, soluble salts and non-adherent particles present on it which would otherwise promote blistering of paint films used for finishing. Generally overflow rinsing and spray rinsing are preferred [186].

**Table 5.** Characteristics of phosphate coatings.

Characteristic	Type of coating		
	Iron Phosphate	Zinc Phosphate	Heavy Phosphate
Coating weight	0.16-0.80 g/m <sup>2</sup>	1.4 - 4.0 g/m <sup>2</sup>	7.5-30 g/m <sup>2</sup>
Types	Cleaner/coater Standard Organic phosphate	Standard Nickel-modified Low-zinc Calcium-modified Manganese-modified	Manganese phosphate Zinc phosphate Ferrous phosphate
Common accelerators	Nitrite/nitrate Chlorate Molybdate	Nitrite/nitrate Chlorate Nitrobenzene Sulphonic acid	None Chlorate Nitrate Nitroguanidine
Operating temp.	Room – 70 °C	Room-70 °C	60-100 °C
Free acid (points)	-2.0 to 2.0	0.5 - 3.0	3.6 - 9.0
Total acid (points)	5-10	10-25	20-40+
Prephosphate conditioners	None	Titanium phosphate None	Manganese Phosphate Titanium phosphate None
Primary use	Paint base for low-corrosion environments	Paint base for high-corrosion environments	Unpainted applications
Limitations	Low painted corrosion resistance; low unpainted corrosion resistance	Poor unpainted corrosion resistance	Expensive, long processing times
Materials needed for tanks	Low-carbon steel	Low-carbon steel, stainless steel or plastic-lined steel	Stainless steel or low-carbon steel
Application method	Spray and immersion	Spray and immersion	Immersion only

### 3.5.5. Chromic acid sealing

The phosphate coatings are usually porous in nature. The porous nature will have a detrimental influence on the corrosion resistance of the phosphate coating unless they are sealed. A hot (70-80 °C) dilute chromic acid rinse is usually used for this purpose. This treatment reduces the porosity by about 50%. It improves the corrosion resistance by the deposition of insoluble chromates on the bare areas of the coating [25]. In addition to the benefits derived from precipitating insoluble salts and passivating any metal that might be exposed, the dilute chromic acid treatment is advantageous in that it helps to dissolve protruding crystals of the phosphate coating [187]. Besides, chromic acid post-treatment leaves a residue that is slightly acidic, which most paints can tolerate. Usually a concen-

tration range of 0.0125-0.050% is used. A gross excess of chromic acid causes blistering, poor adhesion and irregular yellowing of paint [188]. A mixture of chromic acid and phosphoric acid has also been used [188]. Acidic solutions of chromic acid of pH 2-5 are preferred, the free acid being controlled between 0.2 and 0.8 points and the total acid below 5 points.

The role of chromates in improving the passivity of phosphated steel and in improving the paint film adhesion has been the subject of many papers. According to Cheever [189], chromium atoms are distributed over the surface and not just between the phosphate crystals. Wenz and Claus [190] have shown that chromic acid final rinsing completely removes any adsorbed calcium from tap water rinsing after phosphating, deposits some chromium and

alters the Zn/Fe ratio. Maeda and Yamamoto [187] have studied the nature of chromate-treated phosphated surface using XPS. The Cr  $2P_{3/2}$  spectra suggest that the coating mainly consisted of trivalent chromium oxide with a small amount of a hexavalent chromium compound (Fig. 4). Deconvolution of the trivalent chromium peak results in two more peaks which can be attributed to  $Cr_2O_3$  (major part) and  $Cr(OH)_3 \cdot 1.5H_2O$  (minor part), suggesting an intermediate compound (polymerized state) with -ol (Cr-OH) and -oxo (Cr-O-) bonds. From the calculation based on the ratio of the two components, the chemical composition of the chromium oxide(III) was formulated to be  $CrOOH \cdot 0.2H_2O$ . The  $CrOOH \cdot 0.2H_2O$  contributes to increased paint adhesion due to hydrogen bonding with resin components.

Though the chromic acid sealing improves the corrosion resistance, the need for regular disposal of Cr(VI) effluents is a matter of concern because Cr(VI) causes serious occupational and health hazards. Several alternatives for Cr(VI) treatment were proposed (Table 3) [191]. In spite of the development of various alternative treatments, there still exists a strong belief that the extent of corrosion protection provided by them is not as good as that from Cr(VI) treatment and from the point of view of use on an industrial scale, none of these alternative post-treatments have been proved to be a completely acceptable replacement to Cr(VI).

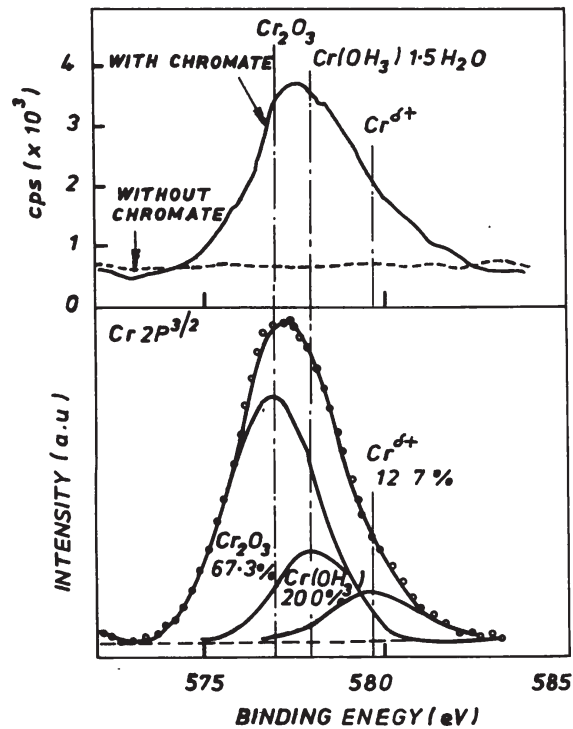
### 3.5.6. Drying

After chromic acid rinsing the parts must be dried before finishing, the conventional methods used being simple evaporation, forced drying by blowing air or by heating [88]. Where evaporation conditions are good, warm air circulating fans and compressed air blow offs are the most economical methods. After drying the phosphated panels are ready for application of further finishes such as paints, oils, varnishes, etc.

## 3.6. Coating characteristics

### 3.6.1. Structure and composition

Phosphate coatings produced on steel, zinc, zinc-coated steel, aluminium and other similar metals show a crystalline structure with crystals ranging from a few to about 100 micrometer in size. Various workers [24, 192, 193] have reported a large number of different constituents of phosphate coatings. Machu [25] listed 30 such phosphate compounds identified in a phosphate coating. Neuhaus and



**Fig. 4.** Cr $2p_{3/2}$  XPS spectra of phosphate coating post-treated with chrome rinse (Parlen 60) (Reprinted from Progress in Organic Coatings, Vol. 33, S. Maeda and M. Yamamoto, The role of chromate treatment after phosphating in paint adhesion, pp. 83-89 (1989) with permission from Elsevier Science).

Gebhardt [192] have tabulated the main phases in phosphate coatings formed on metals from baths of various phosphates (Table 6). The composition of phosphate coatings is influenced by a number of factors such as the method of application (spray or dip), the degree of agitation of the bath, bath chemistry, the type and quantity of accelerator and the presence of other metal ions. Chamberlain and Eisler [194] have found using radioactive tracers that the base layer was formed initially from the metal being attacked during the first few seconds of contact with the phosphating bath producing a very thin film. The film contains oxides and phosphates of the metal being treated. Ferrous phosphate is most likely to be present in the case of steel. The growth of phosphate coating is initiated by the formation of a sub-crystalline layer on which crystalline layer of phosphates build up rapidly. The number of crystals on which growth has occurred is essentially constant with time because nucleation and growth takes place only at a limited constant number of areas

**Table 6.** Phase constituents of phosphate coatings on Fe, Zn and Al.

Metal in the bath	Substrate		
	Fe	Zn	Al
Alkali	$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$	$\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	$\text{AlPO}_4$
Fe	$\text{Fe}_3\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$ (Fe hureaulite)	$\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ $\text{Zn}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	
Mn	$\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ (strengite) $(\text{Mn.Fe})_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$ $\text{Mn}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$ (Mn hureaulite)	$\text{Fe}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$ $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	$\text{Mn}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$
Zn	$\text{Zn}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ (phosphophyllite) $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ (hopeite)	$\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	
ZnCa	$\text{Zn}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ $\text{Zn}_2\text{Ca}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (scholzite) $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$	$\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ $\text{Zn}_2\text{Ca}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$	$\text{Zn}_2\text{Ca}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$

[195]. It is believed that the formation of phosphate coating follows an active site mechanism i.e., only a small percentage of the surface, participates in the nucleation of the growth sites. Machu has postulated that these active sites were the growth areas located predominantly at the grain boundaries of the steel [196].

Light and electron microscopic studies made on zinc phosphated steel, have shown that the formation and growth process occur in three stages.

**1st stage:** Depending on the zinc phosphating process,  $10^4$ - $10^6/\text{cm}^2$  platelet crystals are formed on the surface. These are randomly oriented to the steel substrate; some are parallel, some vertical and others are inclined at an angle. Those platelets, which are not, attached parallel to the surface are needle-like in appearance. These first stage crystals grow primarily laterally over the substrate.

**2nd stage:** It consists of nucleation and growth of several crystals on the upper surface of the original crystals that are attached parallel to the surface. This growth process is usually vertical to the site and gives the appearance of additional needle-like crystals.

**3rd stage:** Finally, a thin layer of zinc phosphate spreads from the base of the original crystals. For paint-base zinc phosphate coatings, the

growth is primarily lateral. For coatings used for oil retention and as bases for cold forming lubricants, considerable vertical growth also occurs.

The crystal habit and size depends on many factors like the bath composition, temperature, method of surface preparation etc. Crystals may take the form of plates, needles and grains having dimension from a few to tens of micrometers.

Many instrumental methods are available for the examination of the constituents of phosphate coatings. These include energy dispersive spectroscopy (EDS), electron spectroscopy for chemical analysis (ESCA) and X-ray diffraction (XRD). Neuhaus *et al.* [193] have reported from XRD analysis that phosphophyllite,  $\text{Zn}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  and hopeite,  $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$  are the essential constituents of zinc phosphate coatings on ferrous substrate, substantiated by others [197, 198] also.

Phosphophyllite is formed essentially at the surface of contact with the basis metal. The quantitative ratio of these phases is variable and depends on the total iron content of the solution. Iron Hureaulite,  $\text{Fe}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$  is formed when the Fe(II) content in the solution is high. This is not stable under atmospheric conditions and has a detrimental influence proportional to its content in the coating.

Miyawaki *et al.* [199] have introduced the concept of 'P ratio' to express quantitatively the proportion of these phases in phosphate coatings. It is defined as:

$$\text{'P ratio'} = \frac{\text{Phosphophyllite}}{\text{Phosphophyllite} + \text{Hopeite}}$$

Several authors [199,200] have correlated the 'P ratio' and corrosion resistance of the phosphate coating. But according to Richardson *et al.* [200] the ratio itself is not sufficient to predict the corrosion resistance.

X-ray and electron diffraction studies have shown that hopeite and phosphophyllite are oriented perpendicular to the plane of the support besides exhibiting that there is an excellent orientation between the substrate and the zinc phosphate coating that follows an epitaxial growth relationship.

(010) - hopeite and (100) - phosphophyllite || (100)- $\alpha$ -Fe

(100) - hopeite and (001) - phosphophyllite ||  $A_0$ - $\alpha$ -Fe and

(001) - hopeite and (010) - phosphophyllite ||  $A_0$ - $\alpha$ -Fe

The formation of primary valency bonds between the coating and the polarized elements of the  $\alpha$ -iron lattices with the production of a two dimensional contact layer of the wustite-type accounts for the excellent adhesion of the coating to the substrate.

### 3.6.2. Coating thickness and coating weight

One of the principal factors involved in the choice of a phosphating bath is in fact the thickness of the deposit that it will provide. Neglecting intercrystalline voids and surface irregularities and considering the phosphate coating as completely homogeneous, the thickness can be measured [201]. Phosphate coatings range in thickness from 1 to 50 microns but for practical purposes the thickness is usually quantified in terms of weight per unit area (usually as g/m<sup>2</sup> or mg/ft<sup>2</sup>) and commonly referred to as coating weight. The reason for the adoption of coating weight rather than coating thickness as the usual measure of coatings is the difficulty in measuring the latter, compounded by the uneven nature of the substrate and of the coating.

According to Lorin [127] the ratio between coating weight (g/m<sup>2</sup>) and coating thickness ( $\mu$ m) varies between 1.5 and 3.5 for the majority of industrial phosphate coatings. For light and medium weight coatings 1  $\mu$ m can be regarded as equivalent to 1.5-2 g/m<sup>2</sup>.

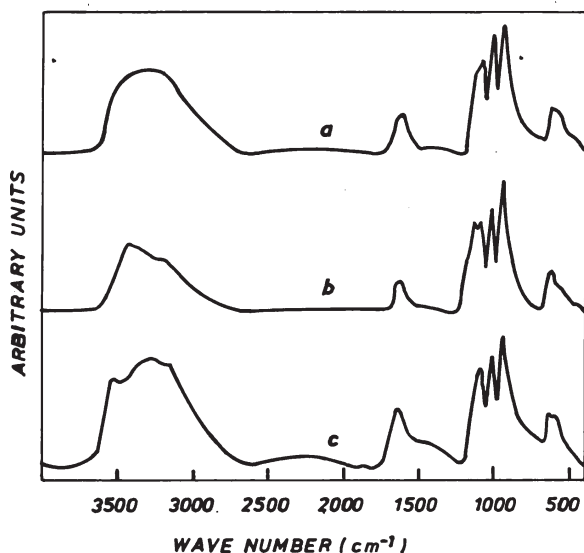
The determination of coating weight is a destructive test, which involves weighing a standard test panel before and after stripping the coating in a medium, which dissolves the coating and not the substrate. Usually methods such as stripping the coating in concentrated hydrochloric acid containing antimony trioxide (20 g/l) as an inhibitor or high concentration of chromic acid solution (5%) or sodium hydroxide (15%) is used. A non-destructive method based on specular reflectance infrared absorption (SRIRA) for the determination of zinc phosphate coating weight has been developed by Cheever [202, 203]. Tony Mansour [204] has shown a good agreement of the results obtained by this method with X-ray fluorescence (XRF) data as well as the gravimetric measurements. Yap *et al.* [205] suggest that XRF is a nondestructive and accurate technique for measuring the thickness of thin phosphate coatings.

The phosphating industry generally uses coating weight as a method of quality control; but it is widely agreed that except at extreme values, coating weight does not directly relate to corrosion performance. Hence coating weight alone is of little value in assessing the quality of coatings and must be considered in relation to other characteristics of the coatings, viz., thickness, structure homogeneity, etc.

### 3.6.3. Coating porosity

The layer of phosphate coating consists of numerous crystals of very different sizes, which have spread from centers of nucleation to join and finally cover the surface. A constitution of this type inherently implies the existence of fissures and channels through to the basis metal at inter-crystalline zones. Porosity is generally fairly low, of the order of 0.5-1.5% of the phosphated surface [25]. It is generally believed that the porosity decreases with increasing thickness of the phosphate coating. Porosity depends upon the type of phosphate solution, the treatment time, the iron content of the bath and, the chemical composition of the coating [206]. In recent years, much attention has been focused on the porosity of phosphate coatings due to the presence of tightly bound carbonaceous residues formed on steel during steel making [207]. Since these cannot be removed by alkaline cleaning process, they interfere with the effective deposition of phosphate coatings resulting in the formation of porous coatings with inferior performance.

Several chemical and electrochemical methods have been developed to determine the porosity of



**Fig. 5.** FTIR absorption-reflection spectra of zinc phosphate coating formed on steel (a) as-prepared; (b) partially dehydrated at 150 °C for 1 hour; (c) partially dehydrated and rehydrated at 95% RH for 70 hours. (Reprinted from Journal of Molecular Structure, Vol. 511-512, A. Stoch, Cz. Paluszkiwicz and E. Dlugon, An effect of methylaminoethoxysilane on zinc phosphate rehydration, pp. 295-299 (1999) with permission from Elsevier Science).

phosphate coatings. The time taken for the deposition of metallic copper from a copper sulphate-sodium chloride solution and the electron microprobe determination of the amount of copper deposited in the bare areas of the coating are the measures of coating porosity [163]. The number of Prussian blue spots formed per unit area of a filter paper soaked in potassium ferricyanide-sodium chloride-gelatin mixture placed on a phosphated sample is yet another method of determination of the porosity of these coatings [208].

Machu's [25] method of determination of porosity of coating by electrochemical means is based on the anodic passivation of uncoated areas in sodium sulphate solution. A more recent electrochemical polarization method is based on the magnitude of current generated by the reduction of oxygen at the cathodically active sites on the porous coating [209,210].

Although porosity of the coating has a detrimental effect on its corrosion performance, it has some advantages too. The pores in the phosphate coatings act as large reservoirs into which organic ma-

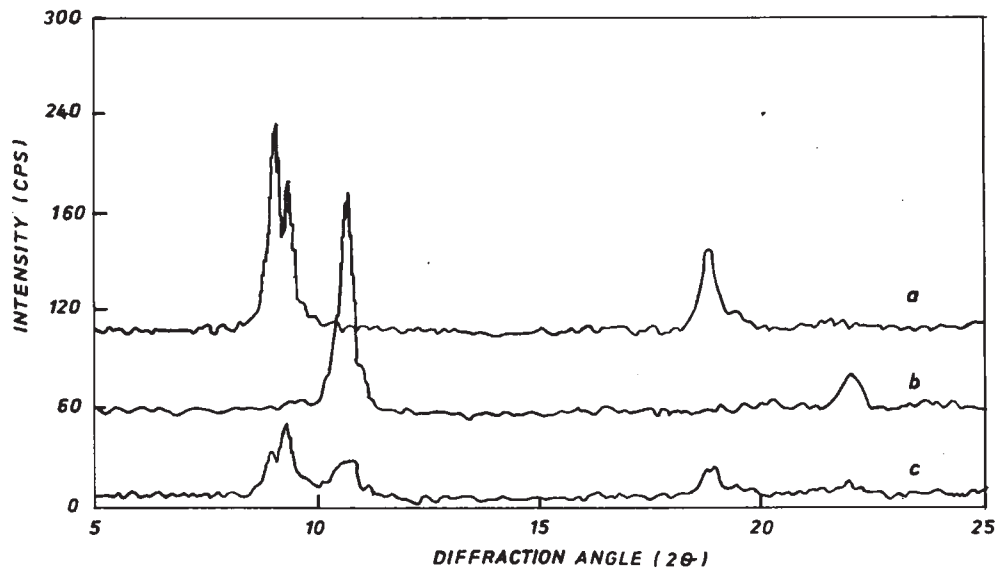
terials can collect [195]. This attribute is made use of in the protection of coated articles by impregnation of oil in the pores. Thus, a homogeneous fine-crystalline coating is desirable with respect to adhesion of a paint film while a coarse-crystalline coating is preferred for protection by oils, varnishes etc.

### 3.6.4. Stability of the phosphate coating

The stability of the phosphate coating is an important characteristic property. Since phosphate coatings serve as an effective pretreatment for subsequent paint finishes, it is imperative that they must be compatible with the applied paint systems. In recent years, numerous developments were made in the paint finishes. Among them, the cathodic electrophoretic deposition has received a widespread acceptance. In order to be compatible with this deposition technology, the phosphate coating must possess an excellent thermal and alkaline stability. The importance of stability of phosphate coating to suit the modern day finishing systems was discussed by several authors [18,19,24,127,211-218].

During cathodic electrophoretic deposition, the decomposition of water produces hydroxyl ions, the creation of which is considered to be critical as they can cause dissolution of the phosphate coating [140, 141]. Several researchers have confirmed the dissolution of phosphate coating in high-pH environments [142-147]. It was found that approximately 30-40% of the phosphate coating gets dissolved during cathodic electrophoretic deposition. This has led to a greater porosity of the phosphate coating. Moreover, the occlusion of the dissolved ions, which are subsequently, concentrated during paint baking affects the corrosion resistance. After cathodic electrocoating the coated panels are usually cured at a temperature of 180 °C for 20 minutes. According to Kojima *et al.* [148] and Sugaya and Kondo [149], under such curing conditions the phosphate coating will undergo a definite weight loss associated with a structural change in the constituent crystals. It is generally advised that the loss in weight should be restricted to less than 15%, which would otherwise cause deterioration of the phosphate coating and a loss in corrosion resistance. The other important factor is the ability of the dehydrated phosphate crystals to revert back to its original hydrated form when subjected to humid service conditions. The dehydration-rehydration phenomenon is further confirmed by X-ray diffraction. During heating at 150 °C for 1 hour the lines at 9.65 and at 19° 2 $\theta$  dimin-





**Fig. 6.** X-ray diffraction pattern of zinc phosphate coating formed on steel (a) as-prepared; (b) partially dehydrated at 150 °C for 1 hour; (c) partially dehydrated and rehydrated at 95% RH for 70 hours. (Reprinted from Journal of Molecular Structure, Vol. 511-512, A. Stoch, Cz. Paluszkiwicz and E. Dlugon, An effect of methylaminoethoxysilane on zinc phosphate rehydration, pp. 295-299 (1999) with permission from Elsevier Science).

ished or disappeared and new lines were observed at 10.90, 11.20 and 22° 2θ. During rehydration the line at 11.20° 2θ diminished while that at 9.65° 2θ grew (Fig. 6). It has been observed that the rehydration of the phosphate crystals induces residual stresses and reduce the phosphate-paint film adhesiveness [150].

Numerous research reports are available to date, which elaborate the behavior of phosphate coatings during chemical and thermal aggressions. The dissolution of zinc phosphate coating in high-pH environments was first reported by Wiggle *et al.* [142]. Later, using sodium hydroxide as a simulated medium, Roberts *et al.* [143] demonstrated the selective leaching of phosphorous from the coating. Van Ooij and de Vries [144] interpreted X-ray photoelectron spectroscopic studies to show that hydroxyl ions exchange phosphate ions in the first few layers of the phosphate coating. Servais *et al.* [140] determined the chemical stability of zinc phosphate coatings by subjecting them to immersion treatment in 0.8 g/l sodium hydroxide solution (pH 12.3) at 40 °C for 3 minutes. Similarly, the effects of high-pH environments on zinc phosphate coatings were determined by Sommer and Leidheiser Jr. [141], using 0.01, 0.1 and 1.0 M sodium hydroxide solutions.

Kwiatkowski *et al.* [151] recommended a borate buffer solution containing 0.01 M ethylenediaminetetraacetic acid (EDTA) as the medium to test the alkaline stability of the coating and suggested its usefulness in predicting the same at a shorter time interval. All these studies uniformly agree that coatings richer in phosphophyllite possess greater alkaline solubility and can serve as effective bases for cathodic electrophoretic painting.

Phosphate coatings undergo marked changes when subjected to variation of temperature. Thermogravimetric technique is usually used to monitor these changes [152]. The changes occurring in zinc phosphate coating on steel upon heating was studied by Kojima *et al.* [148] and Sugaya and Kondo [149]. When heated above room temperature, a gradual loss in weight occurs. This was attributed to a nonstructural weight loss. However, with subsequent increase in temperature dehydration of the constituent phases of the phosphate crystals, occurs. The dehydration of hopeite  $[\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}]$  and phosphophyllite  $[\text{Zn}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}]$  commences respectively at 80 and 110 °C; however, a more pronounced weight loss occurs at approximately 150 °C, where hopeite

loses two molecules of water of hydration. When heated above 150 °C, both phosphophyllite and hopeite are transformed into their dehydrated forms. The hopeite phase is completely dehydrated at a temperature of approximately 240 °C. The weight loss considerably increased between 250 and 600 °C. Above 600 °C sublimation of zinc and phosphorous occurs, which results in complete breakdown of the coating. The change in appearance, colour and morphology of phosphate coatings remain practically unaltered up to 200 °C. However, above this temperature, the grey crystalline phosphate coating changes to a silver grey form and appears dusty. Above 500 °C the colour changes to brown and above 600 °C complete breakdown of coating occurs [148].

Bonara and his co-workers [152,153] have accounted for the observed difference in temperature at which both the hopeite and phosphophyllite crystals lose their water of crystallization. According to them, hopeite crystals seem to possess only one type of crystallization water species, which may be readily released during a progressive heating. In contrast, the phosphophyllite have three different crystallization water types, each with different bond types, thus causing a differential release during progressive heating.

Based on the above facts on thermal stability of phosphate coatings and the normal baking conditions used (180 °C for 20 minutes) for curing cathodic electrocoating, it is quite obvious that both hopeite and phosphophyllite will exist as bihydrated crystals. The rehydration of these bihydrated hopeite and phosphophyllite was a subject of considerable importance as it determines the wet adhesion property. It has now been established that when placed under a rehydration condition, like immersion in an aqueous solution or exposure to high humid atmospheres, the hopeite bihydrated crystals undergo rehydration to the tetrahydrated phase along with the formation of zinc oxide. The formation of these products induces stresses and bond relaxation at the paint-phosphate interface and ultimately affects the adhesiveness. In contrast to this behavior, the phosphophyllite bihydrated crystals are found to resist the rehydration phenomenon. Liebau [233] has accounted for the difference in rehydration behaviour of hopeite and phosphophyllite bihydrate crystals. According to him, in hopeite it is the flexibility of the  $Zn^{2+}$  ion co-ordination state, which can exist in either octahedral or tetrahedral coordination, thus allowing the dehydration process to occur. However, in phosphophyllite, the  $Fe^{2+}$  ions occupy the octahedral co-ordination sites, which are the unsaturated co-ordination states. Hence an ir-

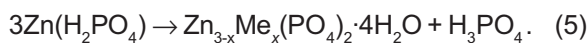
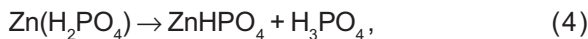
reversible structural modification has resulted during the dehydration process.

Hence it is evident that a phosphate coating richer in phosphophyllite phase is best suited to withstand the environments that occur during cathodic electrophoretic painting, paint curing and under service conditions. This has necessitated modification of the phosphating formulations to produce phosphate coatings richer in phosphophyllite phase. The influence of the phase constituents on the stability of phosphate coatings studied by Sankara Narayanan [213] also confirms this generalization.

The introduction of pre-coated steels such as zinc, zinc alloy coated steels, etc., for automotive body panels present new challenges regarding the stability of phosphate coatings [234]. When coated using a zinc phosphating bath, the zinc and zinc alloy coated steels will produce phosphate coatings, which comprise only the hopeite phase. As stated earlier, phosphate coatings richer in hopeite is not desirable for subsequent cathodic electrocoating finishes. However, these pre-coated steels show good performance with regard to formability and weldability. The extent of perforation and cosmetic corrosion is also less with these materials and they also possess a good surface appearance. Hence to effectively make use of the zinc and zinc alloy coated steels, the phosphating formulation has to be modified to produce coatings that are not richer in hopeite. It is now realized that although low hopeite content is the principle requirement for cathodic electrocoating, it is not essential that the coating should be richer in phosphophyllite as long as the coating has substantial amorphous material.

The introduction of nickel and manganese modified low-zinc phosphating formulations are the most significant modification proposed to cope up with the cathodic electrocoating, particularly in the automobile industry. The presence of  $Ni^{2+}$  and/or  $Mn^{2+}$  ions in these phosphating baths has yielded several advantages. Although there is a decrease in coating weight, crystal formation is observed at an early stage and the crystal size is fine for zinc phosphate crystals obtained from solutions containing  $Ni^{2+}$  and  $Mn^{2+}$  ions. It is confirmed that these heavy metal ions participate in forming the crystal and brings about the crystal refinement and such an effect is found to increase with an increase in their concentration [235,236]. It is also reported that  $Mn^{2+}$  ions are more effective in causing the nucleation of the crystal when compared to the effect of  $Ni^{2+}$  ions [236]. The usefulness of the addition of  $Mn^{2+}$  ion has been advocated based on several other factors.

Mn<sup>2+</sup> ions demonstrably improve the corrosion resistance of coatings obtained from a low zinc phosphating process. The presence of Mn<sup>2+</sup> ions in low zinc phosphating bath increases the rate of formation of phosphate coatings. Hence, it is possible to decrease the bath temperature, which in turn allows a considerable amount of savings in the heating costs. Moreover, the addition of Mn<sup>2+</sup> ions in the phosphating bath helps to increase the working width of the phosphating bath. Also, the presence of manganese in the zinc phosphate coating resists the formation of white spots on galvanized steel. However, it is also cautioned that if the manganese content exceeds a certain level, a decrease in corrosion resistance may occur. Advanced analytical techniques have shown that the manganese tends to be distributed throughout the coating whereas nickel is concentrated at the interface and the presence of both contributes to maximum performance. Based on the results of the electron spin resonance (ESR) technique, Sato *et al.* [237] confirmed that both nickel and manganese are present in the zinc phosphate films respectively, as Ni(II) and Mn(II). According to them, the nickel and manganese doped hopeite are formed by the following mechanisms:



The chemical structure of the modified hopeite crystal in general was considered as  $\text{Zn}_{3-x}\text{Me}_x(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ , where Me = Ni or Mn. Accordingly, the chemical structure of the doped hopeite when nickel and manganese coexist is suggested as  $\text{Zn}_{3-x-z}(\text{Ni}_x\text{Mn}_z)(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ . The possibility of existence of such a structure was confirmed by various analytical techniques such as electron spin resonance (ESR), extended X-ray absorption fine structure (EXAFS), laser Raman spectroscopy, *etc.* [237-243].

Besides the modification of the phosphating bath by Ni<sup>2+</sup> and/or Mn<sup>2+</sup> ions, developments were also made in modifying the surface of the steel sheets. The formation of a Fe-P coating of about 2 g/m<sup>2</sup> containing a phosphorous content of 0.5% or below, on Zn-Ni or Zn-Fe steel sheets is another notable development [234, 244]. These materials are commonly known as double-layered Fe-P/Zn-Ni and Fe-P/Zn-Fe alloy plated steel sheets. The phosphatability of these steel sheets are highly comparable to that of cold-rolled steel sheets. It is the presence of micro quantity of phosphorous, uniformly dispersed in the iron coatings, which activates the surface and enhances the reaction with the phosphating bath, resulting in the production of

closely packed phosphophyllite rich coating, having a crystal size of 3-5 μm. The formation of such a coating improves the wet adhesion property. Hence the modifications made in the phosphating formulations to produce coatings richer in phosphophyllite, to serve as an effective base for electrocoat finishing systems [225], are rightly justified.

### 3.7. Influence of various factors on coating properties

#### 3.7.1. Nature of the substrate

**3.7.1.1. Composition of the metal.** The presence of alloying elements and their chemical nature cause distinct difference in the extent of phosphatability of the substrate. It is generally believed that steels with small amounts of more noble metals such as chromium, nickel, molybdenum and vanadium can be phosphated without much difficulty. However, if the concentration of these elements exceeds certain limit then the steel will encounter with a decrease in the intensity of acid attack resulting in a poor coating formation and among the noble metals in causing such an effect, chromium is considered to be the most detrimental one [245]. The phosphatability of cold rolled steel containing varying amounts of chromium, nickel and copper is given in Table 7. It is evident from Table 7 that the phosphatability is not affected when the total concentration of chromium, nickel and copper is in the range of 200-300 ppm and gets drastically affected when the total concentration of these metals exceeds 800 ppm. The amount of carbon, phosphorus, sulphur, manganese and silicon can also influence the phosphatability of the steel to a great extent. Low carbon steels undergo phosphating easily and produce superior quality coatings. With increasing carbon content, the rate of phosphating becomes slower and the resultant crystals are larger. In fact, when dealing with the carbon concentration in steel, it is the distribution and the form in which it is present is rather an important criterion in predicting its probable effect on sensitization, nucleation and crystallization. The presence of ferrite crystals improve metal attack while on the other hand increasing concentrations of pearlite leads to coarsening of the phosphate crystals as the crystal nuclei develop only to a small extent on the islands of pearlite [127,246]. The deleterious effect of surface carbon content has been the subject of many investigations and based on the amount of surface carbon, steels have been classified as 'bad' or 'good' with reference to their suitability to phosphating

**Table 7.** Phosphatability of cold rolled steel containing varying amounts of chromium, nickel and copper (after Kim [245]).

Substrate designation	Cu + Ni + Cr (ppm)	Surface roughness ( $R_a$ ) (mm)	Phosphatability*	Coating weight (g/m <sup>2</sup> )	
				In the centre	In the edge
CRS-A	300	<0.8	1	4.32	3.87
CRS-B	200	>1.2	1	4.04	5.39
CRS-C	800	<0.8	5	2.86	3.09
CRS-D	1000	>1.2	4	3.54	3.59

\* Based on visual appearance. Rating: 1 – Good; 5 – Poor.

[247,248]. Grossman [248] has found up to 30 times as much carbon on “bad” steels as on the “good” steel samples. A direct correlation between surface carbon content and the porosity of the phosphate coatings on the one hand and their salt spray resistance when painted on the other hand was found by Hospadaruk *et al.* [207,249]. Wojkowiak and Bender [250] using a multiple regression analysis have confirmed the existence of a positive correlation between the extent of underfilm attack and the surface carbon content of the steel.

Takao *et al.* [251,252] have investigated the effect of phosphorus on the phosphatability of ultra low-carbon steel sheets. According to them, the addition of phosphorus was beneficial in refining the grain size and increasing the surface coverage. Moreover, they have proved that the phosphorus addition helps to improve the perforation corrosion resistance after painting. In contrast, Kargol and Jordan [253] have claimed that phosphorus alloy addition inhibits the hydrogen recombination during the initial stages of phosphating resulting in increased porosity and inferior corrosion performance. The rate of attack of the metal in phosphating solution is also affected by the concentration of sulphur. The phosphatability of the dual-phase (Si-Mn) steel is primarily controlled by the balance of silicon and manganese [254].

Although it is clearly evident that every common constituent element of steel has its own influence in determining its phosphatability either to a greater or smaller extent, the most unfavorable from the phosphating point of view are those which are alloyed with carbide forming elements such as chromium and tungsten, and the surface carbon content. As a result, attempts have been made to eliminate such troublesome factors. Accordingly, the surface carbon content of the steel chosen for phos-

phating has to be within the specified limits. Fujino *et al.* [255] have concluded that a contamination of greater than 8 mg/m<sup>2</sup> deteriorates the phosphate coating and resistance to corrosion after painting. Blumel *et al.* [256] and Balboni [257] have predicted an upper limit of 7 mg/m<sup>2</sup>. But Coduti [258] has concluded that this amount has to be a maximum of 4.3 g/m<sup>2</sup> for good performance since only an average performance has resulted when the concentration lies between 4.3 and 6.4 mg/m<sup>2</sup>.

**3.7.1.2. Structure of the metal surface.** The structure of the metal surface has also its own influence and considered to be equally as important as that of the composition. Ghali [259] has made a thorough study of the surface structure in relation to phosphate treatment. It is generally believed that greater the surface roughness, the higher the weight of the coating deposited per unit of the apparent surface area and the shorter the time of treatment required. Moreover, increasing surface roughness gives a corresponding increase in the fineness of the coating structure whereas polished surfaces respond poorly to phosphating. Beauvais and Bary [260] have reported that if the metal surface possesses a greater number of surface concavities and fissures, there will be an increased acid attack during phosphating resulting in good anchorage of the coating. According to Kim [245], phosphatability can be improved by increasing the surface roughness. Balboni [257] has considered that a surface roughness of 0.76-1.77  $\mu\text{m}$  is acceptable for most of the cases.

The growth of the phosphate coating is considered to be an epitaxial growth phenomena and literature reports have convincingly established the following epitaxial relationships in the case of a zinc phosphate coating on mild steel constituting the phosphophyllite ( $\text{FeZn}_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ ) and the hopeite

( $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ ), by means of X-ray diffraction. According to Ursini [261, 262] the orientation relationship (412) phosphophyllite //(111)  $\text{Fe}_\alpha$  role is very important for epitaxial growth on cold rolled steel and for an increasing adhesive bond. Laukonis [142] has studied the role of the oxide films on phosphating of steel and concluded that it is easier to deposit zinc phosphate coatings on ferric oxides than on ferrous oxides. Hence it is evident that it is not only the surface roughness but also the orientation and the presence of the oxide film will influence the phosphating process to a considerable extent.

**3.7.1.3. Surface preparation.** The cleaning methods adopted can also influence the phosphating of steel sheets. It is essential to remove any greasy contaminants and corrosion products from the surface to obtain a good phosphate finish. Degreasing in organic solvents usually promotes the formation of fine-grained coatings while strong alkaline solutions and pickling in mineral acids yield coarse coatings. Though, the prevention of the excessive metal attack during pickling is effected by potent inhibitors, it is generally observed that surfaces that have been pickled with an effective pickling inhibitor are difficult to phosphate unless a strong alkaline cleaning operation is employed to remove the inhibitor residues. Moreover, it is believed that the smut formed during pickling operation can also influence the amount and crystal size of the phosphate coating [188]. However, there are reports available, which are successfully employing potent inhibitors in the pickling bath, which eliminates the usual detrimental effects on phosphating. It is claimed that the inhibitors adsorbed onto the metal surface reduces the amount of hydrogen in the surface layer of the phosphated metal and the phosphate coating produced in such a way are satisfactory for lowering friction, facilitating cold working and as undercoats for paint [263].

**3.7.1.4. Surface activation.** The activating effect of colloidal titanium phosphate was discovered by Jernstedt [264] and latter explored by several others [265]. The mechanism of the activation has been established by Tegehall [266]. The colloids in the aqueous dispersion are disc shaped particles which have the composition of  $\text{Na}_4\text{TiO}(\text{PO}_4)_2 \cdot 0.7\text{H}_2\text{O}$ . These particles are physically adsorbed on the metal surface during the application of colloidal dispersion. When the activated substrate comes in contact to a zinc phosphating bath, an ion exchange between the sodium ions on the surface of the titanium phosphate particles and the zinc ions of the phosphating solution takes place [267]. The ion-exchanged

particles act as nucleation agents for the zinc phosphate crystals because they have nearly the same stoichiometry and offer a crystallographic plane for an epitaxial growth.

The rate of nucleation of the phosphate coating may be markedly increased by imposing an additional activation of the cleaned metal surface. A process for activating steel surface prior to phosphating was patented by Yamamoto *et al.* [268] and Donofrio [269]. Hamilton [270] has proposed a combination of acid cleaning and a phosphating compound for surface activation, while Hamilton and Schneider [271] and Morrison and Deilter [272] have proposed a highly alkaline titanated cleaner prior to phosphating. Use of 1-2% disodium phosphate solution containing 0.01% of titanium compounds have been extensively used in industries [273]. Other compounds like dilute solutions of cupric or nickel sulphates, oxalic acid and polyphosphonates help in increasing the number of initial nuclei formed during phosphating and their subsequent growth, to yield thin and compact coatings of fine-grained nature.

#### 3.7.1.5. Thermal treatments and machining.

Thermal or thermo-chemical treatments cause the formation of heterogeneous phases, which usually alter the grain size. Since the initial metal attack during phosphating occurs mainly at the grain boundaries, the size of the grains becomes an important factor in influencing phosphating and dictates the effect of thermal or thermo-chemical treatments. Moreover, upon thermal treatment, the distribution of the constituent elements of heterogeneous alloys may vary and depending upon which the cathodic and anodic sites on the surface will result and decides the phosphatability. When studying the effects of annealing of a 0.3Mn-0.2Ti modified steel at 280 °C in  $\text{H}_2\text{-N}_2$  atmosphere, Usuki *et al.* [274] has concluded that such a treatment leads to the formation of manganese oxide and titanium oxide. Since the surface concentration of manganese is 3-4 times as large as that of titanium, the treatment enhances the phosphatability of the modified steel by promoting the formation of a predominant proportion of manganese oxide on the surface. Like wise, Hada *et al.* [275] have studied the effect of thermal treatment on the phosphatability of the uncoated side of one-side painted steel. When heated for 2 min. at 280 °C, the crystal size and the coating weight were increased and the 'P' ratio was declined causing an inferior paint adhesion. On the other hand when heated for a longer period there results the diffusion of manganese from the bulk to the surface thus improving the phosphatability.

The influence of cold-rolling and the conditions of annealing on the formation of phosphate coatings were studied by several authors [276-278]. According to Shimada and Maeda [278], increased deformation during cold-rolling and a high-treatment temperature favour the phosphate coating formation with a good surface coverage whereas a rapid rise in temperature in the heat treatment yields an unfavourable condition. Cavanagh and Ruble [279] have showed that tempering treatments following surface hardening processes has a significant effect on the response of steel to phosphating. Machined surfaces accept phosphate coating very easily and often experience a very high rate of deposition.

### 3.7.2. Phosphating parameters

The composition of the phosphating solution and the concentration of its constituents determine the nature of the coatings formed. Higher concentrations of heavy metal ions in accelerated phosphating solutions yield coatings of better protective value [280]. Concerning the acidity of the bath, the free acid value (*FA*), total acid value (*TA*) and their ratio (*FA:TA*) should be maintained at the required optimum level to obtain coatings of improved quality. Increase in total acid pointage generally produce coatings of higher coating weight and the free acid value is considered to be critical since the initial etching attack of the free phosphoric acid present in the bath forms the basis of phosphate coating formation. As the conversion of soluble primary phosphate into insoluble heavy metal tertiary phosphate takes place with the regeneration of phosphoric acid, it is believed that 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 coating. Higher temperatures favour easy precipitation of tertiary phosphates in a shorter time. Hence, more amount of phosphoric acid is needed for the baths operating at higher temperatures. In contrast, in the case of phosphating baths operated at room temperature, the possibility of the increase in acidity during continuous operation is more likely [129,130] and is normally neutralized by the addition of the carbonate of the metal, which forms the coating (Zinc carbonate in zinc phosphating bath). Hence, depending upon the working temperatures and the concentration of the constituents in the bath, the free phosphoric acid content must be chosen to maintain the equilibrium conditions. Too much of phosphoric acid not only delays the

formation of the coating, but also leads to excessive metal loss.

Literature reports have revealed the effects of insufficient metal dissolution as well as the high acidity of the phosphating bath [281,282]. According to Kanamaru *et al.* [281] when the dissolution of iron from the steel during phosphating is insufficient, the hopeite epitaxial growth plane conforms to the phosphophyllite epitaxial growth plane (100) and mixed crystals with a high Zn/P ratio grow along the steel surface whereas when the dissolution is sufficient, the iron concentration in the solution increases, the intrinsically free precipitation of phosphophyllite without the restraint of epitaxy becomes predominant and phosphate crystals with a lower Zn/P ratio grow. However, when the acid concentration is very high, the phosphated material was found to be susceptible to hydrogen embrittlement. The effect is compounded if the exposure time is also increased and it is generally believed that even the relief treatments that are normally practiced are not effective when the acid concentration is abnormally high [282]. Hence, it is clearly evident that the acid coefficient must be maintained properly to produce good quality coatings. Usually, baths of higher acid coefficients form more fine-grained coatings. The conversion ratio, defined as the ratio of amount of iron dissolved during phosphating and the corresponding coating weight [31] is considered to be important as they can predict the efficiency of the phosphating process. However, the inability to generalize its definition for many phosphating baths limits its acceptance as a control parameter in phosphating operations [283].

El-Mallah *et al.* [284] have considered the pH of the bath as initial pH and the pH at which the consumption of all the free phosphoric acid completes as the final pH and correlates the difference between them with the extent of phosphatability. According to them, reducing the difference between the initial and final pH leads to the acceleration of the phosphating process and in causing such an effect the heavy metals and reducing agents such as hydrazine, potassium borohydride were evaluated. Several additives have been attempted to maintain the pH of the phosphating baths. In this respect, organic acids and their salts proved their ability to buffer the pH of an iron phosphating bath made up with hard water [285]. Similarly, the decrease of the total and free acidity by means of some buffer additives to prevent any significant dissolution of zinc coating during the phosphatization of zinc coated steels.

The concentration of the accelerators is also very important. Though increase in accelerator concentration favours better coating formation, too high concentration may cause passivation of metal surface and inhibit the growth. When phosphating bath is modified by the addition of surface active agents, the concentration of accelerator should be optimized in accordance with the influence of these additives [286]. The iron content of the bath is also very critical. Although, a small quantity of iron salts favour phosphate precipitation (Break-in of the bath), the corrosion performance is largely affected as the fraction of the ferrous salts in the coating is increased [287]. The unfavourable effect of Fe(II) is usually decreased by the addition of complexing agents like Trilon B [288]. A method for controlling the iron content of zinc phosphating bath was proposed by Hill [289]. In the case of an iron phosphating bath, the ratio of ferrous to ferric iron in solution has been related to the tendency for flash rusting. The frequency and intensity of flash rust increases as the ratio of ferrous to ferric iron in solution decreased [290].

Addition of specific compounds to the phosphating baths has also their own influence on phosphating. The incorporation of calcium ions in a zinc phosphating bath has resulted in a considerable change in the crystal structure, grain-size and corrosion resistance of the phosphate coatings. In fact, the structure of the zinc phosphate coating changes from the phosphophyllite-hopeite to schlozite-hopeite [291]. The reduction in grain-size (25  $\mu\text{m}$  to 4  $\mu\text{m}$ ) and the improvement in the compactness of the coating and corrosion resistance, makes this kind of modification of zinc phosphating baths as an important type of phosphating and it has been classified as calcium-modified zinc phosphating [172]. Similarly, the inclusion of manganese and nickel ions in the zinc phosphating bath proves to be useful in refining the crystal size and improving the corrosion resistance of the resultant phosphate coatings. It has been established that manganese and nickel modified zinc phosphate deposits on steel have an ordered structure and possess a high corrosion resistance [292]. The immense use of manganese and nickel ions in modifying the hopeite deposits obtained on galvanized steel in such a way that the modified hopeite deposit becomes equivalent to phosphophyllite to withstand the thermal and chemical aggressions, was very well established [293] and as a result of such a pronounced influence of the nickel and manganese ions, they have also been classified as nickel and manganese modi-

fied zinc phosphating [172]. Moreover, such modifications have led to the development of tri-cation phosphating baths consisting of zinc, manganese and nickel ions which explored its potential utility to phosphate aluminum, steel and galvanized steel using the same formulation [294-296]. Besides these major types of modifications, phosphating baths have experienced a variety of additives incorporated in the bath intended for a specific purpose. Each additive has its own influence on the phosphatability of steel depending upon the operating conditions [297-301]. Sankara Narayanan *et al.* [41] have classified the type of special additives used in phosphating and the purpose of their use. The favourable condition and the precautions in using these additives were recommended in the respective documents.

Every phosphating bath reported in literature has a specific operating temperature and the baths were formulated in such a way that an equilibrium condition of the conversion of soluble primary phosphate to insoluble tertiary phosphate exists at that temperature. Insufficient reach of temperature does not favour the precipitation of tertiary phosphate resulted from the conversion. However, when the baths were overheated above the recommended operating temperature, it causes an early conversion of the primary phosphate to tertiary phosphate before the metal has been treated and as a result increases the free acidity of the bath, which consequently delays the precipitation of the phosphate coating. Hence, in an operating line, which has operating time, this effect leads to the production of phosphate coatings with a poor coating weight and inferior corrosion performance. Sankara Narayanan and Subbaiyan [302] have discussed the decisive role of overheating the phosphating baths and outlines the possible way of eliminating the difficulties encountered due to this problem.

Likewise, every formulation has been assigned a fixed operating time based on the kinetics of the phosphating process using the particular bath followed by coating weight measurements or potential measurements with respect to the treatment time. It has been established by many workers that increasing the treatment time beyond the saturation point do not have any influence on the performance of the coating. But it has been warned that any attempt of reducing the treatment time to decrease the amount of phosphate deposition will be disasters.

The method of deposition of phosphate coating or the phosphating methodology can influence the

coating formation to a great extent. The most commonly used methods of deposition namely the dip and spray process, although have received considerable attention, it is believed that the dip process is most likely to produce an equiaxed structure which is considered to be beneficial from the corrosion protection point of view. The influence of permanent magnetic field during phosphating is studied by Bikulcius *et al.* [303]. According to them, when exposed to perpendicular magnetic field, the zinc phosphate coating results in larger crystallites with lower corrosion resistance whereas the effect of parallel magnetic field is insignificant. However, the application of a magnetic field either in perpendicular or parallel mode results in a fine-grained, uniform and more compact zinc calcium phosphate coating.

Electrochemical method of phosphating always yields a heavy coating weight [148,304]. In recent years, studies have been attempted in electrochemical phosphating to produce phosphate coatings richer in a particular phase by selecting an appropriate applied potential [147]. The success of this kind of phosphating methodology has been restricted by the difficulties encountered in adding 'electrics' to the existing process plants. Mechanical vibration of steel during phosphating is considered as a method for obtaining a fine grained phosphate coating. However, the amount of coating formed is found to be inversely proportional to the frequency of vibration [305]. Ultrasonically induced cavitation produces a great number of active centres, which results in a high rate of nucleation. This leads to a uniform fine-grained phosphate coating with low porosity [307,308].

### 3.8. Processing problems and remedial measures

Maintenance of the bath parameters and operating conditions at an optimum level is a major and complicated process, especially in continuous and large-scale phosphating. In actual practice, the finishers have come across several situations that the bath is not working properly. These problems viz., overheating of the bath, creation of an excess acidity at the metal/solution interface especially in the case of cold phosphating, change in acidity of the bath due to carryover of the alkaline solution used for degreasing, the local increase in acidity due to the scaling of the heating coils and so on, were discussed elsewhere [129, 302]. Moreover, baths that have been used for a long time are rendered ineffective due to the formation of sludge of ferric phos-

phate. Sludging occurs to a greater extent in unaccelerated and highly acidic baths and has to be removed periodically to assure proper bath operation [18,19]. In order to maintain bath parameters and to enhance bath life, make-up solutions and solids are usually required. These additives are so formulated that they can be handled easily and are inexpensive.

### 3.9. Defects in coatings and remedies

The most commonly encountered defects in phosphated parts are low corrosion resistance, stained coating with variable corrosion resistance and coatings covered with a loose white powdery deposit. The possible cause for these defects are insufficient care in degreasing and cleaning, incorrect acid coefficient, incorrect solution composition, use of incorrect operating conditions, incorrect maintenance of chemicals, excessive sludge formation and faults in after-treatment. These causes, either singly or in combination, lead to these defects.

Low corrosion resistance of coatings may be a result of incorrect acid coefficient, incorrect bath parameters and operating conditions, presence of certain metallic impurities like aluminium, antimony, tin and lead compounds and the presence of chloride ions in the bath. Improper sealing and abnormally thin coatings may also lead to inferior corrosion resistance. Stained coatings may be formed due to improper cleaning and degreasing. Incorrect distribution of articles in the phosphating bath and wrong ratio of work surface to solution volume may be other causes. Over heating of the phosphating bath, make-up during processing, heavy sludging and sludge suspended in the bath leads to the formation of coatings with a loose powdery deposit.

Proper cleaning and degreasing, correct maintenance of work surface to solution volume ratio, control of bath parameters and operating conditions within the strict limits, avoidance of overheating and excessive sludge formation will yield coatings of consistent good quality and corrosion resistance.

### 3.10. Characterization of phosphate coatings

A variety of instrumental methods, which include, scanning electron microscopy (SEM), electron probe microanalysis (EPMA), X-ray diffraction (XRD), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), electron spin resonance (ESR), X-ray fluorescence (XRF), extended X-ray absorption fine structure (EXFAS), Fourier transform



infra red spectroscopy (FTIR), Raman spectroscopy, differential thermal analysis (DTA), differential scanning calorimetry (DSC), secondary ion mass spectrometry (SIMS), atomic force microscopy (AFM), glow discharge optical emission spectrometry (GDOES), quartz crystal impedance system (QCIS), conversion electron Mossbauer spectrometry (CEMS), acoustic emission (AE) testing, etc. were used to characterize phosphate coatings [308-340].

SEM is the most commonly and widely used technique for characterizing phosphate coatings. It is used to determine the morphology and crystal size of phosphate coatings. SEM serves as an effective tool to study the nucleation and growth of the phosphate coatings and makes evident of the fact that the initial growth of the phosphate coating is kinetically controlled and at a latter stage it tends towards mass transport control [322]. SEM also substantiates the fact that preconditioning the substrate before phosphating enables the formation of a fine-grained and adherent phosphate coating.

EPMA is used in the determination of the porosity of phosphate coatings in which the number of copper spots deposited in the pores following immersion in copper sulphate solution (pH 5.0) [323].

XRD is primarily used to detect the phase constituents present in phosphate coatings – the phosphophyllite and hopeite phases in zinc phosphate coating. Though the manganese and nickel modification of zinc phosphate coating reveals only the presence of hopeite phase, there observed to be significant variations in the orientations of the hopeite crystals as evidenced by the relative intensities of the H(311), H(241) and H(220), H (040) peaks. XRD is also used to characterize phosphate coatings in terms their 'P' ratio.

Van Ooij *et al.* [324] applied high resolution Auger electron spectroscopy (AES) in combination with energy dispersive X-ray spectrometry (EDX) to study the nature of chromium post passivation treatment. According to them, Cr(III) was not detected at the metal/phosphate boundary but on the surface of phosphate crystals and that the Fe/Zn ratio was increased in the surface and subsurface layers.

XPS is used to detect the nature of various species in phosphate coating. The presence of fatty acid-like contaminants on the metal substrates can be identified from the C 1s spectra. Similarly, the Zn 2p<sub>3/2</sub> and P 2p spectra enable identification of Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. Besides, the formation of ZnO or Zn(OH)<sub>2</sub> and NaHPO<sub>4</sub> could be identified from the Zn 2p<sub>3/2</sub> and P 2p spectra, respectively. The Fe 2p<sub>3/2</sub> will give an idea about the presence of Fe<sub>2</sub>O<sub>3</sub> and FePO<sub>4</sub> in

the coating [187]. Cu 2p spectra obtained from the sample phosphated using a solution containing 1 ppm of Cu<sup>2+</sup> ions show two components at binding energies 933.6 eV and 932.2 eV [325]. The former signifies Cu<sup>2+</sup>, although the latter could arise from either Cu<sup>+</sup> or Cu metal. All evidence supports the Cu deposition occurring during the phosphating process.

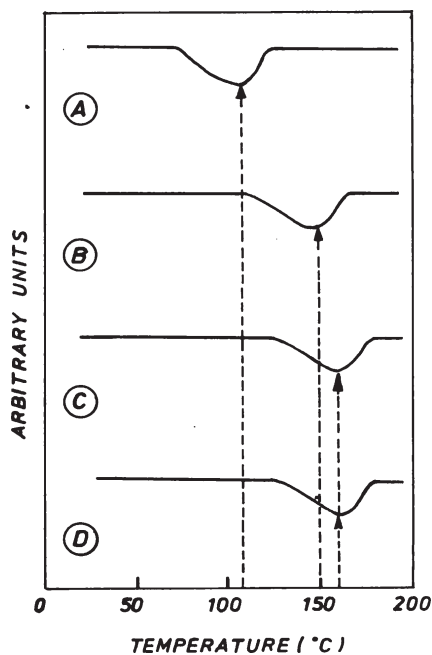
ESR is used to confirm the modified structure of hopeite films formed on the surface of pre-treated steel sheets. The zinc phosphate film formed from the bath that does not contain manganese or nickel ions exhibits no ESR signal. This is because ESR could only detect paramagnetic transition metal ions with an unpaired electron whereas in zinc phosphate coating the ten electron spins of zinc (II) metal ions (3d<sup>10</sup>) in the 'd' orbitals are paired with one another. However, ESR detects the manganese and nickel components in the modified zinc phosphate coating and proves that manganese and nickel exist as Mn(II) and Ni(II) in these coatings [316].

XRF is used to determine the nature of nickel in nickel modified zinc phosphate coating. The XRF spectrum obtained for metallic nickel is compared with that of the modified zinc phosphate coating. The Ni L<sub>α</sub> peak of metallic nickel occurs at 34.18° whereas the Ni L<sub>α</sub> peak of the nickel component of modified phosphate coatings occurs at 34.06°, indicating that the nickel component in the films is not in the metallic state [316].

EXFAS was used to assess the crystal structure of manganese modified zinc phosphate coating [318]. The radial distributions of the first neighbouring atoms appeared at a distance of 0.146 nm for unmodified hopeite and at 0.144 nm for manganese modified hopeite. This decrease is due to the disorderness of modified zinc phosphate coating following the introduction of manganese. EXFAS study also confirms that the manganese component is substituted for zinc component in the octahedral structure.

SIMS was used to detect the presence of titanium, which are adsorbed on to the metal surface and act as sites for crystal nucleation [313].

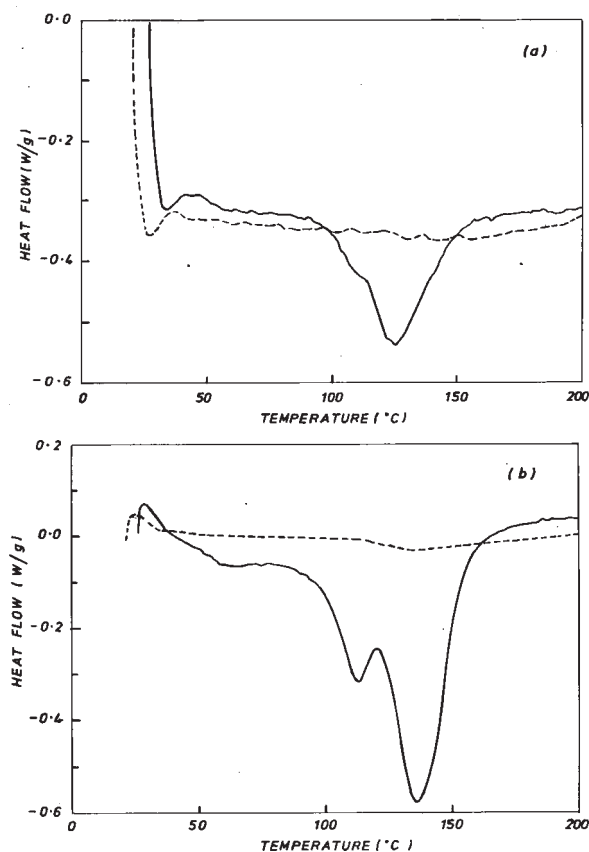
The crystal structure of hopeite and phosphophyllite are hydrated. So once heated, dehydration reactions are expected to occur. Differential thermal analysis (DTA) performed on phosphate coatings shows that there is a clear disparity in the dehydration process of these two phases as evidenced by a 50 °C difference in temperature in the endothermic peaks corresponding to hopeite and phosphophyllite phases. In the case of nickel and



**Fig. 7.** Thermal behaviour of zinc phosphate crystals as hopeite and phosphophyllite studied by differential thermal analyzer: Curve A: Unmodified hopeite; Curve B: Hopeite with 1.8 wt.% Ni + Mn; Curve C: Hopeite with 5.6 wt.% Ni + Mn; Curve D: Phosphophyllite (Reprinted from *Surface & Coatings Technology*, Vol. 30, N. Sato, Effects of heavy metal additions and crystal modification on the zinc phosphating of electrogalvanized steel sheet, pp. 171-181 (1987) with permission from Elsevier Science).

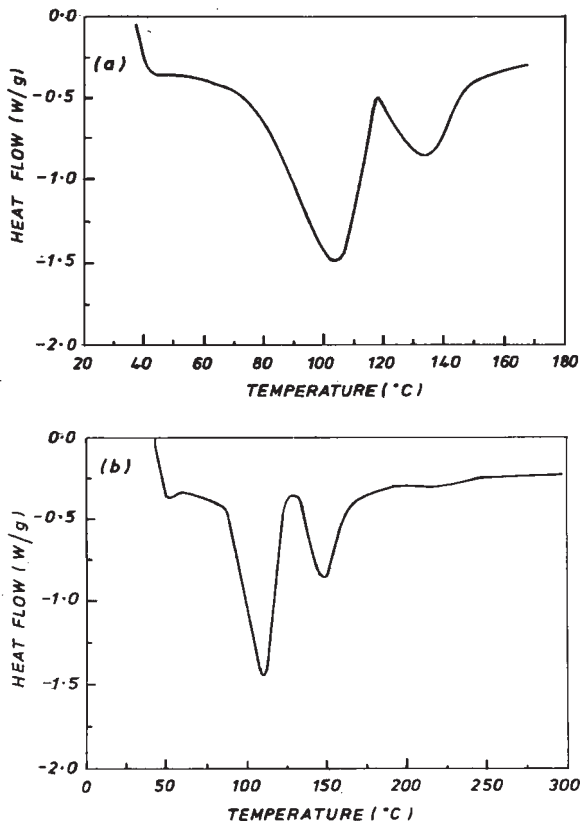
manganese modified zinc phosphate coatings the temperature of the endothermic peaks shifts to higher temperatures and becomes equivalent to the endothermic peak of phosphophyllite (Fig. 7) [326].

DSC is used to assess the thermal behavior of phosphate coatings. Manganese and nickel modified zinc phosphate coatings formed on steel and electrozinc coated steel, in the as deposited condition, show strong endothermic peaks at temperatures below 175 °C associated with the loss of water molecules from the phosphate. On the other hand the DSC traces obtained for these phosphate coatings after stripping the cured paint film exhibit no strong endothermic peak over the temperature range up to 200 °C, confirming that under paint stoving conditions the more labile water molecules have been stripped from the phosphate coating (Fig. 8) [313].



**Fig. 8.** DSC curves of nickel and manganese modified zinc phosphate coating formed on (a) steel and (b) electrozinc coated steel. Solid line represents before stoving and broken line represents after stoving and removal of paint. (Source: R.A. Choudhery and C.J. Vance in *Advances in Corrosion Protection by Organic Coatings*, D. Scantelbury and M. Kendig (Eds.), The Electrochemical Society, NJ, 1989, p.64. Reproduced by permission of The Electrochemical Society, Inc.).

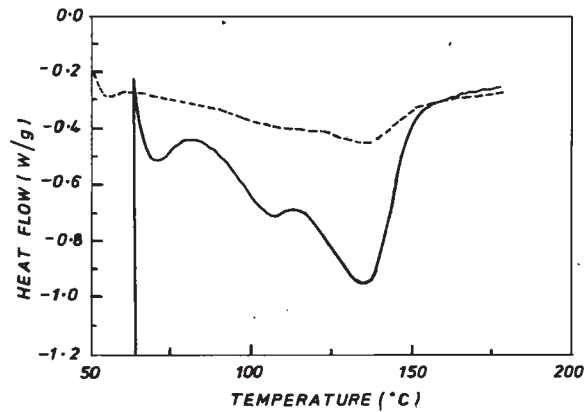
DSC also proves the ability of nickel and manganese modified zinc phosphate coating in resisting the rehydration compared to unmodified zinc phosphate coating. Unmodified zinc phosphate coatings obtained on zinc coated steel exhibit two endothermic peaks at 103 and 135 °C with a total heat flow of 100 J/g. After exposure to 100% RH for 63 hours, these endothermic peaks appear again, with a slight shift in peak temperature towards higher temperatures, indicating that the unmodified zinc phosphate coating is completely rehydrated (Fig. 9). In contrast, manganese and nickel modified zinc phosphate coating exhibit a much stronger resistance to the rehydration process when subjected



**Fig. 9.** DSC curves of unmodified zinc phosphate coating (a) before stoving; and (b) after stoving and rehydrated at 100%RH for 63 hours. (Source: R.A. Choudhery and C.J. Vance in *Advances in Corrosion Protection by Organic Coatings*, D. Scantelbury and M. Kendig (Eds.), The Electrochemical Society, NJ, 1989, p.64. Reproduced by permission of The Electrochemical Society, Inc.).

to similar conditions (Fig. 10) [313]. The main limitation of DSC is that the phosphate coating has to be physically removed from the substrate.

Handke has demonstrated the use of FTIR to study the mechanism of phosphate coating formation [327]. FTIR is sufficiently sensitive to distinguish between different types of coatings in terms of composition and crystallinity [313]. FTIR is also sensitive to the degree of hydration of phosphate coatings. The FTIR spectra of nickel and manganese modified zinc phosphate coating on cold rolled steel (CRS) and zinc coated steel (ZCS) under conditions namely, before heating, after stoving at 180 °C for 20 minutes and after exposure to 100% RH for 14 days was analyzed (Figs. 11 and 12). The assignments of the FTIR spectra for CRS and ZCS



**Fig. 10.** DSC curves for nickel and manganese modified zinc phosphate coating. Solid line represents before stoving and broken line represents after stoving and subsequent rehydration. (Source: R.A. Choudhery and C.J. Vance in *Advances in Corrosion Protection by Organic Coatings*, D. Scantelbury and M. Kendig (Eds.), The Electrochemical Society, NJ, 1989, p.64. Reproduced by permission of The Electrochemical Society, Inc.).

are given in Tables 8 and 9, respectively. The FTIR spectra of phosphate coatings on CRS and ZCS are similar before heating. On heating there are significant changes in the FTIR spectra of ZCS while the changes for steel are less noticeable. On exposing to 100% RH it is evident that phosphate coatings formed on ZCS shows greater tendency to rehydrate, indicated by the increase in intensity of all peaks associated with water vibrations. On the other hand phosphate coating formed on CRS exhibit very little tendency to rehydrate; the spectrum essentially remains constant.

The infrared and Raman spectra of  $\alpha$ -hopeite and phosphophyllite are shown in Figs. 13-15 [341]. They resemble the room temperature spectra reported by Hill and Jones [342] and Hill [343]. The infrared and Raman spectra of both compounds display a large number of bands. In addition, the infrared and Raman spectra of these compounds resemble each other very strongly. Hence distinction of the respective peaks in phosphate coatings is not easy. However, there are some peaks, which are different for these compounds, are useful in identifying these compounds. For example the Raman bands at 1150, 1055 and 310  $\text{cm}^{-1}$  are typical for  $\alpha$ -hopeite whereas the Raman bands at 1135, 1070 and 118  $\text{cm}^{-1}$  are useful for identifying phosphophyllite in phosphate coating.

**Table 8.** The assignments of the FTIR spectra of nickel and manganese modified zinc phosphate coating on cold rolled steel (after Choudhery and Vance [313]).

Wavenumber (cm <sup>-1</sup> )	Shape/Intensity	Assignment Before heating for 20 minutes	After stoving at 180 °C	After exposure to 100% RH for 14 days
3536	Sharp/Strong	Free O-H	Lost	All peaks similar to stoved sample with only a slight increase in peak height
3214	V. broad/Strong	OH/H <sub>2</sub> O stretching	Broadens	
1643	Sharp/Medium-St	H <sub>2</sub> O bending	Shifts to 1629	
1145	W. Sharp/Strong	P-O stretching	Shoulder 1170 appears and shoulder at 1082 now a peak	
1121	Sharp/Strong	P-O stretching	Shoulder 1170 appears and shoulder at 1082 now a peak	
1080	Sh./Strong	P-O stretching	Shoulder 1170 appears and shoulder at 1082 now a peak	
1020	Sharp/Strong	P-O stretching	Shoulder 1170 appears and shoulder at 1082 now a peak	
997	Sharp/Strong	H <sub>2</sub> O rocking	Lost	
933	Sharp/Strong	P-O stretching	–	
643	Sharp/Medium	O-P-O bending/ H <sub>2</sub> O wagging	Broadens	

The influence of metal components in hopeite films was investigated using Infrared and Raman spectra [243]. The IR spectra of hopeite films exhibit peaks at 3500 to 3000, 1640, 1200 to 900 and 640 cm<sup>-1</sup>. The peaks at 3500 to 3000 cm<sup>-1</sup> correspond to the stretching vibration of O-H in H<sub>2</sub>O, the peak at 1640 cm<sup>-1</sup> to the deformation of H-O-H in H<sub>2</sub>O and the three peaks at 1200 to 900 and that at 640 cm<sup>-1</sup> to PO<sub>4</sub><sup>3-</sup> in the hopeite films. There are four basic vibrations for PO<sub>4</sub><sup>3-</sup>, namely,  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$  and  $\nu_4$  in which  $\nu_1$  and  $\nu_2$  are inactive in IR absorption whereas  $\nu_3$  and  $\nu_4$  are active. Hence the three peaks at 1200 to 900 cm<sup>-1</sup> correspond to the  $\nu_3$  mode and that at 640 cm<sup>-1</sup> to the  $\nu_4$  mode. A comparison of the IR spectra of nickel and manganese modified hopeite with unmodified hopeite indicate that the incorporation of nickel and manganese into the hopeite films

affects the coordination state of PO<sub>4</sub><sup>3-</sup> and cause splitting or shifting of peaks. The three peaks at 1200 to 900 cm<sup>-1</sup> corresponding to the  $\nu_3$  mode of hopeite film shows splitting and the peak at higher wavenumber is shifted by 10 cm<sup>-1</sup> towards the lower wavenumber. The  $\nu_4$  peak of nickel and manganese modified hopeite generates a new peak at 580 cm<sup>-1</sup>.

Laser Raman spectra of hopeite films exhibit four peaks in the region between 1150 and 930 cm<sup>-1</sup>, with the main peak appearing at 996 cm<sup>-1</sup>. These four peaks are due to PO<sub>4</sub><sup>3-</sup>, which has four basic vibration modes  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$  and  $\nu_4$ , all of them are Raman active. If the PO<sub>4</sub><sup>3-</sup> in the hopeite film exists as a perfect regular tetrahedron, then only peaks of  $\nu_1$  and  $\nu_3$  should appear. But in practice, there are four peaks. PO<sub>4</sub><sup>3-</sup> in hopeite films affects the sym-

**Table 9.** The assignments of the FTIR spectra of nickel and manganese modified zinc phosphate coating on zinc coated steel (after choudhery and vance [313]).

Wavenumber (cm <sup>-1</sup> )	Shape/Intensity	Assignment Before heating for 20 minutes	After stoving at 180 °C	After exposure to 100% RH for 14 days
3545	Sharp/Strong	Free O-H	Lost	Water stretching peaks intensify. Spectrum begins to resemble the one obtained for sample before heating
3290	V. broad/Strong	OH/H <sub>2</sub> O stretching	Broadens	
1635	Sharp/Strong	H <sub>2</sub> O bending	Shifts to 1649	
1135	Sh./Strong	P-O stretching	Shoulder 1184 appears and shoulder at 1026 now a peak	
1098	Sharp/Strong	P-O stretching	Shoulder 1184 appears and shoulder at 1026 now a peak	
1069	Sharp/Strong	P-O stretching	Shoulder 1184 appears and shoulder at 1026 now a peak	
1026	Sh./Strong	P-O stretching	Shoulder 1184 appears and shoulder at 1026 now a peak	
1003	Sharp/Strong	H <sub>2</sub> O rocking	Lost	
925	Sharp/Strong	P-O stretching	—	
638	Sharp/Medium	O-P-O bending/ H <sub>2</sub> O waging	Broadens	

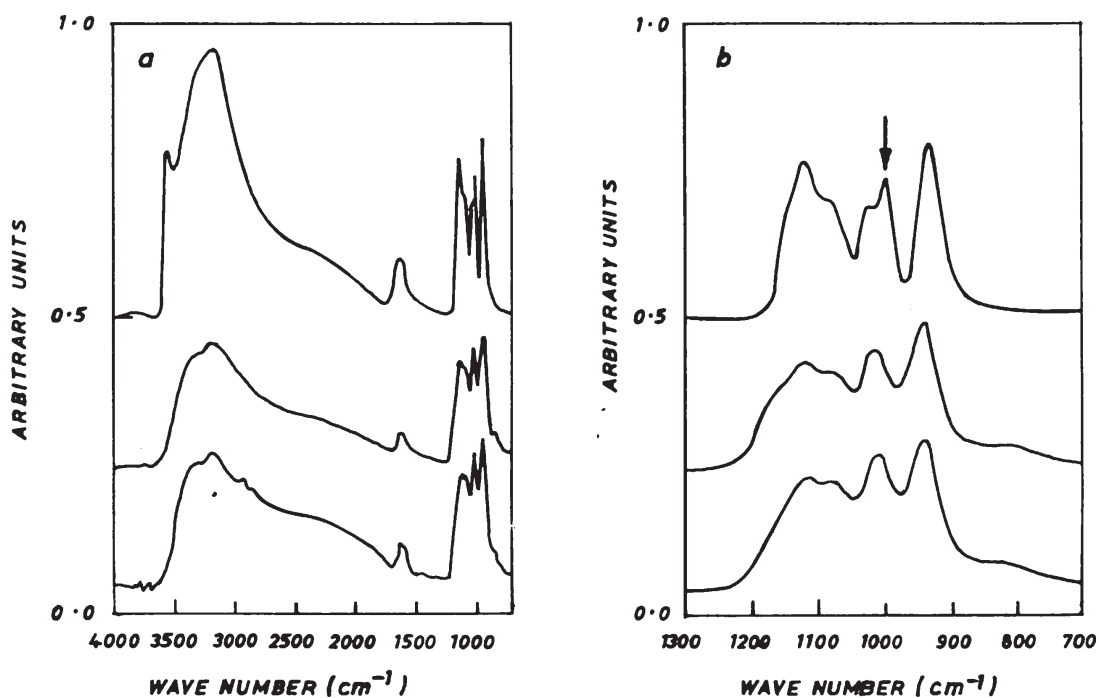
metry of the regular tetrahedron structure by interaction with the surrounding crystalline structure so that the symmetry will become distorted. As a result, the degeneracy of the vibration modes will be united and split and hence results in four peaks.

Three peaks, except for the main peak, correspond to the stretching vibration mode of  $\nu_3$ , which split into three peaks; the main peak around 900 cm<sup>-1</sup> corresponds to the symmetrical stretching vibration of  $\nu_1$ . The level of interaction of PO<sub>4</sub><sup>3-</sup> with its surroundings affects the number of basic vibrations, the Raman band or the intensity of the Raman spectrum. With the incorporation of manganese or nickel in the hopeite films, the Raman band of the main peak as well as the three peaks of  $\nu_3$  are shifted to a lower wavelength. Increasing the metal content in hopeite films has an increasing effect on the data of

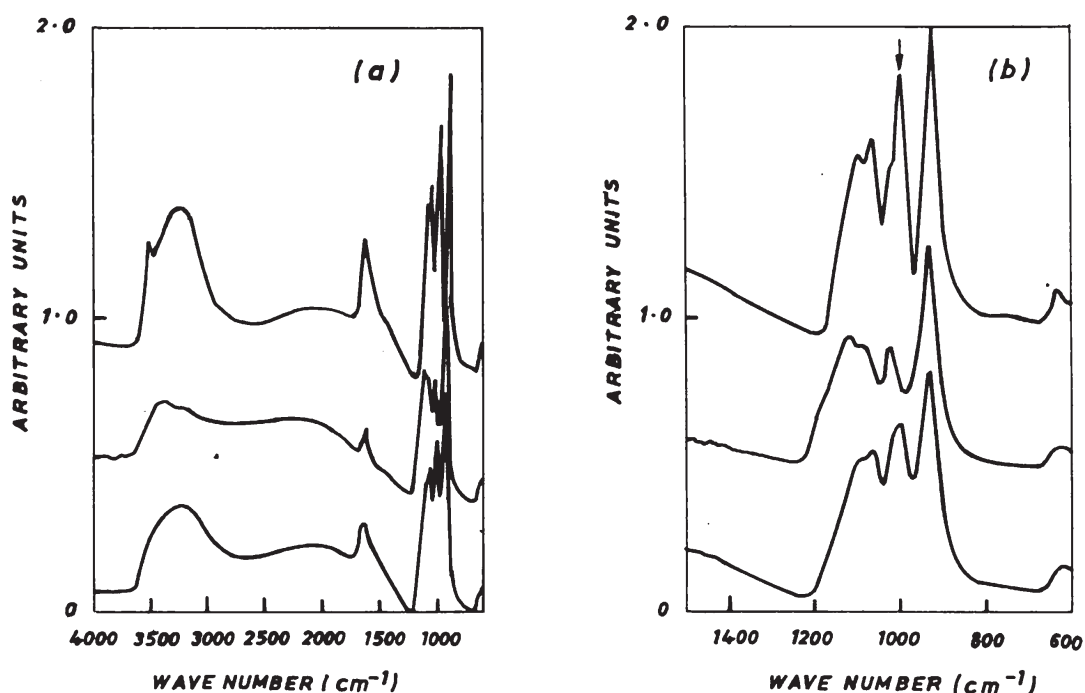
Raman band. Raman spectra showed a sensitivity to the degree of modification of hopeite films by metal components to a greater extent than did IR spectra.

AFM is used to study the effect of surface preconditioning on phosphatability of zinc coated steel. AFM is useful in getting a better understanding of the activation process [328].

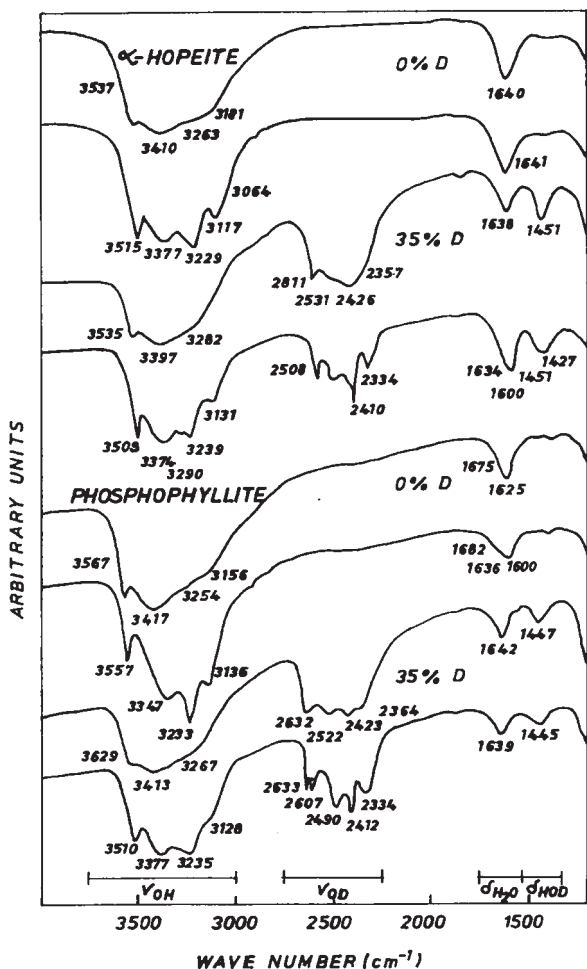
Quartz crystal impedance system (QCIS) was used to study the formation of phosphate coating from a manganese modified low-zinc phosphating bath [329]. It involves rapid and simultaneous measurement of admittance spectra of the zinc coated piezoelectric quartz crystal resonator (PQC). By measuring the equivalent circuit parameters and frequency shift of the zinc coated PQC resonator, the growth kinetics of the phosphating process can be



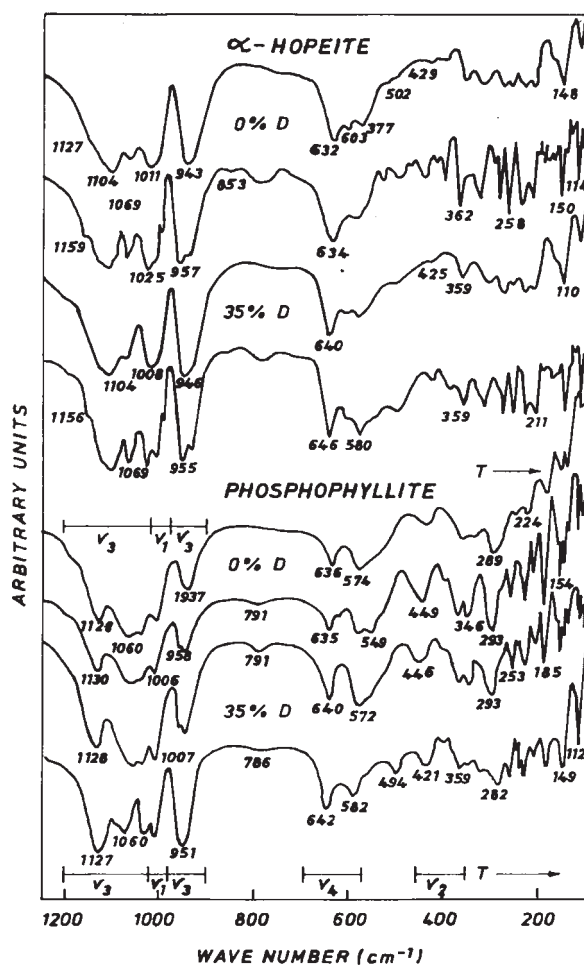
**Fig. 11.** FTIR Spectra of nickel and manganese modified zinc phosphate coating formed on steel. (a) Full range; and (b) Selected range. The top, middle and bottom spectra represent before stoving, after stoving and after stoving with subsequent rehydration, respectively. (Source: R.A. Choudhery and C.J. Vance in *Advances in Corrosion Protection by Organic Coatings*, D. Scantelbury and M. Kendig (Eds.), The Electrochemical Society, NJ, 1989, p.64. Reproduced by permission of The Electrochemical Society, Inc.).



**Fig. 12.** FTIR Spectra of nickel and manganese modified zinc phosphate coating formed on zinc. (a) Full range; and (b) Selected range. The top, middle and bottom spectra represent before stoving, after stoving and after stoving with subsequent rehydration, respectively. (Source: R.A. Choudhery and C.J. Vance in *Advances in Corrosion Protection by Organic Coatings*, D. Scantelbury and M. Kendig (Eds.), The Electrochemical Society, NJ, 1989, p.64. Reproduced by permission of The Electrochemical Society, Inc.).



**Fig. 13.** Infrared spectra of  $\alpha$ -hopeite and phosphophyllite in the region 4000–1400  $\text{cm}^{-1}$  (Reprinted from *Spectrochimica Acta Part A*, Vol. 57, O. Pawlig, V. Schellenschlager, H.D. Lutz and R. Trettin, *Vibrational analysis of iron and zinc phosphate conversion coating constituents*, pp. 581-590 (2001) with permission from Elsevier Science).

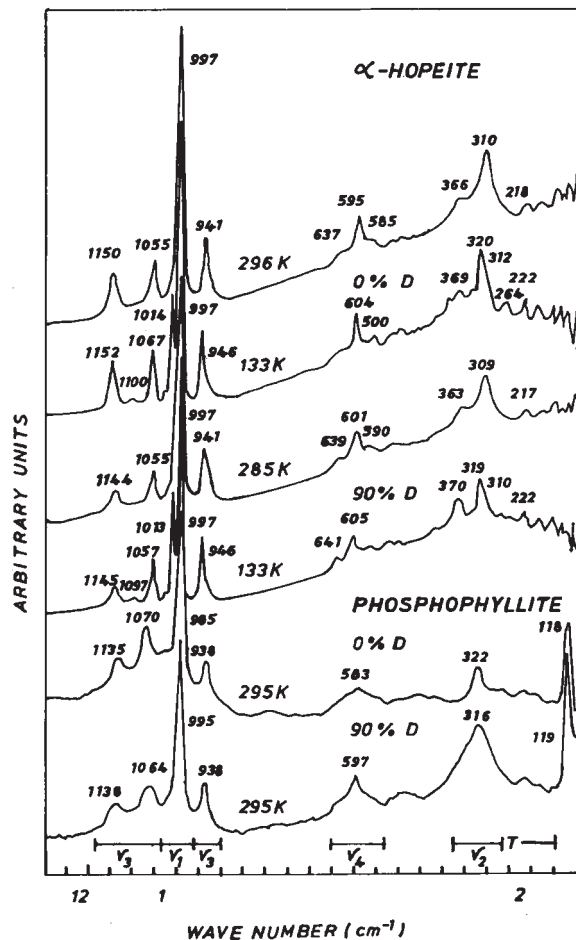


**Fig. 14.** Infrared spectra of  $\alpha$ -hopeite and phosphophyllite in the region 1200–100  $\text{cm}^{-1}$  (Reprinted from *Spectrochimica Acta Part A*, Vol. 57, O. Pawlig, V. Schellenschlager, H.D. Lutz and R. Trettin, *Vibrational analysis of iron and zinc phosphate conversion coating constituents*, pp. 581-590 (2001) with permission from Elsevier Science).

monitored. QCIS is also used to measure the change in viscoelasticity of zinc phosphate coatings, which decreases with increase in phosphating time and the concentration of sodium nitrite [330].

The utility of GDOES in the analysis of phosphate coatings has been attempted by several authors [331-334] and phosphate coatings deposited on cold-rolled, hot-dipped galvanized, galvanized, electrogalvanized and Zn-Ni or Zn-Fe electroalloy-coated sheets were characterized. It has been reported [331] that the profiles of the elemental distribution throughout the film thickness can be obtained with high sensitivity. GDOES provides more detailed information on the constituent elements, depth, di-

rection and the crystal growth process than conventional chemical and X-ray methods. Quantification of the results has also been attempted in the case of GDOES based on the integrated intensity of the constituent elements. Maeda *et al.* [331] have suggested the possibility of utilizing this method for quantitative determination, after establishing a linear relationship between integrated intensity and coating thickness of phosphorus and nickel. GDOES is considered to be the most appropriate method for depth profiling thick phosphate coatings [335]. GDOES due to its higher detection sensitivity compared to XPS, confirms the adsorption of titanium phosphate on zinc coated steel [328].



**Fig. 15.** Raman spectra of  $\alpha$ -hopeite and phosphophyllite in the region 1300–100  $\text{cm}^{-1}$  (Reprinted from *Spectrochimica Acta Part A*, Vo. 57, O. Pawlig, V. Schellenschlager, H.D. Lutz and R. Trettin, *Vibrational analysis of iron and zinc phosphate conversion coating constituents*, pp. 581-590 (2001) with permission from Elsevier Science).

AE is also used as a tool to characterize phosphate coatings [336-340]. Phosphate coating exhibit only a single peak during AE in a ring-down count-rate against strain curves. The amplitude distribution verses events curve recorded for steel/phosphate systems at a strain rate of 10 percent showed emissions with amplitudes only below 40 dB. Room and Rawlings [338, 339] have shown that it is possible to assign the source of failure mechanism to the peaks of amplitude distribution. Each failure mechanism was characterized by events centred on specific amplitudes. In their study they attribute the peak at 22 dB to the cracking of the hopeite needles and the peak at 26 dB to the adhesion fail-

ure between the phosphophyllite and hopeite. Hence it is evident that with the help of AE testing it is possible to detect the onset of a process such as cracking of the coating and/or adhesion failure and the extent to which these failures shall occur.

### 3.11. Testing the quality of phosphate coatings

Methods to evaluate the quality of phosphate coatings involve the determination of its physical characteristics as well as the performance in corrosive environments. Kwiatkowski *et al.* [344] have reviewed the testing methods of phosphate coatings.

#### 3.11.1. Evaluation of physical characteristics

(a) *Examination of physical appearance.* Phosphate films on steel may range in colour from light gray to dark gray, depending on the type of bath and the grade of steel substrate used. After sufficiently strong scratching of phosphate coating with a fingernail, a white scratch should appear on the surface without causing an injury to the coating visible to the naked eye.

(b) *Determination of coating thickness and coating weight.* The local thickness of phosphate coatings on steel is usually determined by magnetic, electromagnetic and microscopic methods [18,19,127,128]. The average thickness is usually expressed in  $\text{g/m}^2$  or  $\text{mg/ft}^2$ . Destructive methods of determination of coating weight are widely adopted. These methods involve the determination of change in weight of a coated specimen after dissolution of the coating in a suitable medium. Concentrated hydrochloric acid containing 20 g/l of antimony trioxide is usually used at room temperature for this purpose. Other solutions commonly used are 5% solution of chromic acid at room temperature and 20% sodium hydroxide at 90 °C. The difference in weight after coating removal is divided by the surface area of the work in  $\text{m}^2$  to obtain unit coating weight in  $\text{g/m}^2$ .

(c) *Determination of acid resistance.* It is calculated as the difference in weight per unit area of the panel before phosphating and after stripping off the coating; and is expressed in  $\text{g/m}^2$ .

(d) *Testing of physical properties.* The absorption value and hygroscopicity are the important parameters relating to the physical properties of the phosphate coating. Evaluation of the absorption value of the phosphate coating involves the measure of the gain in weight per unit area when subjected to immersion in diacetone alcohol for



two minutes and allowed to drain the excess for three minutes [345]. The gain in weight of the phosphated panels, when subjected to a humid atmosphere in a closed container at room temperature for six hours, gave the hygroscopicity of the coating [345].

(e) *Estimation of porosity.* Estimation of the porosity of the phosphate coating involves both chemical and electrochemical methods. The chemical (Ferroxyl indicator) method was based on formation of blue spots (Prussian blue) on a filter paper dipped in potassium ferricyanide - sodium chloride - gelatin mixture when applied over the phosphated surface for one minute. The number of blue spots per sq. cm gives a measure of the porosity of the coating. The electrochemical method of determination was based on the measurement of the oxygen reduction current density when immersed in air-saturated sodium hydroxide solution (pH 12). The current density values measured at -550 mV, where oxygen reduction is the dominant reaction at the uncoated areas reveals the porosity of the coating [209,210]. Although, both the Ferroxyl test and the electrochemical test are used in an industrial scale to assess the porosity of phosphated steel, the former method is found to be qualitative and not very effective in distinguishing the porosities of panels phosphated using different baths. In contrast, the electrochemical method is far reliable besides its simplicity in operation and quicker measurements of the porosity. The advantage of the electrochemical method has been discussed elsewhere [209, 346].

(f) *Determination of thermal and chemical stabilities.* The thermal stability of the coating was usually determined by calculating the percentage loss in weight when the phosphated panels were subjected to drying at 120 and 180 °C.

The chemical stability of the coating, in particular, the alkaline stability is very important as it determines the effectiveness of the phosphate coating as a base for cathodic electrophoretic finishes. This is determined by calculating the percentage residual coating when immersed in alkaline media. Immersion in sodium hydroxide solution is recommended to test the alkaline stability. Recently, Kwiatkowski *et al.* [347] have recommended a borate buffer solution containing 0.01M EDTA as the medium to test the alkaline stability of the coating and proved its usefulness in predicting the same. A similar calculation of the percentage residual coating when

subjected to immersion treatments in buffered solutions of varying pH from 2-14 can give an insight about ability of the phosphate coatings to withstand different chemical aggressions and to prove their effectiveness in preventing the cosmetic corrosion [219].

(g) *Evaluation of surface morphology.* The surface morphology of the phosphate coating is usually assessed by scanning electron microscope (SEM). This technique reveals the distinct features of the crystal structure, grain size of the crystallites, the coating coverage and uniformity; the parameters that determine the performance of the coating.

(h) *Determination of 'P ratio'.* The 'P ratio' is usually determined by measuring the intensity of the characteristic planes of the constituent crystallites of the phosphate coating. In a zinc phosphate coating, which consists essentially of hopeite ( $Zn_3(PO_4)_2 \cdot 4H_2O$ ) and phosphophyllite ( $Zn_2Fe(PO_4)_2 \cdot 4H_2O$ ), the 'P ratio' is defined as [199]:

$$\text{'P ratio'} = \frac{P}{P + H}$$

Where  $P$  – Intensity of the characteristic planes of phosphophyllite and  $H$  – Intensity of the characteristic planes of hopeite.

(i) *Adhesion measurements.* The standard laboratory method of estimation of adhesion is the peel off test, which involves the determination of the extent of adhesion at scribed areas using a pressure sensitive adhesive tape. Usually adhesion in the dry state will be good since it mainly depends on the cohesive failure of the paint film. Wet adhesion is of prime importance and is usually determined after subjecting the painted panels to immersion treatment in de-ionized water at 45 °C for 240 hours. Depending upon the extent of peeling, rating will be made between 0 and 5B as per ASTM D 3359-87 [348].

### 3.11.2. Evaluation of corrosion performance

(a) *Rapid preliminary quality control tests.* Preliminary investigation of coating quality for on-line monitoring mainly involves two empirical tests of which one involves inspection for rust spots after immersion in 3% sodium chloride solution for 5-30 minutes and the other is concerned with the time taken for metallic copper deposition from a copper sulphate-sodium chloride-hydrochloric acid mixture.

(b) *Laboratory corrosion resistance tests.* The most frequently used laboratory tests for evaluating

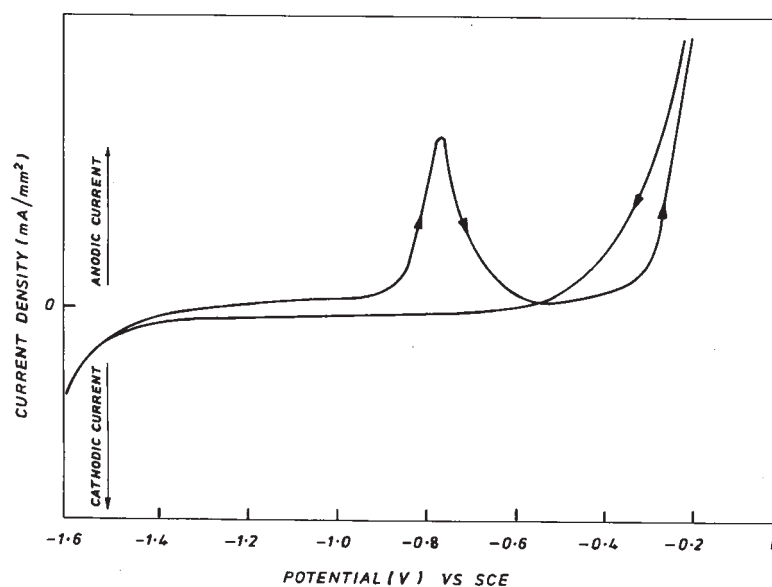
the corrosion resistance of phosphate coatings include (i) immersion test, (ii) salt spray (fog) test, (iii) humidity test and (iv) A.R.E. salt droplet test.

- (i) *Immersion test.* This test consists of determining the time required for the first appearance of corrosion on the basis metal when immersed in 3% sodium chloride solution. The change in weight expressed as  $\text{g/m}^2$  for every 24-hour period of immersion is also determined and correlated to the corrosion resistance of the coating.
- (ii) *Salt spray test.* Evaluation of corrosion resistance of the phosphated and finished panels is performed by subjecting them to a salt mist of 5% sodium chloride solution in a salt spray chamber for a specified length of time. The extent of spread of corrosion from a scribe made on the panel, rated after ASTM B 117-85 specifications, is a measure of the corrosion resistance of the phosphate coating [349].
- (iii) *Humidity test.* This test is used for the evaluation of phosphated panels with and without further finishes. By subjecting the phosphated panels to highly humid conditions (90-95% relative humidity) at slightly elevated temperatures (42-48 °C), assessment of corrosion likely to be induced due to the porosity of the coating can be made. The extent of blistering of paints due to the presence of soluble salts on phosphated and finished panels when subjected for 1000 hours in the humidity chamber is also related to its corrosion performance.

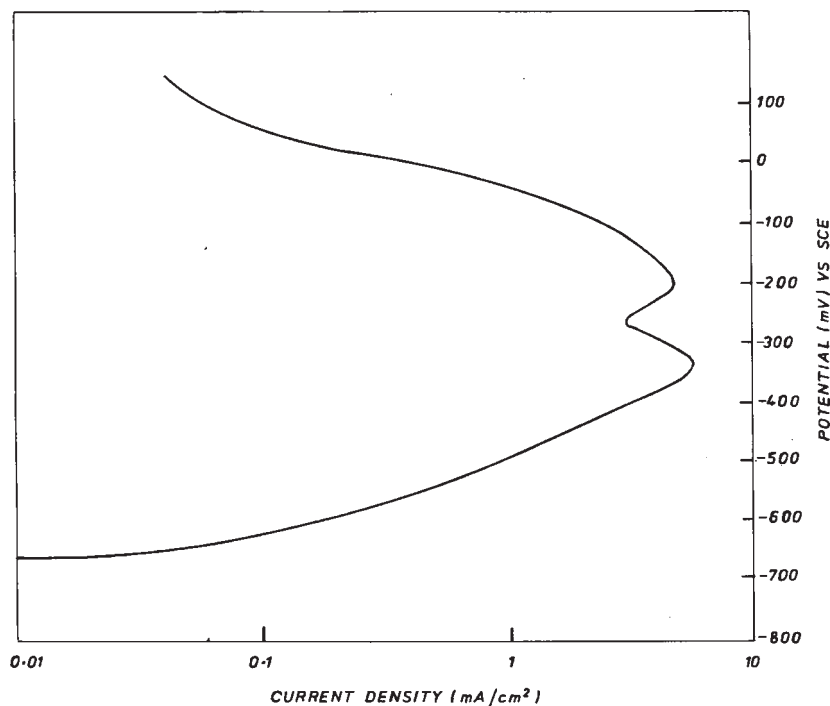
(iv) *A.R.E. salt droplet test.* This test consists of the evaluation of the corrosion resistance of the phosphated panels by determining the loss in weight after five days of exposure in humid condition inside a closed cabinet at room temperature with a single spray of synthetic seawater on each day [350].

(c) *Electrochemical methods of testing.* The electrochemical methods of testing the phosphate coating mainly involves the anodic polarization studies in 0.6M ammonium nitrate [346,351] and AC impedance measurements in 3% sodium chloride solution [352-363].

Zurilla and Hospadaruk [209] proposed a method to assess the porosity of phosphated steel based on oxygen reduction current density in air saturated 0.1 N sodium hydroxide solution. Since cathodic reduction of oxygen occurs at the uncoated areas, the measure of current density values at a fixed potential ( $-550$  mV vs. SCE) reveal the porosity of the coating. Kiss and Coll-Palagos [355] utilized cyclic voltammetry to evaluate the porosity of phosphate coatings. Fig. 16 shows the typical cyclic voltammogram obtained for zinc phosphate coated steel in 5% sodium chloride solution (pH 6.5; 25 °C). The voltammogram can be classified into three major regions based on the potential values. The anodic peak observed between  $-550$  mV and  $-950$  mV is believed to be due to the oxidation of Fe,  $\text{Fe}^{2+}$  and/or the formation of a complex compound in the pores of the phosphated steel and its intensity is



**Fig. 16.** Cyclic voltammogram obtained from zinc phosphate coated steel in 5 wt.% sodium chloride solution (pH 6.5; 25 °C) (After Kiss and Coll-Palagos [355]).



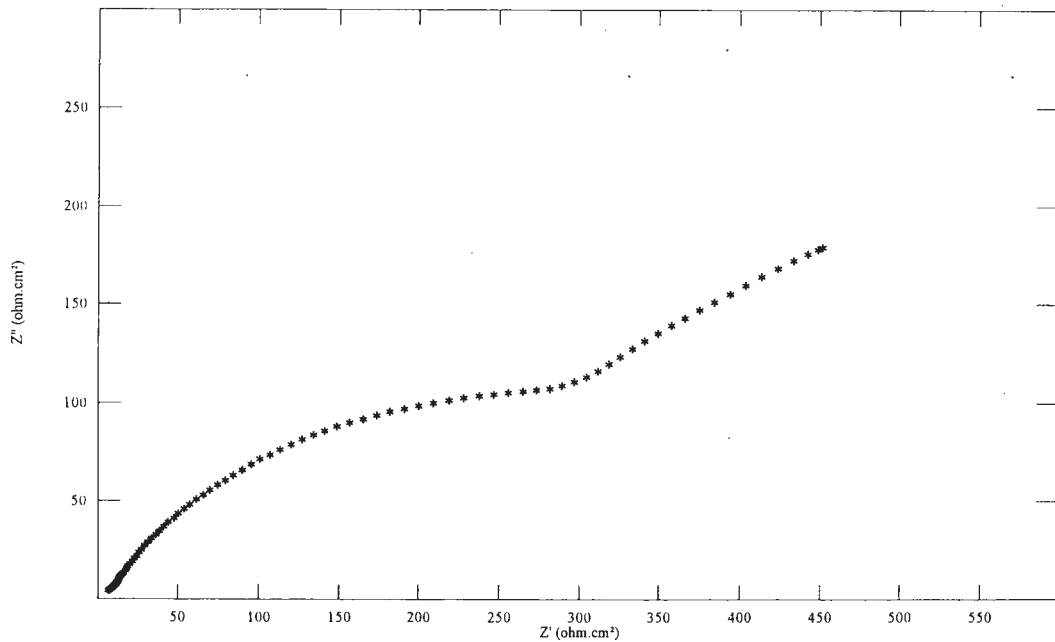
**Fig. 17.** Anodic polarization curve obtained for zinc phosphate coated steel in 0.6 M ammonium nitrate.

related to the porosity of the phosphate coating. Kiss and Coll-Palagos [355] termed this peak as 'porosity peak'. The peak height at  $-800$  mV or the integrated area under this anodic peak was used to predict the porosity.

Anodic polarization study in 0.6 M ammonium nitrate solution is one of the recommended methods of electrochemical evaluation of corrosion resistance of phosphate coatings (Fig. 17) [346]. During anodic polarization in 0.6 M ammonium nitrate solution, at potentials more negative than  $-0.33$  V, phosphated steel undergoes active dissolution. Above  $-0.33$  V, the first passivation region occurs due to the adsorption of hydroxide ions at the electrode surface. The occurrence of the second active region is due to the replacement of hydroxide ions by phosphate ions available at the electrode/solution interface. Replacement of the adsorbed phosphate ions by nitrate causes the occurrence of the second passive region. Hence it is clear that these active and passive regions are the result of the competitive and potential dependent adsorption of anions at the electrode surface. It should be noted here that the appearance of this second current density maximum is specific to phosphated steel and it is not observed for uncoated steel when tested under similar conditions. Hence the value of the

second current density maximum can be used to evaluate the corrosion resistance of different phosphate coatings [346].

The other important method of evaluation of the corrosion resistance of phosphate coatings is the electrochemical impedance spectroscopy (EIS). It provides a rapid, nondestructive means of evaluating corrosion rate and mechanism of corrosion of phosphate coatings. Literature reports on the evaluation phosphate coatings [357-363] suggest that the corrosion behaviour of phosphate coatings in contact with the corrosive medium (3.5% NaCl) can be explained on the basis of a porous film model since the electrolyte/coating-metal interface approximates such a model. Accordingly, the phosphated substrates are considered as partially blocked electrodes when comes in contact with 3.5% NaCl solution. This implies that the metal substrate is corroding in the same way when unprotected in a much smaller area where coverage is lacking. Since the capacitive and resistive contributions vary directly and indirectly, respectively, with respect to the area, based on these measured parameters, predictions on the corrosion rate of different phosphate coatings can be easily made. Fig. 18 shows the Nyquist plot obtained for zinc phosphate coated steel in 3.5% NaCl solution exhibiting a semicircle in the high fre-



**Fig. 18.** Nyquist plot obtained for zinc phosphate coated steel in 3.5 wt.% sodium chloride solution.

quency region followed by a linear portion in the low frequency region. An equivalent electrical circuit model, which involves charge transfer resistance ( $R_{ct}$ ), the double layer capacitance ( $C_{dl}$ ) and the Warburg impedance ( $Z_w$ ) can be proposed to simulate the behaviour of phosphate coating in 3.5% NaCl solution. The change in the values of these parameters with time gives an account of how the coating degradation has occurred and helps to establish a mechanistic pathway. High values of charge transfer resistance and low values of double layer capacitance signify a coating of better performance. The appearance of Warburg impedance suggests that corrosion of phosphated steel is a diffusion controlled. [352-354,362-365].

### 3.12. Applications

Phosphate coatings have been put to a wide variety of applications; salient among them is the corrosion protection, as bases for paint, to provide wear resistance and an aid in cold forming of steel [18,19,24,127,128,366,367].

Phosphate coatings provide an effective physical barrier to protect corrosion-prone metals against their environment. Due to their insulating nature, the phosphate coatings prevent the onset and spreading of corrosion. These coatings provide effective corrosion protection to ferrous and non-ferrous met-

als alike. 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 [368]. They can be used as an excellent base for more recent methods of paint applications such as electrophoretic painting and powder coating [369,370] and shown to improve the corrosion resistance of steel coated subsequently with cadmium, zinc, nickel, etc., both in industrial as well as marine atmospheres [371]. The application of phosphate coating also improves the adhesive bonding of plain carbon steels [372].

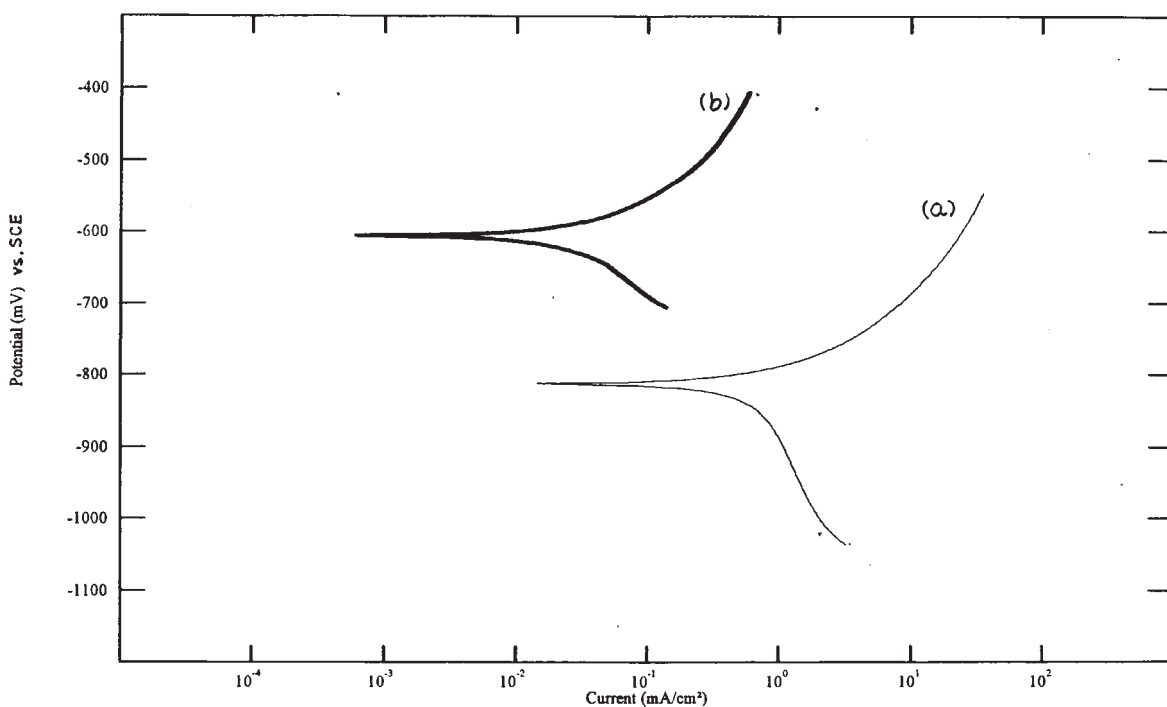
The mechanism of pyrite oxidation in acidic media involves preferential release of iron into the medium. The phosphate treatment results in the formation of iron phosphate coating and significantly reduces the chemical oxidation of pyrite [373]. The formation of a phosphate layer on the surface of iron powders induces a significant improvement of the oxidation resistance in the temperature range of 300-700°C [374]. The oxidation resistance of ultrafine copper powder is increases by phosphating [375]. Rebeyrat *et al.* [376] based on thermogravimetric experiments suggest that phosphating of bulk  $\alpha$ -iron significantly decreases the gain in weight due to oxidation.

The Nd–Fe–B type magnets are highly susceptible to attack from both climatic and corrosive environments, which result in corrosion of the alloy and deterioration in both its physical and magnetic properties. The poor corrosion resistance of Nd–Fe–B type magnets in many aggressive environments is associated with the presence of ~ 35 wt.% of neodymium in their composition. Neodymium, along with other rare earth (RE) elements belongs among the most electrochemically active metals. The application of a zinc phosphate coating proved to be a most useful method to improve the corrosion resistance of NdFeB magnet [377,378]. The improvement in corrosion resistance of NdFeB magnet following the application of a zinc phosphate coating is shown in Fig. 19.

Phosphating is a widely used method of reducing wear on machine elements and moving parts [379,380]. Phosphate coatings function as lubricants, 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 [381]. The manganese phosphates widely used in automotive industry are the best to improve the ease of sliding and the reduction of associated wear of two steel surfaces sliding one against the other. The phosphate coatings pos-

sess no intrinsic lubricating properties but can absorb or hold a considerable quantity of lubricant by virtue of their porosity [382,383]. This combination favours an easier running-in at higher surface pressures by forming a non-metallic barrier that separates the two metal surfaces and reduces the danger of seizure and associated pitting. There is also less noise produced at such surfaces and they have an in-built capacity, in emergencies, to run dry for a limited period [384]. Phosphating increases the sliding distance to scuffing as well as the scuffing load, whilst marginally reducing the coefficient of friction. No advantage was found in phosphating dry sliding surfaces. Phosphating reduces the likelihood of adhesive wear in marginal or poorly lubricated sliding couples. The choice of phosphate coating is primarily dependent on the surface finish of the sliding counterface; thin coatings are suitable for smooth surfaces whereas against rougher surfaces thicker coatings are preferred [385].

The power used in deep drawing operations, sets up a great amount of friction between the steel surface and the die. This will decrease the speed of drawing operation and the service life of tools and dies [386,387]. Application of light to medium weight non-metallic zinc phosphate coating to steel surfaces, which permit the distribution and retention of a uniform film of lubricant over the entire surface,



**Fig. 19.** Potentiodynamic polarization curves of NdFeB magnet in 3.5% sodium chloride solution (a) Uncoated NdFeB magnet; and (b) Zinc phosphate coated NdFeB magnet.

prevents metal to metal contact and makes possible the cold forming and extrusion of more difficult shapes, than is possible without the coating [85,388-390]. A combination of zinc phosphate and lubricant film prevents welding and scratching of steel in drawing operations and greatly decreases the rejections. Bustamante *et al.* [391] suggest the usefulness of pre-phosphate coating of zinc and zinc alloy coated steel sheet in preventing the damage during the forming process.

Phosphate coating is used as an absorbent coating in laser surface hardening of steel [392-394]. Although, all the three major type of phosphate coatings, namely, the manganese, zinc and iron phosphate coatings were used as absorbent coatings, the former was found to be frequently employed in majority of the cases. Besides these, phosphate coatings have also been found to be useful as thermal control coatings in satellite components [395].

### 3.13. Environmental impact

The environmental impact of metal finishing operations is a matter of serious concern and phosphate pretreatment operation is no exception to this. The wastes generated from phosphate pretreatment line can be broadly classified into liquid wastes arising from acid pickling, alkaline cleaning, rinsing stages and chromic acid sealing stage, *etc.* and solid wastes arising from the sludges formed during phosphating. It is estimated that the total outlet of wastewater is about 20,800 g/m<sup>2</sup> and the solid residue generated in the whole phosphating process is about 49.0 g/m<sup>2</sup>. The phosphating process discharges 400 g/m<sup>2</sup> CO<sub>2</sub>-equivalent mass to the environment, which demonstrates that conventional phosphating, has some green house effect. Fortunately, the influence on human health is not so heavy since the average local toxic level (LTL) is estimated to be 1.6 ppm/ppm [396]. Unlike the wastewater discharge, the environment cannot absorb the solid residue. The phosphating sludges are generally considered as hazardous waste materials and are, therefore, subject to strict regulations as to disposal. It is estimated that fifty million pounds of sludge results from phosphating operations each year. Hence it is not only desirable but also mandatory to identify a means for recovering various sludge components.

Phosphating sludge, in general, has 20 wt.% iron, 10 wt.% zinc, 1-3 wt.% manganese, <1 wt.% nickel and 50-55 wt.% phosphate (composition on dry basis). Hence efforts are focused on the recovery of zinc, iron and phosphate for preparing phosphating

solution and/or make-up feed. Among the various methods proposed for reclaiming phosphating sludge, pyrometallurgical processing - reduction sintering processes, for recovering the metals zinc, iron and nickel in addition to sodium phosphate; wet chemical processing by leaching constituents with acids and bases and reusing them in the preparation of phosphating solutions; and digestion with mineral acids, removal of constituents and their re-use are prevalent.

United States Patent 5,350,517 [397] describes a process in which the phosphating sludge is digested with nitric acid, the iron is selectively extracted with liquid/liquid extraction and the extract thus obtained is reused in the preparation of zinc phosphating solution. The extractant used is monoester of 2-ethylhexyl alcohol with phosphoric acid in kerosene. The use of mineral acids for extracting zinc and phosphate ions from the phosphating sludge and subsequent use of the extract as a phosphating solution is also suggested in the British Patent 1545515 [398]. Besides, this patent also suggests the possibility of leaching phosphate from the undissolved residue containing iron and phosphate ions with alkali so that, ultimately, an iron-containing residue remains behind. The phosphate in the alkaline liquor is precipitated as zinc phosphate and may also be used for the preparation of phosphating solution.

United States Patent 5,376,342 [399] describes a process which involves the following stages: (i) dissolution of the sludge in phosphoric acid; (ii) filtration of undissolved solids; (iii) precipitation and recovery of iron phosphate; and (iv) addition of requisite metals to the zinc and phosphate containing aqueous phase and recycling the resultant zinc phosphate solution to the zinc phosphating operation as a make-up feed. The iron phosphate, which precipitates in the process, may be used as an animal feed additive.

Mixing the phosphating sludge with an alkaline solution, drying the mixture and sintering it at 500-1300 °C in the presence of a reductant converts phosphate in the sludge to a water soluble phosphate salt, reduces the zinc and iron to their metallic state and volatilizes the zinc from the reaction zone. Leaching the sintered cake with water recovers the soluble phosphate and the iron [400].

United States Patent 5273667 [401] describes a process which involves collecting the phosphate sludge, dewatering using a filtering process, drying the dewatered sludge at an elevated temperature to a moisture content of less than 10 wt.% and reduc-

ing the particle size of the dried sludge to less than about 20 mesh. The dried and ground phosphate sludge has been found to be an excellent lubricant additive, which is suitable for use in lubricant formulations designed for the metal treatment, metal forming and industrial lubrication.

United States Patent 4986977 [402] suggests a method for treating the phosphating sludge with an aqueous base to achieve a pH greater than 10 that results in precipitation of iron hydroxide. The iron hydroxide is recovered and the aqueous phase is acidified to a pH of 7-10 to cause precipitation of zinc hydroxide.

Baldy [403] suggests that the phosphating sludge generated from automotive pretreatment process may contain up to 25 wt.% of oil and removal of oil is essential for the full recovery of all useful components. The removal of oil is accomplished by the addition of H<sub>2</sub>O<sub>2</sub> to an acidic dispersion of the sludge that displaces the oil from the remaining mixture. According to him, the recovery of zinc phosphate sludge involves the following four stages: Phase I is the separation of oil from the sludge. Phase II is the extraction of zinc, manganese and nickel from the sludge following digestion with phosphoric acid. Phase III is the conversion of the iron phosphate residue from phase II to pigment grade iron oxide and sodium phosphate that may be acidified to an iron phosphate concentrate.

The use of phosphating sludge in the process of clinker production is suggested as one of the possible mode of reclamation of such waste by Caponero and Tenorio [404]. Their study proves that an addition of up to 7.0% of phosphating sludge to the raw cement meal of Portland cement did not cause any damage to the clinkerization process. X-ray diffraction analysis shows that there is no significant modification in the yielded clinker proportional to the sludge additions, neither is there atypical phases formed with additions up to 5.0% of phosphating sludge. Differential thermal analysis of the mixture with up to 7.0% dry sludge additions does not show any significant difference from the analysis of the cement clinker raw meal. Additions of the phosphating sludge up to 5.0% significantly modify only the zinc content of the clinker that was produced. The major element of the sludge, zinc, shows an average of incorporation of 75%.

#### 4. SUMMARY

This review outlines the various aspects of phosphating. Although, numerous modifications were proposed recently, on the deposition technologies

to achieve different types of coatings and desirable properties such as improved corrosion resistance, wear resistance, etc., phosphate conversion coating still plays a vital part in the automobile, process and appliance industries, as it has unique advantages in the cost-wise placement among all the emerging deposition technologies and pays off the finisher with a handful of profit.

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