



ACCELERATION OF LOW TEMPERATURE ZINC PHOSPHATING; GALVANIC COUPLING VS. ELECTROCHEMICAL TREATMENT

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ABSTRACT

Galvanic coupling and electrochemical treatment are some of the possible methods of acceleration of low temperature phosphating. Galvanic coupling of mild steel substrate with the cathode materials such as titanium, copper, brass, nickel and stainless steel accelerates iron dissolution and enables an earlier attainment of the point of incipient precipitation (PIP), that is, the point at which saturation of metal dissolution occurs and higher coating weight results and thus possess better corrosion resistance. Electrochemical treatment influences the phosphating process in a different way. The present paper aims to compare these two methods of low temperature zinc phosphating process and identify the viability of these process for industrial application.

Key words: Zinc phosphating, Galvanic coupling, Anodic coating, Cathodic coating.

INTRODUCTION

Low temperature phosphating baths needs to be accelerated by chemical or mechanical or electrochemical methods¹⁻⁴. In this review, two different low temperature phosphating processes, one accelerated by galvanic coupling and the other accelerated by electrochemical treatment is compared. Our earlier papers⁵⁻⁸ have addressed the influence of galvanic coupling on the deposition of phosphate coating on mild steel and evaluation of their corrosion behavior. Galvanic coupling of mild steel substrates with the other cathode materials proved to be beneficial in accelerating the low temperature phosphating process. Both cathodic and anodic treatment influence the deposition of zinc phosphate coatings on mild steel anode⁹⁻¹³. The objective of this review is to compare these two different techniques in acceleration of low temperature zinc phosphate coatings and their effectiveness in corrosion resistance.

EXPERIMENTAL

Phosphating processes

The chemical composition of the bath, control parameters and operating conditions used for acceleration using galvanic coupling and for cathodic and anodic electrochemical treatments are given in Table 1.

Table 1: Chemical composition, control parameters and operating conditions of zinc phosphating bath

Variable	Galvanic coupling	Cathodic treatment	Anodic treatment
ZnO (g/L)	5	2.04	2.04
H ₃ PO ₄ (85%) (mL/L)	11.3	16	16
NaOH (g/L)	-	6.7	6.7
NaNO ₂ (g/L)	2	-	0.5
Control parameters			
pH	2.70	2.90	2.90
FA Value (Points)	3	3.8	3.6
TA Value (Points)	2.5	29.7	29.0
FA : TA	1 : 8 : 33	1 : 7.82	1 : 8.06
Operating condition			
Temperature (°C)	27	27	27
Time (min)	30 min	60	60
Current density (mA/cm ²)	-	4,5 and 6	4,5 and 6

In the case of electrochemical treatment and galvanic coupling method, the bath components are essentially the same except there is a little difference in the quantities used. NaOH is used in the electrochemical treatment, which is not used in the galvanic coupling method. NaNO₂ is used in the galvanic coupling method as an accelerator. During anodic treatment, NaNO₂ is added to prevent polarization of the cathode. The composition of the MS substrate and the cathode materials used for phosphating using galvanic coupling were given elsewhere⁵.

The size of the MS substrates used for the galvanic coupling method and the electrochemical treatment were 8 cm × 6 cm × 0.2 cm and 6 cm × 5 cm × 0.2 cm, respectively. The details of surface preparation of mild steel substrates, experimental setup used for the cathodic and anodic electrochemical treatments and the galvanic coupling method were given in the earlier papers^{5,9,11}.

In the case of galvanic coupling method, the mild steel anode is galvanically coupled to cathode materials such as titanium (Ti), copper (Cu), brass (BR), nickel (Ni) and stainless steel (SS) of varying area ratios (anode to cathode area ratio 1 : 1, 1 : 2 and 1 : 3) and immersed in zinc phosphating bath for 30 minutes and the coating was deposited⁵.

In the electrochemical treatment, deposition of coatings were carried out under galvanostatic conditions at 4, 5 and 6 mA/cm² applied using a potentiostat/galvanostat (ACM. Instruments, UK : Model : Gill AC)^{9,11}.

The structural characteristics of the coatings were evaluated by X-ray diffraction measurements using Cu K α radiation. The surface morphology of the coatings was assessed by scanning electron microscope (SEM). The corrosion resistance of phosphate coatings was evaluated by immersion test, salt spray test and potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) studies. The details of the corrosion studies were reported elsewhere^{7,10,12,13}.

The ability of these coatings to prevent underfilm corrosion was assessed by salt spray test. Salt spray test was conducted by painting the phosphated steels with synthetic enamel paint (white). The edges of the painted substrates were scribed to the base metal with a sharp need be so that the base metal is exposed to the salt mist in the salt spray chamber (ASTMB 117-63). The spreading of corrosion from the X scribe, after 94 hours of exposure, was assessed and photographed^{8,10}.

Mechanism of coating formation

In anodic treatment and in the galvanic coupling method, the mechanism of coating formation is similar. i.e., the coating formation proceeds through two stages: metal dissolution and deposition of coating are the predominant reactions during the first and second stages. In the case of anodic treatment, the onset of phosphate coating occurs following the initial metal dissolution, displacement of protons away from the interface and attainment of point of incipient precipitation. Though there was progressive increase in iron dissolution, the coating weight was not increased as expected. The availability of regenerated phosphoric acid at the interface causes a drop in local pH, which attacks the base metal as well as the phosphate coating¹¹.

In cathodic treatment, during the initial stages, a thin layer of zinc deposits on the surface of the mild steel substrate with a simultaneous hydrogen evolution reaction. The consumption of available H^+ ions at the metal-solution interface results in a progressive rise in the interfacial pH and favors the conversion of soluble primary phosphate to insoluble tertiary phosphate. As a result, deposition of zinc phosphate occurs over the thin layer of zinc. The continued deposition of zinc and hydrogen evolution enables further deposition of zinc phosphate on adjacent areas. The available metallic sites (zinc) decrease with the progress in coating formation and it reaches almost a constant value. The mechanistic aspects associated with cathodic treatment resemble those of electrochemical deposition while the anodic treatment resembles the conventional phosphating process but with accelerated metal dissolution. The cathodic treatment enables the formation of a zinc-zinc phosphate composite coating on mild steel whereas the anodic treatment leads to the deposition of zinc phosphate and zinc-iron phosphate⁹.

Under phosphating using galvanic coupling, both metal dissolution and coating formation occur at the mild steel substrate whereas hydrogen evolution occurs at the cathode material (Ti/Cu/Ni/BR/SS). The decrease in the induction period is one of the significant effects of galvanic coupling. This is due to the higher dissolution of metal resulting from galvanic coupling which forces quicker consumption of free phosphoric acid at the metal solution interface and enables an earlier attainment of the point of incipient precipitation. The continuous evolution of hydrogen at the cathode enables deposition of zinc phosphate on the entire surface of anode. In the conventional phosphating, the hydrogen evolution also occurs at the mild steel anode but in phosphating using galvanic coupling, the surface sites for hydrogen evolution are shifted from mild steel anode to stainless steel or titanium cathode. Hence, it is presumed that more surface sites are available for phosphate coating formation which results in the increased coating weight⁵.

Characteristics of the coatings obtained by cathodic and anodic electrochemical treatments

The coatings obtained by cathodic treatment are gray in colour with bright metallic luster whereas those obtained by anodic treatment and galvanic coupling method are grayish white with no metallic luster. All the coatings obtained were uniform and exhibit excellent adhesion to the mild steel substrate when evaluated by a pull-off test with a pressure sensitive adhesive tape.

The porosity of phosphate coatings was assessed by the electrochemical method, which measures the oxygen reduction current density at -550 mV vs. SCE indicates the amount of porosity involved. The oxygen reduction current density values for coatings obtained by anodic treatment are in the range of 15-20 $\mu A/cm^2$, which indicates that coatings are relatively more porous than those obtained by chemical treatment. The

mild steel substrates coated using galvanic coupling have a low porosity value (in the range of 4-12 $\mu\text{A}/\text{cm}^2$) as compared to electrochemical treatment or conventional phosphating⁵.

From the X-ray diffraction studies, it was reported that the coatings obtained by cathodic treatment are rich in hopeite phase $\{\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}\}$ with elemental zinc. Unlike the phosphate coatings obtained by chemical treatment, they are mostly free from phosphophyllite phase $\{\text{Zn}_2\text{Fe}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}\}$ ⁹. Coatings obtained by anodic treatment though consists of both hopeite and phosphophyllite phases similar to those obtained by chemical treatment, they are rich in phosphophyllite phase¹¹. The phosphate coating resulting from galvanic coupling is richer in phosphophyllite phase, which is advantageous towards the alkaline conditions created during electrophoretic painting⁵.

The surface morphology of coatings obtained by cathodic treatment exhibits the formation of plate-or-flower-like-crystals, which is characteristics of the hopeite phase. The surface morphology of coatings obtained by anodic treatment exhibits the formation of needle-like crystals, which is characteristics of the phosphophyllite phase. SEM images of phosphate coatings obtained under galvanic coupling condition confirmed the presence of phosphophyllite rich phase and the more uniform and compact coating with reduced porosity^{5,9,11}.

Immersion test in 3.5% NaCl

Comparison of loss in weight in 3.5% NaCl after 24 hours of immersion of zinc phosphated (developed using galvanic coupling, chemical and electrochemical treatment methods) mild steel panels was shown in Fig. 1. The loss in weight due to corrosion after 24 h of immersion in 3.5% NaCl solution is 24.12 g/m^2 for uncoated mild steel, 13.12 g/m^2 for chemically phosphated mild steel, 1.3-1.7 g/m^2 for mild steels phosphated using cathodic treatment, 11.4-12.9 g/m^2 for mild steels phosphated using anodic treatment and 0.04 to 0.57 g/m^2 for mild steel substrates phosphated under galvanically coupled condition. This shows that the extent of corrosion protection offered by the phosphate coatings obtained by using galvanic coupling condition is higher when compared to chemical and electrochemical phosphating. Anodic treatment also offers much higher corrosion protection than the cathodic treatment and chemical method of phosphating^{5,9,11}.

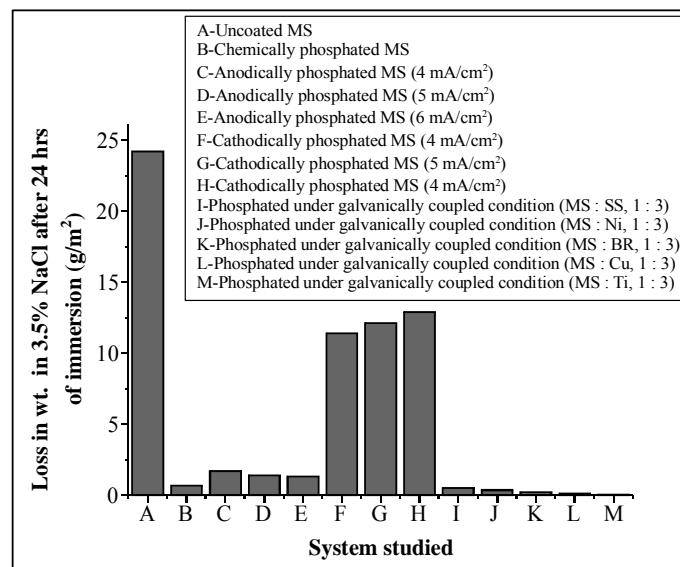


Fig. 1 : Comparison of loss in weight in 3.5% NaCl after 24 hrs of immersion of zinc phosphated mild steel panels using galvanic coupling, chemical and electrochemical treatment methods

Salt spray test

The spreading of corrosion from the 'X' –scribe after 96 h of salt spray test is relatively less for mild steel substrates phosphated under galvanically coupled condition and by anodic and cathodic treatments compared to that of unphosphated mild steel and demonstrate the effectiveness of phosphate coatings obtained by these treatments in resisting alkaline attack^{8,12,13,10}.

Potentiodynamic polarization and EIS studies

From the potentiodynamic polarization results, it is shown that the corrosion resistance offered by the zinc-zinc phosphate composite coatings obtained by cathodic treatment is very low in 3.5% NaCl solution. This is due to the dissolution of zinc from these coatings. In cathodic treatment increase in the immersion time (50 hrs) during phosphating increases the formation of non metallic nature of zinc phosphate coating which increases the corrosion resistance of the phosphated panels¹⁰. Corrosion potential of zinc phosphated mild steel panels in 3.5% NaCl developed using galvanic coupling, chemical and electrochemical treatment methods is compared in Fig. 2.

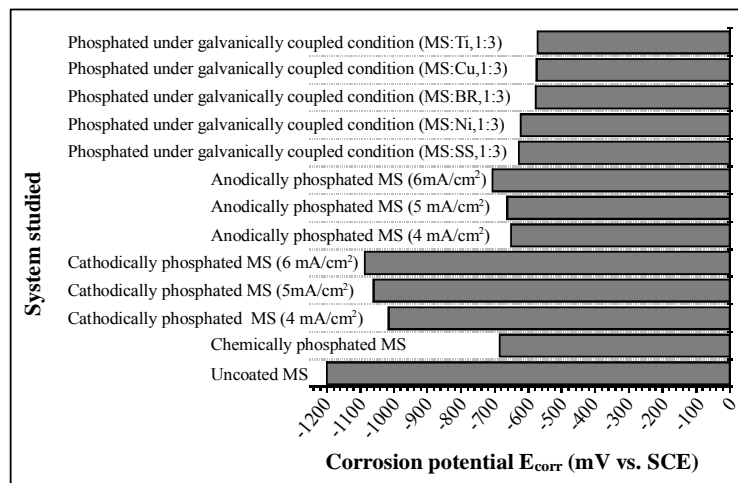


Fig. 2: Comparison of corrosion potential of zinc phosphated mild steel panels in 3.5% NaCl developed using galvanic coupling, chemical and electrochemical treatment methods

The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) of phosphate coatings obtained by anodic treatment at 6 mA/cm² are quite similar to those obtained by chemical treatment¹³. The E_{corr} values for the phosphated mild steel substrates using galvanic coupling shift towards less negative potential. The extent of shift in potential is largely a function of phosphate coating weight and the porosity of the coating. A larger anodic shift in corrosion potential is observed for panels phosphated using mild steel-titanium couple with 1 : 3 area ratio. Corrosion current densities of the phosphated mild steel substrates in 3.5 % NaCl developed using different phosphating processes are compared in Fig. 3. Lower current density is observed for substrates phosphated under galvanically coupled condition than the ones phosphated by other techniques⁷.

Electrochemical impedance spectroscopic results of cathodically phosphated mild steel exhibited a very low charge transfer resistance (around 10 ohm.cm²) (Fig. 4). The Nyquist plot of cathodic treatment exhibits a small semi circle and an inductive loop in the initial period and improvement of corrosion resistance was observed with time¹⁰. The Nyquist plot of phosphate coatings obtained by anodic treatment exhibit a semi-circle in the high frequency region followed by a diffusion tail in the low frequency region¹⁴. The appearance of a diffusion tail in the low frequency region is characteristic of Warburg impedance

behaviour and suggests that the corrosion of phosphate coatings in 3.5% sodium chloride solution is a diffusion controlled process. Usually the Nyquist plot of conventionally phosphated mild steel consists of a semi circle in the high frequency region followed by a diffusion tail in the low frequency region. Similar trend was obtained for anodically phosphated mild steel and for phosphate coatings obtained under galvanically coupled conditions, indicating that the process involves a single time constant. Literature reports on the evaluation of phosphate coatings suggest that capacitive and resistive contributions of the phosphate coatings in 3.5% NaCl vary directly and indirectly respectively with regard to the area of the coated panel.

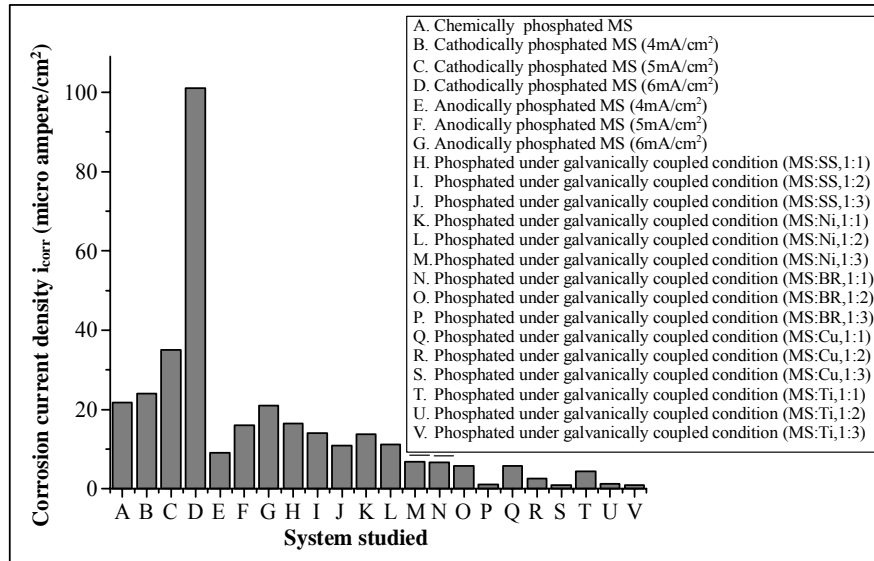


Fig. 3: Comparison of corrosion current density of zinc phosphated mild steel panels in 3.5% NaCl developed using galvanic coupling, chemical and electrochemical treatment methods

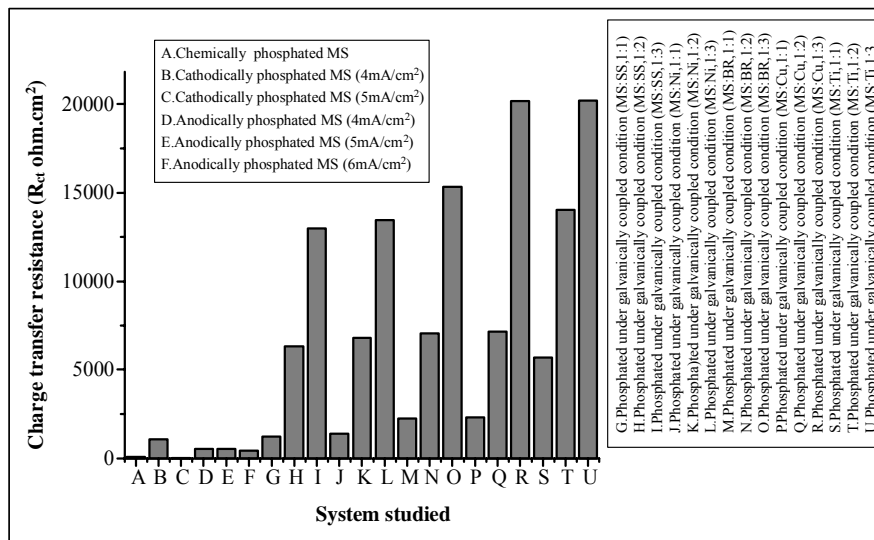


Fig. 4: Comparison of charge transfer resistance of zinc phosphated mild steel panels in 3.5% NaCl developed using galvanic coupling, chemical and electrochemical treatment methods

In electrochemical reactions, as a precipitated film, phosphate coating acts as a mechanical barrier between the substrate and the aggressive solution. Appearance of Warburg impedance confirms that the

mechanical barrier hinders the penetration of the aggressive species (here, 3.5% NaCl solution) and contributes to the protection behavior of phosphated panels. The reaction resistance increases with the thickness of the phosphate coatings¹⁵. The impedance studies confirmed that the corrosion behavior of the phosphated MS substrates under galvanically coupled condition in 3.5% sodium chloride solution is a diffusion-controlled process following the appearance of a Warburg impedance. The high values of charge transfer resistance and low values of double layer capacitance (Fig. 5) obtained for panels coated under galvanically coupled condition showed their better ability in preventing the on-set of corrosion⁷.

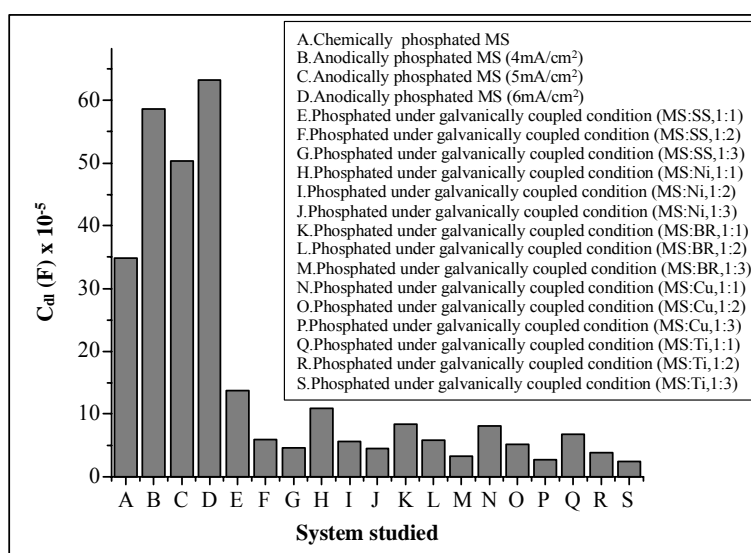


Fig. 5: Comparison of double layer capacitance of zinc phosphated mild steel panels in 3.5% NaCl developed using galvanic coupling, chemical and electrochemical treatment methods

Table 2: Comparison of zinc phosphating using galvanic coupling and electrochemical treatment methods

Parameter	Phosphating using galvanic coupling	Electrochemical treatment	
		Cathodic treatment	Anodic treatment
Bath constituents	Essential constituents-ZnO, H ₃ PO ₄ and NaNO ₂	Essential constituents-ZnO, H ₃ PO ₄ and NaOH	Essential constituents - ZnO, H ₃ PO ₄ , NaOH and NaNO ₂
Special additive	No Special additives	No special additives	No Special additives
Requirement of accelerator	Other than NaNO ₂ , cathode materials such as titanium, copper, brass, nickel and stainless steel were used to accelerate phosphating.	No accelerator is necessary	Accelerator addition is essential to prevent polarization of the cathode
Energy requirement	Capable of producing good quality coatings at low temp. without electrical energy	Capable of producing good quality coatings at low temperature at the expense of electrical energy	Capable of producing good quality coating at low temperature at the expense of electrical energy
Eco-friendliness	Less eco-friendly	More eco-friendly	Less eco-friendly

Cont...

Parameter	Phosphating using galvanic coupling	Electrochemical treatment	
		Cathodic treatment	Anodic treatment
Operational problem	No specific problem	Distintegration of graphite cathode; use of anode bag is essential to get good quality deposits.	Deposition of metallic zinc at the graphite cathode
Iron dissolution	The anodic to cathodic area ratio influences iron dissolution and it is high when compared to chemical phosphating	No iron dissolution	Heavy iron dissolution
Coating Weight	High. Increase in cathodic area exerts a strong influence on the mild steel anode and increases the extent of metal dissolution which in turn influences the amount of coating formation	High; permits to build the desired coating weight by increasing the deposition time	Medium; similar to conventional phosphating process
Sludge formation	Medium sludge formation	No sludge formation	Heavy sludge formation
Reaction at Mild steel and at cathode	Iron dissolution and phosphate deposition at mild steel and hydrogen evolution at cathode material	Deposition of zinc and zinc phosphate; hydrogen evolution at mild steel	Iron dissolution; phosphate deposition at mild steel and hydrogen evolution and deposition of metallic zinc at the graphite cathode
Means of attainment of PIP	Drifting protons away from the mild steel vicinity	Proton consumption for H ₂ evolution reaction	Drifting of protons away from the electrode vicinity
Coating composition	Zinc-iron phosphate (Phosphophyllite); Zinc phosphate (Hopeite)	Zinc phosphate (Hopeite phase); Metallic zinc	Zinc-iron phosphate (Phosphophyllite); Zinc phosphate (hopeite); Iron phosphate
Time taken for the attainment of PIP (Induction time)	Induction time decreases	Induction time increases	Induction time is similar to that of the conventional chemical phosphating
Colour and appearance	Gray	Gray with bright crystalline luster	Grayish white with no metallic luster
Uniformity of the coating	More uniform than conventional chemical phosphating	Uniform	Uniform
Surface morphology	Needle like crystals	Plate/flower-like crystals	Needle-like-crystals
Adhesion	Good	Good	Good
Porosity	Very low porosity (4-12 uA/Cm ²)	Very low porosity	More porous (15-20 uA/Cm ²) than conventional phosphating process

Cont...

Parameter	Phosphating using galvanic coupling	Electrochemical treatment	
		Cathodic treatment	Anodic treatment
Thermal stability	High when compared to conventional and electrochemical phosphating	Comparable with anodic and conventional phosphating process	Comparable with cathodic and conventional phosphating process
Chemical stability	High when compared to conventional and electrochemical phosphating	Relatively lower than conventional and anodic phosphating process	Relatively higher than cathodic phosphating process. Resembles that of conventional phosphating process
Immersion test	No red rust formation after 12 h of immersion in 3.5% NaCl solution, solution remains colourless. Weight loss after 24 h is lower than conventional phosphating and	No red rust formation after 12 h of immersion; solution remains colourless. Weight loss after 24 h is considerably lower than conventional and anodic phosphating process	No red rust formation after 12 h of immersion solution remains colourless. Weight loss after 24 h is lower than conventional phosphating; relatively higher than cathodic phosphating.
Salt spray test	Prevents spreading of corrosion from the scribe. Red rust formation at the scribe	Prevents spreading of corrosion from the scribe. White rust formation at the scribe	Prevents spreading of corrosion from the scribe. Red rust formation at the scribe
Potentiodynamic Polarization studies	E_{corr} Shift towards more anodic values (-685 mV-573 mV Vs SCE). I_{corr} of the phosphated MS decreases in the following order of the galvanic couple used during phosphating : M S-S S > MS-Ni > MS-BR > MS-Cu > MS-Ti. Increase in the cathodic to anodic area ratio (from 1:1-1:3) decreases the corrosion rate.	Greater shift in E_{corr} values towards cathodic values compared to uncoated mild steel (-1000 to -1100 mV Vs. SCE). With increase in immersion time the E_{corr} values shift towards more anodic values.	A slight shift in E_{corr} Values towards anodic values compared to uncoated mild steel (680 to 700 mV Vs SCE)
Electrochemical impedance studies	Nyquist plot exhibits only one semicircle. Appearance of Warburg impedance confirms that it is a diffusion controlled process. The corrosion resistance increases with the increase in the coating weight.	Nyquist plot exhibits a small semicircle and an inductive loop in the initial period. improvement of corrosion resistance with time	Nyquist plot exhibits a semicircle and a diffusion tail; semi-infinite and finite length diffusion behavior. Behaves like conventionally phosphated mild steel.

CONCLUSION

A comparison of the mechanism, characteristic properties and corrosion resistance of phosphate coatings obtained by phosphating using galvanic coupling and phosphating by electrochemical treatment is being done. It provides an insight on the strength and limitations of these treatment methods. Phosphating

using galvanic coupling increases the phosphate coating weight, uniformity of the coating and decreases the porosity of the coating which in turn increases the corrosion resistance of these coatings. The processing time is also shorter when compared to electrochemical phosphating and the process is cost effective as no electrical energy is involved. The limitations of using galvanic coupling method for phosphating is formation of higher amount of sludge and the use of sodium nitrite during phosphating. Phosphate coatings obtained by electrochemical treatment showed little less protection ability in 3.5% NaCl solution when compared to the galvanic coupling method. But the advantage of the cathodic treatment is its environmental friendliness where no NaNO_2 is used and in the anodic treatment only less amount of NaNO_2 is used when compared to galvanic coupling method. Out of this comparison, it can be concluded that phosphating using galvanic coupling and anodic phosphating are more viable for industrial usage.

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