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Summaries

Effect of conversion coatings on the performance of chlorinated rubber primer on aluminium

Aluminum gets attacked by different media and several surface treatments are used for effectively reducing corrosion. Of these, the versatile method is anodising the aluminum surface, the others being chromating and phosphating. However, these treatments give only short-term protection. The application of protective paint coatings over the surface gives long-term corrosion protection. The bond strength of paint coatings over bare aluminium is found to be far from satisfactory and hence conversion coatings are first given over which paints are applied. This paper deals with a study of the comparative performance of coatings with different conversion coatings applied over aluminium. The performance of the coatings has been assessed by adhesion tests, salt-spray tests and electro-chemical impedance tests. SEM (scanning electron microscopy) studies are also carried out to examine the surface morphology of the pretreated surfaces of aluminium.

L'effet des revêtements de conversion sur la performance de la peinture primaire au caoutchouc chloré appliquée à l'aluminium

L'aluminium est susceptible d'attaque par des moyens variés et il existe plusieurs traitements de surface pour réduire la corrosion superficielle d'une manière efficace. Parmi ces traitements, la méthode la plus versatile est d'anodiser la surface de l'aluminium, d'autres méthodes en étant le chromatge et le phosphatage. Cependant ces traitements ne fournissent qu'une protection de courte durée. L'application d'une peinture protectrice sur la surface lui donne une protection de longue durée contre la corrosion. La force du lien des revêtements de peinture sur l'aluminium nu a été trouvée loin d'être satisfaisante, donc on a appliqué d'abord des revêtements de conversion sur lesquels des peintures ont été appliquées. Nous présentons ici l'étude comparée de la performance des peintures appliquées sur des revêtements de conversion variés, eux-mêmes appliqués à l'aluminium. La performance des revêtements a été évaluée par le moyen des tests d'adhésion, des tests au brouillard salin, et de l'impédance électrochimique. Des études SEM (scannage par microscopie électronique) ont aussi été effectuées pour examiner la morphologie de la surface de l'aluminium pré-traité.

Der Effekt von Reaktionslacken auf die Leistung eines chlorierten Gummi Primers auf Aluminium

Aluminium wird von verschiedenen Medien angegriffen und bedarf daher mehrerer Oberflächenbehandlungen um Korrosion effektiv zu verringern. Eine sehr vielseitige Methode ist die Anodisierung der Aluminiumoberfläche; die anderen gängingen Methoden sind Chromierung und Phosphatierung, allerdings geben diese beiden nur eine kurzfristige Schutzwirkung. Das Auftragen einer schützenden Farbschicht gibt langfristigen Korrosionsschutz. Die Haftkraft von Farben und Lacken auf unbehandeltem Aluminium ist sehr unbefriedigend, und aus diesem Grund wird die Aluminiumoberfläche zuerst mit einem Reaktionslack vorbehandelt. Diese Studie vergleicht die Leistung und Merkmale von Lacken, die über verschiedene Reaktionslacke auf Aluminium aufgetragen wurden. Die Leistung der Lacke wurde mittels Adhäsionstests, Salz-Sprüh-Tests und elektrochemischen Impedanz-Tests geprüft. Die Oberflächenmorphologie der vorbehandelten Aluminiumoberflächen wurde mittels SEM studiert.

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Introduction

Surface preparation before painting plays a very important role in imparting adhesion to the coating and thus protecting the metal substrate against corrosion. Corrosion prevention by organic coatings is not solely obtained due to their performance. The pretreatment of metals before painting usually includes a phosphate, chromophosphate, conversion layer with a post rinse which has traditionally been an aqueous chromate solution. The corrosion performance is normally assessed on the basis of coating degradation, water uptake, the condition of the metal surface, and interface delamination of the tested samples. Traditionally the performances of the coatings are evaluated by conventional corrosion techniques, which include salt-spray humidity, atmospheric exposure and immersion tests.[1] However, more recently electrochemical methods have also gained acceptance. The primary application of these techniques is to measure and/or to predict the useful system life time. The advantages of using Electrochemical Impedence Spectroscopy (EIS) over dc and conventional techniques are numerous and the characterisation of coating/metal systems with EIS has been widely reviewed.[2-6]

There have been several pretreatment methods developed in the past to improve the adhesion of the paint to the metal surface.[7] The pretreatment processes developed range from surface cleaning to the surface conversion into different oxides to improve the adhesion of the paints to the metal surface.[8]

It has been a common practice to resort to the conversion of aluminium surfaces to achieve good adhesion of the primers or paints. The chromate conversion coating process, which has excellent corrosion protection properties, has been used now for several years to protect the metal from corrosion.[9] The use of chromates has come under severe restrictions because of their health hazards and has necessitated a need for environmentally benign corrosion-protection processes.[10]

Experimental

High purity aluminium (A1 – 99.99%, Si – 1ppm, Fe – 1ppm, Cu – 1ppm) was employed in all conversion coating experiments conducted in the laboratory. Aluminium panels of 150mm x 100mm, or 75mm x 50mm were used for the experiments. Degreasing was effected with trichloroethylene, then the panels were pickled in 5% NaOH solutions at 70°C for two minutes, followed by rinsing in running water, and then thoroughly with distilled water, subsequently etching the surface with 1:1 metric acid prior to the conversion coating process. Conversion coating treatment was carried out in different bath compositions by immersing the specimens in:

i)
ZnO	5g/l
H_3PO_4	11.3ml/l
$NaNO_2$	1.2g/l
NaF	0.5 to 1.0g/l
Time	10 to 15 minutes
Temp	30°C

ii)
ZnO	5g/l
H_3PO_4	11.3ml/l
$MnPO_4$	1.0g/l
$NaNO_2$	1.2g/l
NaF	0.5 to 1.0g/l
Time	10 to 15 minutes
Temp	30°C

iii)
CrO_3	16g/l
H_3PO_4	50ml/l
Time	5 minutes
Temp	45ºC

iv)
CrO_3	4g/l
$K_2Cr_2O_7$	3.5g/l
$NaNO_3$	0.6g/l
NaF	0.5 to 1.0g/l
HNO_3	3.5ml/l
Time	3 minutes
Temp	30°C

After phosphating, the panels were thoroughly rinsed in distilled water and then immersed for 10 to 15 seconds at 313 318K in 0.5% CrO_3, thus passivating the surface, after which they were dried in a stream of hot air or dried at 323 to 333 The low thickness coatings of phosphate, chromophosph and chromate on aluminium panels were measured with Electrophysik, mini-test 600 FN. Then a chlorinated rub coating of 50μ thickness was given on all the treated surface aluminum and cured at room temperature for 21 days.

Salt-spray exposure was conducted according to ASTM B11 which specified exposure in an enclosed chamber at 30°±5 to a fog generated from a 5% sodium chloride solution. T panels were inspected at periodic intervals and assigned a rat ing based on visual appearance.

For EIS testing, glass tubes were mounted on panels with organic coating as well as a conversion coating in order expose an area of 1cm². To the glass tube 3% NaCl solution added. Platinum foil and saturated calomel electrodes we placed in the glass tube containing 3% NaCl. The impedan measurements were made as a function of frequency betwe 10⁵KHz to 10⁷mHz using a sinusoidal voltage modulation 20mV. The experiments were conducted using a PAR mod 6310 impedance analyser. The pull-off test was conducted controlled phosphated chromophosphated and chromate panels, using a tTensometer 20 model. SEM Model Hitachi 3000H was utilised for surface examination studies.

Results and Discussion

Results from the impedance measurements are shown in or to relate them directly to the anti-corrosion primer perfo mance. The corrosion resistance of the primer was related the effects of different surface preparations on the aluminiu substratum. To determine the influence of the surface prepa
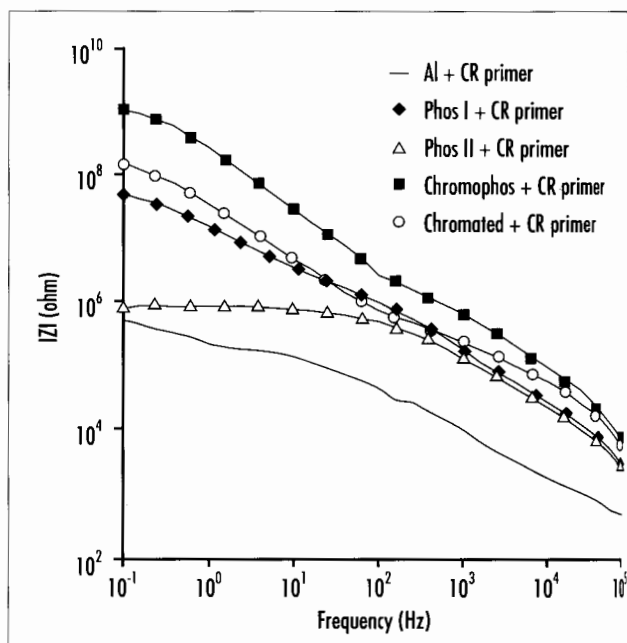

Figure 1:

tion, the authors had to compare the spectra of the samples to identify the stages of deterioration. At time t is approximately 1 hour (see Figure 1), when the specimen was assumed to be dry, its behaviour was capacitive for all the investigated frequency range 10^5 to 10^9Hz. Along with this behaviour, some electrochemical processes also happened under the primer along the interface conversion coating/substrate which was influenced by the surface preparation methods.

After ten days of immersion (see Figure 2) it was observed that the impedance of barrier-type conversion coatings was subjected to relatively large changes which could be attributed to processes of ion/water transport through the primer or to changes in the primer or at the interface primer/metal substrate due to the initial corrosion process, even when the visual appearance of the primer was obviously unchanged.
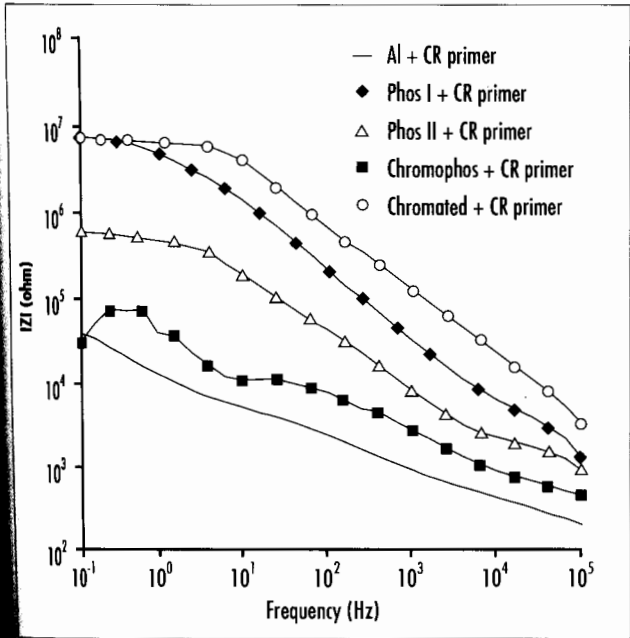

Figure 2:

Initially the coating acted as a pure dielectric, separating the metallic substrate from the aggressive external environment, and this behaviour resulted in a pure capacitive behaviour. The second step was water and ion uptake within the film, either homogeneously through the film or heterogeneously due to defects.

The impedance values for the coating system [z] were in the range of 1 x 10^6ohm cm². After 10 days of exposure, the [z] values were 1 x 10^5ohms cm². Similarly the impedance values of conversion coated panels viz phosphated, chromophosphated, and chromated showed a marginal decrease in [z] value of 1 x 10^7ohms cm² for phosphated and chromated, 1 x 10^5ohms cm² for phosphated II, and 1 x 10^6ohms cm² for chromophosphated respectively. The reason for the decrease in [z] value is due to the ingress of water in the primer and passivated aluminium substrate.

Finally, after 17 days of exposure (see Figure 3), it was found that the order of the variation of impedance values for chlorinated rubber primer over the conversion coating layer was found to be less. After 17 days of exposure, a decrease of impedance values was observed in all the conversion-coated primer systems. However, higher impedance values were observed for phosphate I and chromate primer systems, and the values were 10^5 to 10^6ohms cm² and 1 x 10^7ohms cm² respec-
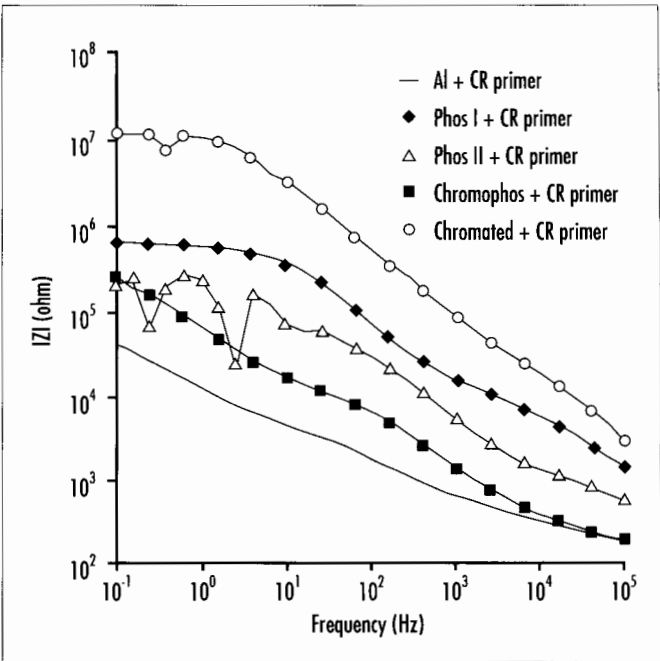

Figure 3:

In overall trends, the surface treatment by chromating and the application of a chlorinated rubber primer showed better performance.

Comparison between SST (salt-spray test) and EIS results

Salt-spray tests were also carried out in order to compare the EIS results with them. Results obtained after 720 hours of exposure indicated the absence of any corrosion spot on all systems. These results lead to the conclusions that all coatings exhibit non-distinguishable protective properties. In EIS the undamaged test area was exposed to 3% NaCl solution. EIS measured the diffusion of the electrolyte through the coating layer as well as the corrosion and the delamination at the coating/metal interface in a 100% wet solution. In SST, on the other hand, the coated metal was exposed directly to the electrolyte. The chromate rinse on a zinc phosphate system showed higher protection. Chromate conversion coatings showed an increase of impedance value due to the accumulation of chromium compounds in the primer. Conversion coatings alone on the aluminium panels, especially in the baths of phosphate in presence of Mn^{2+} and chromophosphate, lasted 80 hours in the SST, whereas coatings from baths of zinc phosphate lasted up to 220 hours.

Adhesion

Table 1 summarises the adhesion properties of organic coatings coated over various surface pretreatments. Conversion coatings were mainly employed to improve metal-polymer bonds. The adhesion performances of polymer-metal interfaces were attributed to mechanical interlocking.

One of the most important factors relating to the adhesion of coating materials to the substrate is the stability when exposed to water or high humidity. Out of the conversion coatings of phosphate, chromophosphate and chromate, the adhesion of chromate coatings to the aluminium surface was generally very good, because the coating had been formed by a reaction taking place at the metal-solution interface, and this facilitated the incorporation of chromium into the chlorinated rubber primer.

Table 1: Adhesion values of different coating systems with primers

S no	Surface pretreatment	Tensometer readings Newtons/mm^2
1	Aluminium alkaline cleaning with acid etching	3.89
2	ZnO-5g/l, H$_3$PO$_4$ – 11.3 ml/l NaNO$_2$ – 1.2g/l NaF – 0.5 – 1.0 g/l Time – 10–15 mins, Temp 30°C	3.3
3	ZnO-5g/l, H$_3$PO$_4$ – 11.3ml/l MnPO4 – 1.0 g/l NaNO$_2$ – 1.2g/l NaF – 0.5 – 1.0 g/l Time – 10–15 mins, Temp 30°C	4.4
4	CrO3 – 10 g/l, H$_3$PO$_4$ – 50 ml/l Time 5 mins Temp. 45°C	5.0
5	CrO$_3$ – 4g/l, K$_2$Cr$_2$O$_7$ – 3.5 g/l, NaNO$_2$ – 0.5 – 1.0 g/l. NaF – 0.5 – 1.0 g/l, HNO$_3$ – 3-5 ml/l, Time – 3 mins, Temp. 30°C	6.8

Chromophosphate coatings considerably improved paint adhesion rather than phosphate coatings. It was observed that zinc-phosphated samples delaminated at the phosphate-substrate interface. The zinc phosphate coating was found to be less porous and less degraded. The thin zinc phosphate coatings contributed to higher pore resistance. The better interface adhesion in the zinc phosphate system with the chlorinated rubber primer must be related to the surface properties of the phosphate, whereas the manganese addition to the zinc phosphate bath II enhanced the adhesion properties due to the porous nature of Mn and the zinc phosphate system. The phosphate coatings obtained in the presence of Mn^{2+} increased the bonding between the paint and the metal due to the enhanced adhesion.[11]

It was clearly evident that alkaline cleaning and acid etching before the conversion coating operation improved the adhesion of the chlorinated rubber primer coating due to the removal of any strong organic contamination and to alteration of the oxide layer.

From this study, it could be concluded that developed conversion coatings helped in the improvement of corrosion performance as well as adhesion.

Scanning electron micrographs are shown in Figures 4, 5, 6, and 7 for pure aluminium, and after phosphating, chromating and chromophosphating respectively. From Figure 5 it was observed that the deposition of phosphates on the aluminium surface was not uniform. At some spots there was a grain growth which resulted in larger grains of 100m, and less porous in nature. From Figure 6 it was observed that the grain size of chromates was much lower than the phosphate deposits. The deposits were uniform with little tendency to grain growth. Figure 7 shows that the pattern of chromophosphate deposits was far better than the two already mentioned. The deposits were uniform and porous, and the grain size was approximately
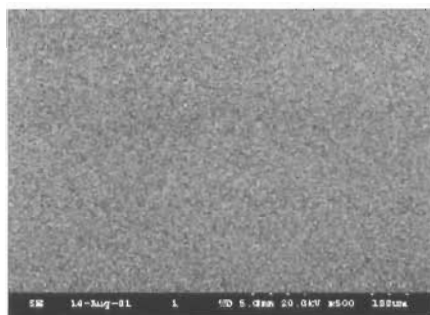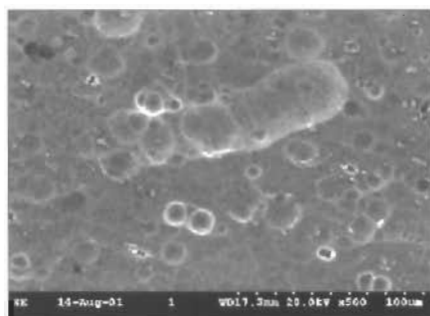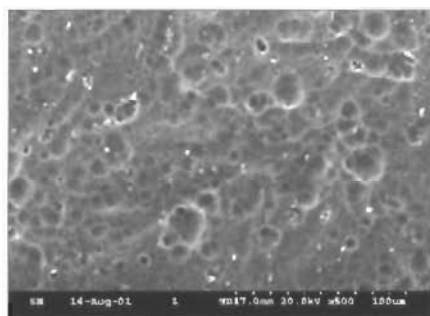

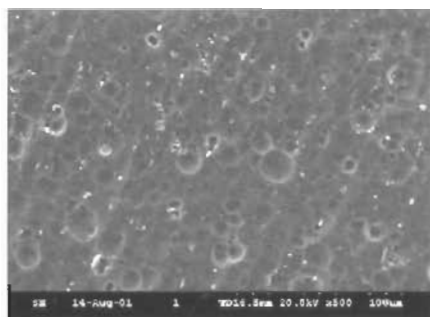Figure 4:

Figure 5:

Figure 6:

Figure 7:

20µ. In overall trends, chromophosphate coating deposits exhibited uniform coverage.

Conclusion

1. Surface treatment with a chromate conversion coating system on the aluminium surface was more effective than the phosphate or the chromophosphate system.
2. The addition of manganese to the phosphating bath enhanced adhesion properties as evidenced from the performance of baths I and II
3. SEM studies showed that the nature of the deposits was uniform from both the chromate and chromophosphate baths, but it was non-uniform in the phosphate bath.
4. Overall trends showed that chromate conversion systems exhibited better performance than the phosphate or chromophosphate conversion systems.

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