

STUDIES ON MANGANESE PHOSPHATING OF STEEL

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A new manganese phosphating bath which produces coating relatively at lower temperature within a reasonable time by the use of chemical accelerators has been developed. Bath formulation and operating conditions have been optimized by coating weight determinations. Corrosion resistance property of the resultant coatings has been evaluated in 3% NaCl by electrochemical methods such as potentiodynamic polarisation, linear polarisation and impedance measurements. Results of the electrochemical techniques have been complemented by salt spray, humidity and immersion tests. Porosity coatings has also been studied. Results show that the newer manganese phosphate bath gives good coatings at 353 K within 30 minutes. Addition of nitrates of various metals as accelerator produces thicker coatings. Corrosion studies have shown that the corrosion resistance of the resultant coatings are much superior than the conventional coatings.

Keywords: Phosphating, conversion coating, steel, manganese phosphating.

INTRODUCTION

Phosphate coatings are transformations of metal surface into a coating having non-metallic and non-conductive properties. They are widely used commercial processes to pretreat surfaces i) to receive and retain paint and to protect surfaces against underpaint corrosion, ii) for bonding with other coatings, iii) for metal forming operations such as cold extrusion by providing a base for drawing compounds and lubricants and iv) to improve corrosion resistance by providing a good base for waxes and rust preventive oils. The most widespread use of phosphate coating is to prolong the useful life of paint finishes and hence it plays a significant role in the entire metal finishing industry. Manganese phosphate coatings are mostly used where high coating thicknesses are necessary. Most of the manganese phosphating bath which are in current use require high temperature 363 - 368 K and longer treatment time (60 - 150 min) which is a luxury for energy conscious industries. It is therefore necessary either to reduce the treatment temperature or time or both. In view of the above, the present work aims to develop a newer manganese phosphating bath which operates at a much lower temperature and time. Attempts have been made to standardise conditions for

phosphating and to develop a newer bath formulation which results in a thicker, corrosion resistant coating.

EXPERIMENTAL

Mild steel specimens of size 5 cm x 2 cm were used for coating weight and other evaluation while specimens of size 5 cm x 1 cm were used for electrochemical studies. Specimens were pickled in inhibited hydrochloric acid solution for 5 minutes, washed with water, rinsed with distilled water and dried.

For phosphating, the bath containing phosphoric acid and manganese salt were used. Phosphating was done by a simple immersion for 10 - 60 minutes. Various addition agents A, B and C were added in the concentration range 0.01 to 1%. The performance of the resultant coatings were evaluated in 3% sodium chloride.

Coating weight determination and visual examination of the surface were used for studying the coating formation while complete immersion tests in 3% NaCl, salt spray test, humidity test and polarisation technique were used for evaluating the coating performance. The porosity of the coating was assessed by the chemical method [1], water absorption test, and by monitoring the oxygen reduction

current in a solution of 0.01 N NaOH (pH 12) at a cathodic potential of $-550 \text{ mV}_{\text{SCE}}$ [2].

RESULTS AND DISCUSSION

Coating weight

Although various bath control parameters are involved in phosphating operation, coating weight is used as the prime factor in assessing the quality of phosphating and is widely practised in industries. The coating weight is used as one of the tools to standardise the bath and operating parameters. To study the influence of bath variables on the coating weight, certain parameters have been varied while the others are kept constant. The variables were: Ratio of phosphoric acid to manganese salt (A/S ratio), Treatment time (10-60 min), Operating temperature (343-363 K), type and accelerator concentration.

Effect of A/S ratio

Coating weights of phosphated samples were determined for samples treated in various A/S ratio using 5% phosphoric acid and manganese salt concentration in the range of 1.25 to 5% at 348 K for various treatment time (10 to 60 minutes) and shown in Fig. 1. This study indicates that the coating weight is maximum only when the A/S ratio is 4:1 and it is minimum at 1:1. It also shows that the increase in the coating weight is very high within 30 minutes.

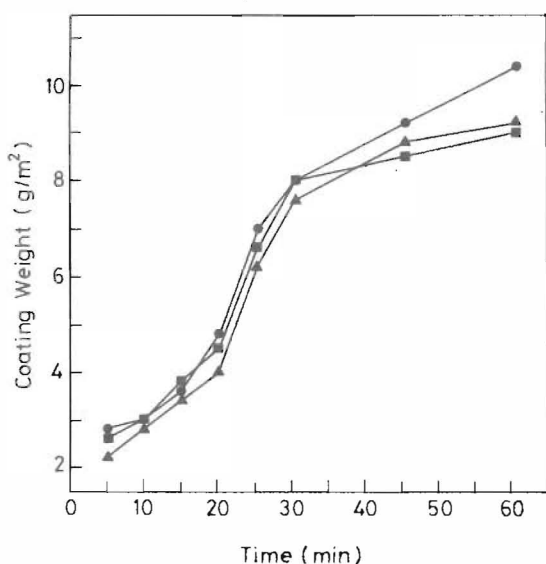


Fig. 1: Effect of A/S ratio on the coating weight of phosphated steel (▲) A/S ratio 1:1; (■) A/S ratio 2:1; (●) A/S ratio 4:1

Similar coating weight determination study indicates that increasing the phosphoric acid content either above or lesser than 5% resulted in thin coatings. The results reveal that phosphoric acid content as well as A/S ratio are critical factors in formulating the manganese phosphating bath.

Effect of treatment time and temperature

Coating weights were determined for samples treated in the bath containing 5% phosphoric acid and 1.25% manganese salt for various immersion time (10 to 60 minutes) at 343 - 363 K. The results are given in Fig. 2 which shows that for the formation of phosphate layer, the optimum temperature and time being 353 K and 30 minutes respectively.

Effect of accelerator

Nitrates of various metal cations are added in the concentration range of 0.01 to 0.1% and its effect on coating weights have been studied and given in Fig. 3. The operating temperature and time were 353 K and 30 minutes respectively. Thus effective manganese phosphating formulation is phosphoric acid 5% - temperature 353 K; manganese salt 1.25% - time 30 min and accelerator 0.05%.

Polarisation technique

Though the standard test for determining the corrosion resistance of phosphating coating involves the use of accelerated salt spray test, which is time consuming, electrochemical methods based on polarisation is utilised for

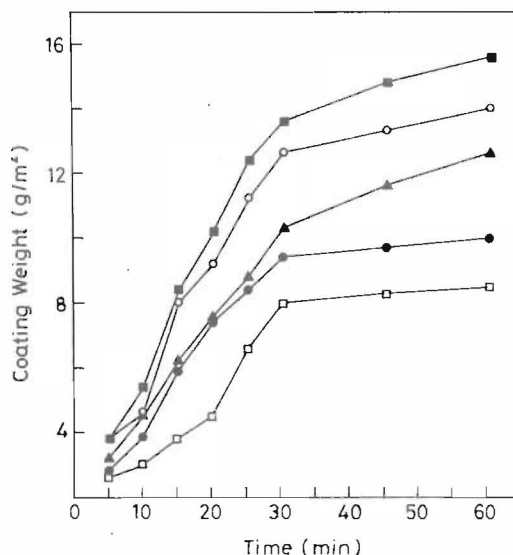


Fig. 2: Effect of temperature on the coating weight of phosphated steel (■) 343 K; (●) 348 K; (▲) 353 K; (○) 358 K; (◆) 363 K

rapid characterisation of coating [3-6]. Typical polarisation curve for mild steel with and without phosphate coating in 3% NaCl is given in Fig. 4 and the polarisation parameters are summarised in Table I.

Polarisation parameters are very useful for differentiating the corrosion performance of phosphate coatings from different baths. The corrosion current values for phosphated samples are much lower. This indicates that dissolution of base metal shows down in presence of phosphate coatings because of barrier and the less soluble nature of the coating in the corrosive environment than the base metal. Moreover, phosphate coating consists of a relatively non-conducting layer of strengite, $Mn_3(PO_4)_2 \cdot 2H_2O$ and Huealite $(Mn,Fe)_5 H_2(PO_4)_4 \cdot 8H_2O$.

Anodic Tafel slope is higher in presence of coating indicating that the dissolution of the base metal takes place through a different mechanism. Thinner coatings (lower coating weight) from bath IV shows very low corrosion current. This may be due to either low porosity or insoluble nature of the coating or both. Generally solubility of the coating depends mainly on the structure and chemical composition.

In additive containing baths, especially in bath II and IV, the chemical accelerator, accelerates the base metal dissolution and thus a higher concentration of ferrous ion is introduced in the bath. Thus produced ferrous ion accumulates at the metal/solution interface and redeposits in the coating as

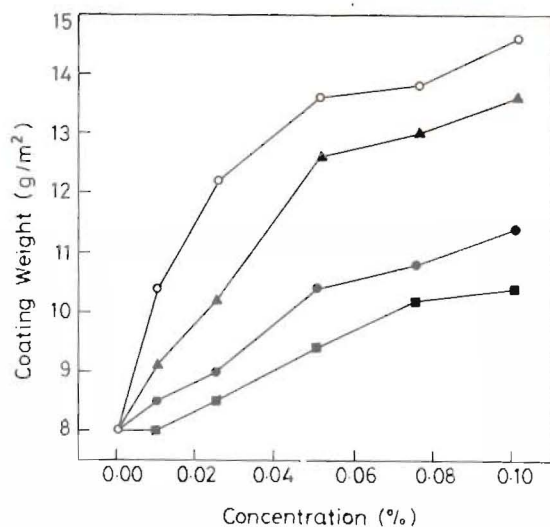


Fig. 3: Influence of additives on coating weight of phosphated steel (■) Blank; (●) With additive C; (▲) With additive A; (○) With additive B

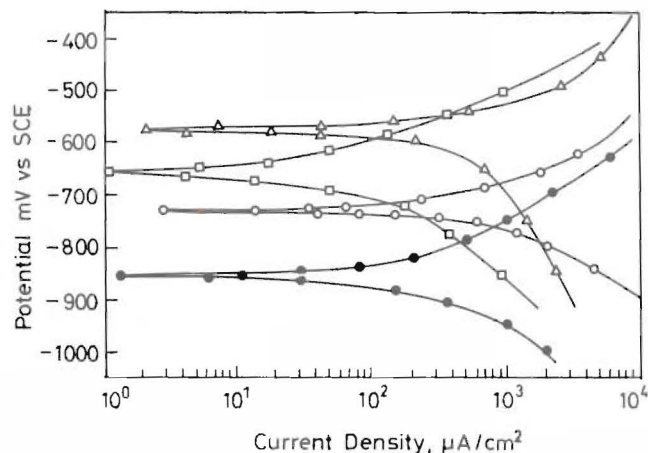


Fig. 4: Polarisation behaviour of phosphated steel in 3% NaCl (○) Blank; (●) With additive 'A' (▲) With additive 'B'; (□) With additive 'C'

manganese-iron phosphate (Huealite). The high corrosion resistance of such coatings was attributed not only to their higher content of Huealite, but also to their low porosity as mentioned latter.

Polarisation resistance, R_p , measured from linear polarisation resistance method is also given in Table I. From Table I, it is clear that presence of manganese phosphate coating increases the polarisation resistance in 3% NaCl which means that the corrosion resistance of phosphate coated samples is improved. The very high polarisation resistance value for the coating from baths II and IV indicates that the protection of the coatings from these baths is better than that of other baths. These results are in good agreement with those of potentiodynamic polarisation measurements and the accelerated tests.

TABLE I: Results of polarisation studies of phosphated steel in 3% NaCl

Bath	Accelerator	Corrosion potential mV vs SCE	Corrosion current $\mu A/cm^2$	Tafel slope b_a	$R_p \Omega cm^2$
Control	----	-725	10 mA	40	52
I	----	-560	300	65	200
II	A	-850	100	90	350
III	B	-750	140	120	250
IV	C	-650	30	160	400

TABLE II: Results of other tests

Type of phosphate	Immersion test	Humidity test	Salt spray test
Pickled steel	Solution turns brownish yellow and the specimen corroded severely	Heavily rusted	Severely corroded
Zinc phosphated	Slight colouration of the solution and few rust spots	Slightly corroded	Slightly corroded
Manganese phosphated from Bath I	-do-	-do-	-do-
Bath II	Very slight colouration of solution	Few spots	Few spots
Bath III	-do-	-do-	-do-
Bath IV	-do-	-do-	-do-

* Immersion in 3% NaCl for 24 hours

** 100% R H for 24 hours

*** 3% NaCl salt spray for 96 hours

Other tests

Phosphated samples were also subjected to immersion in 3% sodium chloride, salt spray test and humidity tests and the results are given in Table II. These data show that presence of phosphate coating retard the corrosive attack, but these tests are not able to differentiate the corrosion performance of various phosphate coatings. Anyway the results of the electrochemical tests were complemented by these results.

Coating porosity

Porosity of manganese phosphate coatings depend on many factors such as coating weight, crystal morphology, phosphating bath composition and surface pre-treatment methods etc. The porosity values of the coatings were measured qualitatively (ferroxyl methods and water absorption test) and quantitatively (electrochemical method) and the results are listed in Table III.

The results of the tests indicate that the porosity is low for samples phosphated in bath containing additives. Higher reduction in coating porosity was observed for coating from

 TABLE III: Results of porosity measurements
Effect of additives

Bath	Chemical method		Electro-chemical test $\mu\text{A}/\text{cm}^2$
	Ferroxyl test Points/ cm^2	Water adsorption g/m^2	
	---	6.6	30
I	4-6	31.5	16
II	2-3	23.2	5
III	2-4	29.9	11
IV	1-2	21.1	3

bath IV which has additive C. This may be attributed to the involvement of these additives in the manganese phosphate crystal nucleation process which is the most important reaction in the phosphating process. The density of nuclei formed determines the properties of the manganese phosphate coatings. A large number of nuclei results in a fine grained coating. If the nuclei are to be formed, the solution has to be supersaturated with manganese phosphate which is possible if the hydrogen ion consuming reactions on the steel can be speeded up. The additives are oxidizing in nature and therefore consume hydrogen and speed up the reaction. Thus the solution is supersaturated and more nuclei are formed. In addition to the enhancement of the nucleation, the higher dissolution rate of base metal in presence of additives also results in a faster growth of the phosphate crystals. This results in higher coating weight in shorter time.

Addition of additive C alone brings out improvement in the coating performance due to its influence in crystal re-organisation stage in which the formed phosphate dissolves and re-precipitates very rapidly. During this re-precipitation, some amount of dissolved iron from the base metal co-deposits and this not only re-organise the phosphate crystals but also change the structure of the coating. Due to this re-organisation of the phosphate crystal, the performance of coating gets improved significantly.

CONCLUSION

A new bath has been developed which gives good coating within reasonable time and temperature. The phosphoric acid content and the ratio between acid and manganese salt is a critical factor in formulating the bath and optimum being 5% and 4:1 respectively. Addition of accelerators resulted in better phosphate coating within reasonable time (30 min) and

temperature (353 K). Corrosion studies have shown that phosphate coating improves the corrosion resistance of the base metal. Coatings from bath IV (additive C) is more corrosion resistant. Electrochemical methods can be used to evaluate the corrosion resistance of the resultant coatings. Results are obtained rapidly and complimented by other standard tests which takes much longer time. Porosity measurement shows that the coatings from bath IV (additive C) is less porous. The corrosion protection ability of phosphate coating mainly depends on the porosity rather than thickness of the coating. Since most of the commercial baths available today requires temperature of 368 ± 10 K for 30 min, this is energy saving, economical formulation and will find wider applications.

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