

The Application of Phosphate Treatment for Chromium-Free Insulating Coating on Electrical Steel

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Nowadays, the effective replacements for chromium (+6), such as vanadium compounds, cerium compounds, titanate salts, phosphate and permanganate, are being extensively developed due to RoHS (Restriction of Hazardous Substances) for the hazard of chromium (+6). In this study, the performance and chemical reaction of phosphate salt solutions applied to electrical steel sheet by a roll coating process as an insulating film were investigated. The results show that a solution consisting of Al^{+3} , Mg^{+2} and PO_4^{-3} in the correct composition range provided good surface resistance and good adhesion after annealing within the optimal molar ratio range of $\text{Al}^{+3}/\text{PO}_4^{-3}$, 0.5–0.7/1.0, or of $\text{Mg}^{+2}/\text{PO}_4^{-3}$, 0.5–1.2/1.0. It was also found that both acrylate resin and tetraethoxy silane imparted the adhesion of film before and after annealing. The corrosion resistance of this film descended with the increase in NO_3^- content in the phosphate salt solution due to the $\text{Fe}^{+2,3}$ content becoming in excess in the insulating film. In the heating process, some reducing or oxidation reactions occurred between the phosphate(ite) and the acrylate resin latex. After the above work, an environmentally friendly insulating coating with high performance was achieved, which possessed good properties, such as surface resistance, corrosion resistance, heat resistance and adherence.

1. INTRODUCTION

Chromium (+6) has been widely applied to surface treatment on metal as a corrosion inhibitor on account of its high performance and low cost. However, an effective alternative of chromium (+6) is being extensively developed due to the hazard of chromium (+6). Phosphate salt, which is composed of phosphoric acid, magnesium ion and alumina ion, and is a potential replacement for chromate salt, is widely used as an insulating coating for electrical steel with high electrical resistance.⁽¹⁻²⁾ However, the phosphate coating substantially tends to become powdery during steel-making processes such as slitting, punching, or to become sticky and less rust-resistant due to absorbing moisture in a high humidity environment. To overcome these drawbacks, various coating compositions consisting of zirconium compounds, titanium compounds, silicates and phosphate salts have been studied and disclosed in many patents.⁽³⁻⁶⁾ In one such patent,⁽⁶⁾ zirconium compounds were used to enhance the rust resistance and powdery proof properties of the phosphate insulating coating due to the feasibility of a condensation reaction with phosphoric acid. Additionally, varied silane

compounds have also been widely studied to enhance the corrosion resistance of alumina alloy and steel. Sundararajan and Van Ooij prepared a protective film for use the steel surface by the polymerization of an ethoxysilane coupling agent, 1,2-bis(triethoxysilyl)ethane.⁽⁷⁾ However, such zirconium compounds, titanium compounds and silane coupling agents are expensive and not easily prepared for application. Improving the above poor properties of a phosphate insulating coating may be also achieved cheaply by some adjustments to the treating solution, for example, to the ratio of metallic ion/phosphate ion, and modifying the acid concentration. In this study, the optimal composition of the phosphate coating solution and the effects of additives, including inorganic acid and tetraethoxysilane, on the performance of coating were investigated in order to obtain a cheap chromium-free insulating coating for electrical steel sheet.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

In the following investigation, a coating solution was prepared with phosphoric acid, alumina nitrate,

magnesium oxide and some additives with the purity as listed as the Table 1, and the low silicon & low carbon non-oriented electrical steel sheet classified as 50CS1300 by China Steel Corporation (CSC) was coated with the insulating coating solution to be evaluated.

2.2 Test Procedure and Analyzing Method

The coating solution was prepared by dissolving the above mentioned chemicals in pure water in varied compositions, which were mainly made in various mole ratios of Mg^{+2}/PO_4^{-3} ranging from 0.3 to 1.5/1 as shown in Table 2, and Al^{+3}/PO_4^{-3} from 0.1 to 0.7/1.0 shown in detail as Table 3.

First the coating solution was coated onto the electrical steel sheet manually by bar coater with wet film thickness of about 6.9 micrometer. The coated panel was baked in the oven at the temperature of 300°C for 60 seconds, resulting in an insulating coating with a dry

film thickness of 0.8 gram/m² estimated by the non-volatile volume 10% and specific weight of solution 1.25.

The insulating coating properties of the coated specimen, including adhesion, heat resistance, surface resistance and rust resistance, were evaluated. The adherence of the coating was evaluated by 180°×Φ1/4" bend & 3M tape; and was classified with Grades 0~5. Grade 0 means that the coating fully peeled off; Grades 1~2 implies that the coating moderately peeled off; Grades 3~4 means slightly peeled; and Grade 5 that no peeling took place. Sometimes, electrical steel must be subjected to stress-relief annealing at 600°C~800°C protected by N₂ gas. During annealing, the heat resistance of the insulation film should be evaluated by a different adhesion test. This second adhesion test was executed with 180°×Φ1/4" bending after annealing and was classified with Grades 0~5 similar to the above classification. Rust resistance was measured both by

Table 1 Purity of Chemicals

Chemical	Phosphoric acid	Magnesium oxide	Aluminum hydroxide	TEOS	Nitric acid
purity	>85%	>95%	98%	98%	28%

Table 2 Result of Performance Test of Mg^{+2}/PO_4^{-3} Insulating Coating with Various Compositions

Mg^{+2}/PO_4^{-3}	Interlaminar resistance ($\Omega \cdot cm^2/sheet$)	Adhesion before annealing tested by bending & 3M tape tests (graded from 0~5)	Adhesion after annealing tested by bending test (graded from 0~5)
0.3/1.0	23	0~1	0~1
0.5/1.0	30	0~1	3~4
0.6/1.0	40	0~1	3~4
0.8/1.0	90	0~1	3~4
1.0/1.0	90	0~1	3~4
1.2/1.0	40	0~1	3~4
1.5/1.0	40	0~1	0~1

Table 3 Result of Performance Test of Al^{+3}/PO_4^{-3} Insulating Coating with Various Compositions

Al^{+3}/PO_4^{-3}	Interlaminar resistance ($\Omega \cdot cm^2/sheet$)	Adhesion before annealing tested by bending & 3M tape tests (graded from 0~5)	Adhesion after annealing tested by bending test (graded from 0~5)
0.1/1.0	10.0	0~1	0
0.3/1.0	15.0	0~1	0~1
0.5/1.0	23.3	0~1	3~4
0.7/1.0	40.0	0~1	3~4
0.9/1.0	40.0	0~1	0~1
1.0/1.0	40.0	0~1	0~1

the ratio of rust area after 5 hours salt spray test according to JIS Z2371, and by the corrosion current density with an electrochemical analyzer, Field Machine made by ACM, UK. Interlaminar resistance was measured by the interlaminar resistivity tester, model JIS-C-2550 made by TOEI Industry Ltd.

The elements depth profile and chemical bonding of phosphor in the insulating coating were also studied respectively, by a globe discharge spectrometer (GDS) and by X-ray absorption spectroscopy (XAS) the synchrotron radiation source, the 1.5 GeV third-generation storage ring of the National Synchrotron Radiation Research Center (NSRRC) of Hsinchu, Taiwan.

3. RESULTS AND DISCUSSION

3.1 Relationship of Coating Compositions with Performance of Insulating Coating

3.1.1 Relationship of Mg^{+2}/PO_4^{-3} mole Ratio with Performance of Insulating Coating

The coating solutions composed of Mg^{+2}/PO_4^{-3} were applied by bar coater and sequentially baked to form an insulating film on the electrical steel.

The performances of the insulating films with various mole ratios of Mg^{+2}/PO_4^{-3} were tested and the results are shown in Table 2. The interlaminar resistance ascended from 23.0 $\Omega.cm^2/sheet$ to 90 $\Omega.cm^2/sheet$ with the increases in mole ratio of Mg^{+2}/PO_4^{-3} from 0.3/1.0 to 1.0/1.0. However, when mole ratio of Mg^{+2}/PO_4^{-3} reached 1.2/1.0~1.5/1.0, the interlaminar resistance abruptly descended to 40 $\Omega.cm^2/sheet$.

Before annealing, adhesive properties of the Mg^{+2}/PO_4^{-3} film in this composition range was poor, being graded to Grade 0~1 as shown in Table 2, meaning that the film was almost entirely peeled off after the bending & tape-peeling test. After annealing, the adhesion of the film was impressively improved from Grade 0 to Grade 3~4 with the increases in the molar ratio of Mg^{+2}/PO_4^{-3} to 1.2/1.0.

3.1.2 Relationship of Al^{+3}/PO_4^{-3} mole Ratio with Performance of Insulating Coating

The coating solutions composed of Al^{+3}/PO_4^{-3} applied to electrical steel as an insulating film had a performance similar to the above Mg^{+2}/PO_4^{-3} solution and the test results of the insulating films with various mole ratio of Al^{+3}/PO_4^{-3} are shown in Table 3. The interlaminar resistance ascended from 10.0 $\Omega.cm^2/sheet$ to 40 $\Omega.cm^2/sheet$ with the increases in mole ratio of Al^{+3}/PO_4^{-3} from 0.1/1.0 to 1.0/1.0, respectively.

Before annealing, the adhesive properties of the Al^{+3}/PO_4^{-3} film in this composition range was also poor, graded to Grade 0~1 as shown as Table 3, meaning that the film was almost entirely peeled off after bending & tape-peeling tests. After annealing, the adhesion of the film was enhanced by increasing the amount of Al^{+3} , rising from Grade 0 to Grade 3~4 within the optimal range of Al^{+3}/PO_4^{-3} , 0.5~0.7/1.0.

From the above results, the optimal compositions of Mg^{+2}/PO_4^{-3} and Al^{+3}/PO_4^{-3} were the molar ratios of 0.5~1.2/1.0 and 0.5~0.7/1.0, respectively to obtain the best adhesion of the insulating coating after annealing.

3.1.3 Effect of Additives on Performance of Insulating Coating

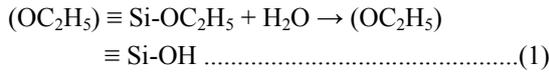
TEOS, acrylate latex resin and nitrate ion was added to the phosphate solutions with 0.3/1.0 Al^{+3}/PO_4^{-3} to further enhance the properties of the insulating film.

TEOS may be hydrolyzed as Equation 1 and can sequentially link with each other in condensation reactions, such as by Equations 2 and 3, in acidic or basic condition. The condensation reaction of TEOS with the hydroxyl group of phosphate compounds is presumed to occur as Equation 4. This reaction will enhance the polymerization of phosphate compound and consequentially improve the properties of the phosphate coating. In the results shown as Table 4, it can be seen that the adherent property of the coating after annealing ascended to Grade 4, with almost no peeling occurring, through the addition of TEOS at the weight ratio of TEOS/ phosphate solution, 10~50/100, and before annealing, also improved slightly to Grade 2 in the weight ratio of 20~50/100.

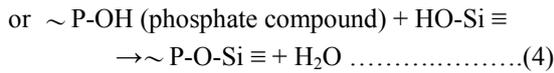
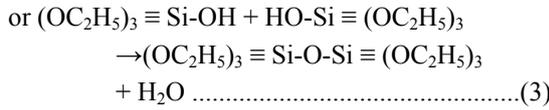
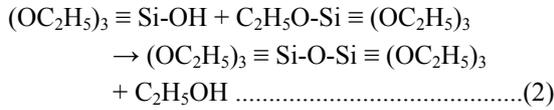
Table 4 Properties of Phosphate Coating with Various Contents of TEOS or Acrylate Resin

TEOS added to phosphate solution				Acrylate latex resin added to phosphate solution			
TEOS/Sol. (by Weight)	Interlaminar resistance ($\Omega.cm^2/sheet$)	Adhesion before annealing	Adhesion after annealing	Resin/Sol. (by Weight)	Interlaminar resistance ($\Omega.cm^2/sheet$)	Adhesion before annealing	Adhesion after annealing
5/100	15.0	0~1	3~4	5/100	15.0	1	0~1
10/100	12.5	1~2	4	10/100	12.5	2	2~3
20/100	12.5	2	4	20/100	12.5	3~4	2~3
50/100	15.0	2	4	50/100	15.0	3~4	2~3

Hydrolysis reaction:



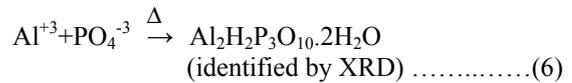
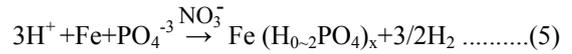
Condensation reaction:



Generally, acrylate resin with good flexibility is added to the inorganic insulating coating to enhance the adhesive property of the inorganic insulating coating before annealing, however acrylate resin could be heat-degraded during annealing and result in a poor adhesive property of the coating after annealing expectantly. It was also observed that adhesive property of the coating before annealing ascended to Grade 3~4, as only slight peeling occurred, at the weight ratio range of resin / phosphate solution of 20~50/100 before annealing, as shown in Table 4. Moreover the heat resistance unexpectedly also improved slightly to Grade 2~3 as evaluated by the bending test, at the weight ratio range of resin / phosphate solution of 10~50/100. Additionally, some cracks were apparent on the surface of the coating with resin due to the heat degradation of organic polymer at 750°C, as observed by SEI (Secondary Electron Image), and shown as Fig. 2. In comparison, no cracks appeared on the surface of pure inorganic coating shown as Fig. 1. From the above results it was inferred that for the coating which was mixed with resin after annealing, the bending stress can be partially

relieved through the cracks. Consequentially, this mixed type coating was determined to be more flexible than the pure inorganic coating and possessed better adhesive properties after annealing.

Nitrate ion plays a role in accelerating the phosphate conversion reaction through the traditional processes such as dipping or spraying. Although, in this study, the chemical mechanisms of film forming of the phosphate insulating coating by both roll coater and drying in place process is different from that of the traditional phosphate conversion coating, nitrate ion was still presumed to be influential in phosphate insulating coatings. Simple film-forming chemical equations for this insulating coating were hypothesized such that at the first stage, with the steel being covered with the coating solution, there is an etching by acid process to form a compound consisting of iron ions and phosphate at the interface between solution and steel, which is accelerated by nitrate ion as Equation 5. Then at the second stage, when the coating solution has been dried at 300°C, $\text{Al}_2\text{H}_2\text{P}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$, which was identified by XRD (X-Ray Diffraction pattern), is precipitated. Finally, an insulating film composed of the phosphate salts combining Fe with Al forms on the steel.



In this study, it was observed that the corrosion resistance of the phosphate films originating from the solutions with varied dosages of nitrate ion decayed with the additive amount of nitrate ion. The corrosion rate measured by electrochemical analyzer accelerated from 0.088 mm/year to 0.22 mm/year within the range of concentrations of NO_3^- from 0% to 21.0% and the

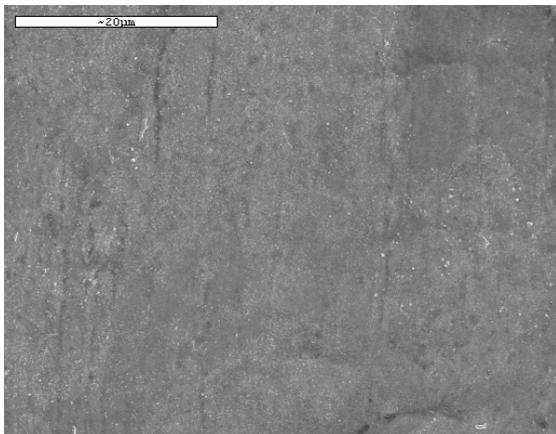


Fig. 1. SEI of phosphate coated samples without resin 750°C.

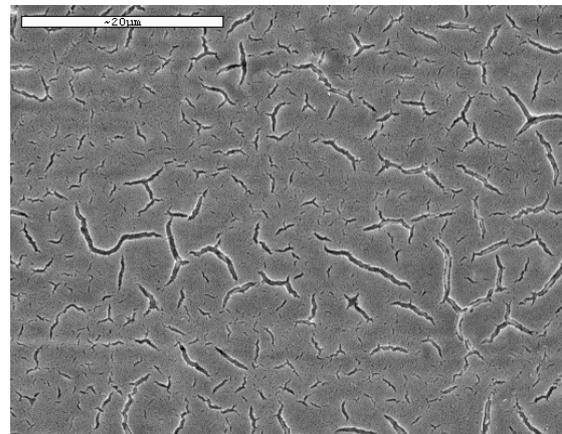


Fig. 2. SEI of phosphate coated samples with resin after annealing at after annealing at 750°C.

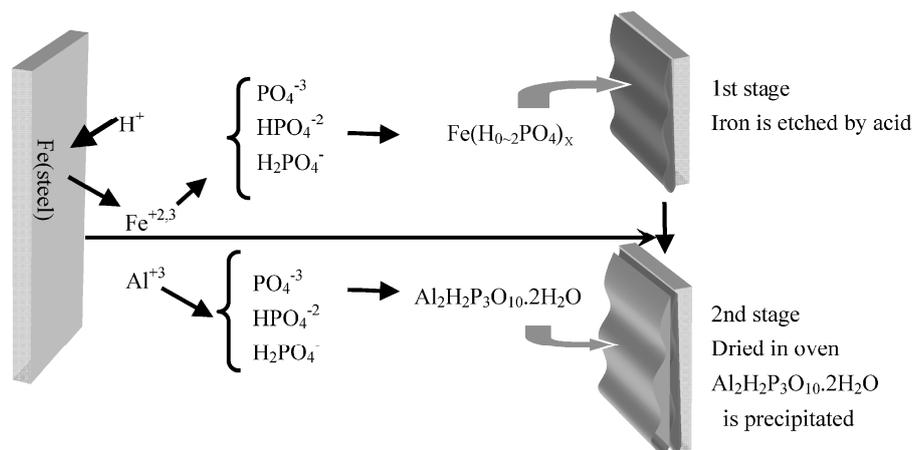


Fig. 3. Schematic diagram of film-forming stages of phosphate insulating coating by both roll coater and drying in place process.

corrosion area also steadily increased from 0% to 80% after SST 5 hours with increasing concentrations of NO₃⁻, as shown in Table 5. Those results reflected the excessive dissolving of iron into the film due to the activity of an acid etching reaction by NO₃⁻ as expressed in Equation 5. In the film, ferrous ion or ferric ion may

form phosphate salt with good properties, but if the ferrous ion or ferric ion becomes in excess, some oxide or hydroxide of iron with poor corrosion resistance is created. In the measurement of element depth profile by GDS, it is shown in Fig. 4 and Table 5 that the concentration of Fe on the skin surface of the insulating

Table 5 Result of Corrosion Rate of the Film Treated with Phosphate Solutions with Varied Concentrations of NO₃⁻

Weight % of NO ₃ ⁻	Atomic % of Fe on the skin surface of the insulating film measured by GDS as Fig. 4	Corrosion rate (mm/year)	Rust area ratio after SST 5 hours
0	25%	0.088	0%
2.8	37%	0.092	10%
15.6	80%	0.180	50%
21	82%	0.220	80%

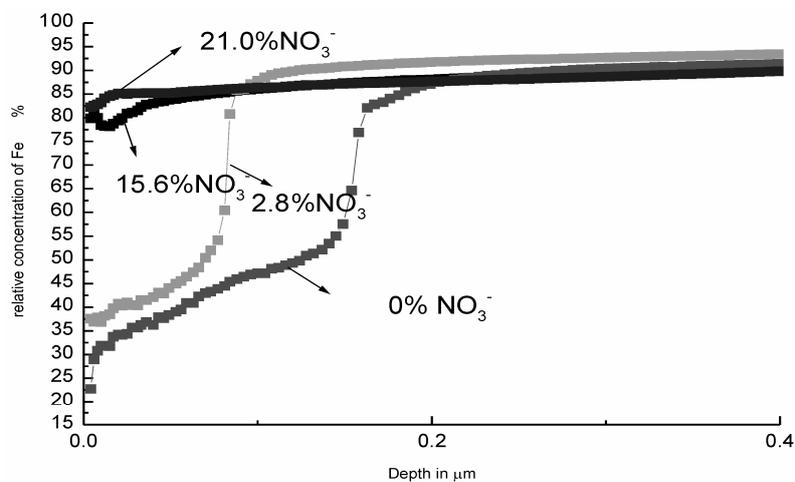


Fig. 4. The depth profile of Fe concentration in the film by GDS.

film increased with the increasing of weight % of NO_3^- , and that more and more oxide or hydroxide of Fe in the film results in a decay of the corrosion resistance.

3.2 Chemical Valence of Phosphor in the Insulating Coating

In the heating process, the dehydration and condensation reactions of phosphate coating are well known, but the change of chemical valence of phosphor has not been studied yet. For samples coated with either H_3PO_3 or Na_2HPO_4 and inorganic additives, such as H_3BO_3 or Al_2O_3 , the absorption spectra of P K edge show no change after the samples were baked at 300°C (see Fig. 5). However, the acrylate resin latex, seems to play roles of both oxidation agent and reducing agent. When latex was mixed with Na_2HPO_4 , a small portion of P^{5+} was reduced to P^{3+} , whereas when latex was mixed with H_3PO_3 , a large portion (about 70%) of P^{3+} was oxidized to P^{5+} . Finally, only the P^{5+} peak appeared in the XANES, as shown in Fig. 6, taken from samples annealed at 750°C in N_2 , indicating that P^{3+} in the coating has been oxidized to P^{5+} . It is also worth noting that the existing of latex makes the oxidation of P^{3+} being less complete.

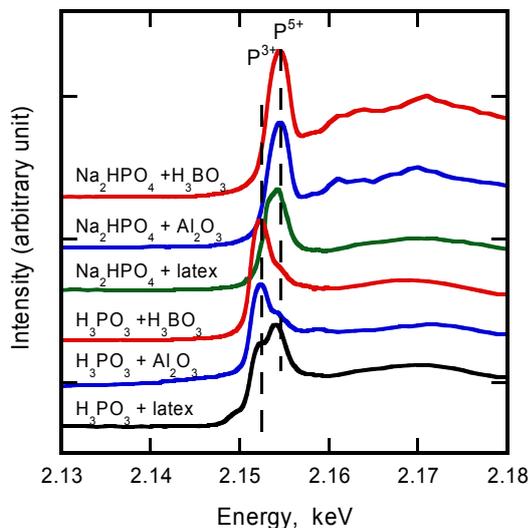


Fig. 5. Near edge absorption spectra taken from phosphate (-phate) coated samples cured at 300°C .

3.3 Performance of Phosphate Insulating Coating Commercialized

An optimal phosphate insulating coating as a replacement for chromate coating has been successfully applied, basically resulting from the above laboratory work. Some coating characteristics were evaluated and compared to those of the chromate one as in the following description.

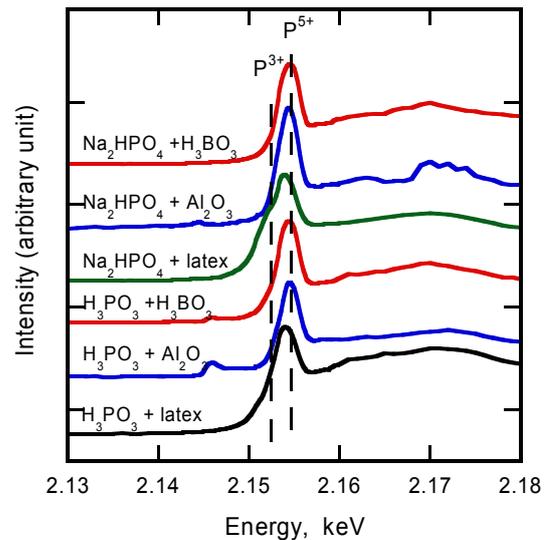


Fig. 6. Near edge absorption spectra taken from phosphate (-phate) coated samples after stress relief annealing.

The adherence of the coatings was evaluated by $180^\circ \times \Phi 1/4$ " bend & 3M tape and Erichsen $1 \text{ kg} / 50 \text{ cm} \times \Phi 1/2$ " impact respectively. The adhesive property of the phosphate coating was the same as that of the chromate one, in both bending and impact tests, respectively classified to be Grade 3 and Grade 2~3, shown as Fig. 7.

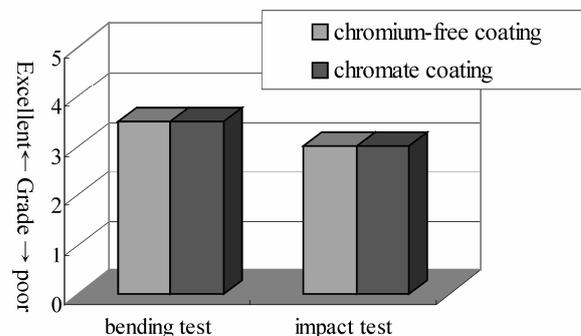


Fig. 7. Adherence of chromium-free (phosphate) and chromate coatings.

The heat resistance was compared at $600^\circ\text{C} \sim 800^\circ\text{C}$ protected by N_2 gas. After annealing, as measured by the bending test, the adhesion grade of phosphate coating was Grade 4, almost no peeling occurred, matching that of the chromate coating at $700^\circ\text{C} \sim 800^\circ\text{C}$. Conversely, at 600°C and 650°C , the adhesion of phosphate coating was evaluated to be Grade 3~4 and Grade 1, respectively, much worse than that of the chromate film, as shown as Fig. 8.

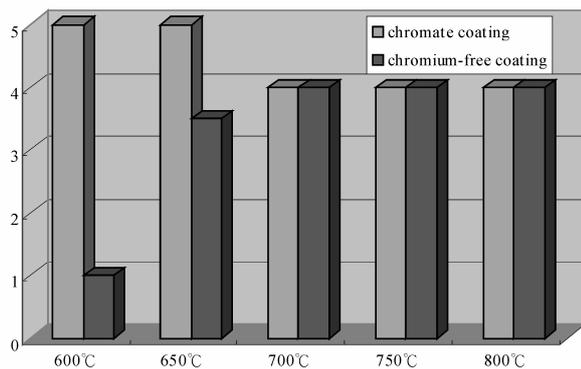


Fig. 8. Adherence of chromium-free (phosphate) and chromate coatings after annealing at varied temperature.

The corrosion and interlaminar resistance of this chromium-free coating with film thickness of 0.5 μm and 0.8 μm were also compared. The results of corrosion test shows that with film thickness of 0.5 μm the rust area of the chromium-free coating was 30~40%, significantly more than the 20~30% of the chromate one, as shown in Fig. 9; however, with a film thickness of 0.8 μm , the rust area of chromium-free coating decreased to about 10%, the same as the rust area of the chromate coating, as shown in Fig. 9. The interlaminar resistance of the chromium-free coating was 20~30 and 30~40 $\Omega\cdot\text{cm}^2/\text{sheet}$, respectively, with film thicknesses of 0.5 μm and 0.8 μm , as shown in Fig. 10, and was clearly superior to that of the chromate one.

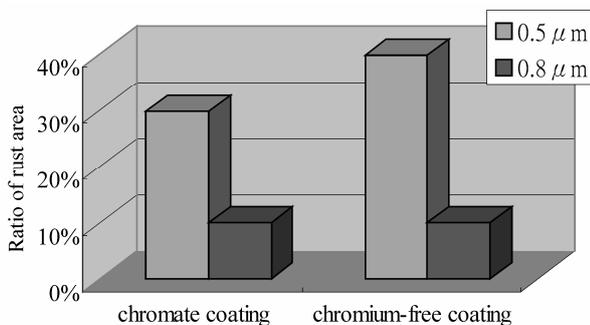


Fig. 9. Ratio of rust area on the insulation film with thickness of 0.5 μm and 0.8 μm after salt spray test.

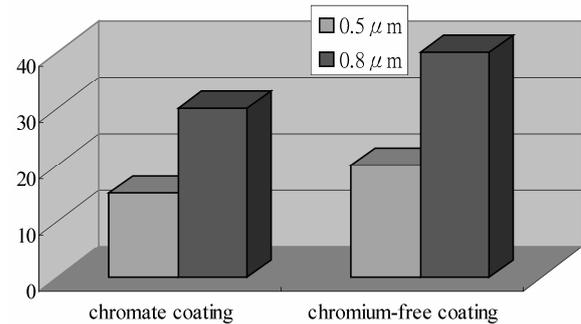


Fig. 10. The comparison of interlaminar resistance between chromium-free and chromate coating with thickness of 0.5 μm and 0.8 μm .

4. CONCLUSIONS

- (1) Phosphate insulating coating, only containing magnesium, aluminum and phosphate ions, on electrical steel can induce good surface resistance and good adhesion properties after annealing within the optimal molar ratio range of $\text{Al}^{+3}/\text{PO}_4^{-3}$, 0.5~0.7/1.0 or of $\text{Mg}^{+2}/\text{PO}_4^{-3}$, 0.5~1.2/1.0.
- (2) Both TEOS and acrylate latex resin can improve the adhesion before and after annealing.
- (3) Nitrate ion negatively affects the corrosion resistance of the phosphate insulating coating due to the excess of ferrous ion or ferric ion in the film resulting from the activating of an acid etching reaction by nitrate ion.
- (4) In the heating process, some reducing or oxidation reactions of phosphorus may occur between phosphate(ite) and the acrylate resin latex.
- (5) A newly developed chromium-free insulating coating has been successfully developed, which is based on an inexpensive phosphate compound and possesses good performances similar to those of chromium-containing coating, such as surface resistance, corrosion resistance, heat resistance and adherence.

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