Improvement in Corrosion Resistance of Aluminium Alloy by Permanganate-based Conversion Coating

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ABSTRACT: *This investigation on permanganate-based conversion coating describes a chromate-free coating and efforts at reducing the environmental foot prints of metal finishing industries. A golden coloured coating on aluminium specimen was obtained from the permanganate coating (PMC) bath with nominal pH of 7.9. Results from scanning electron microscopy (SEM) examination showed that the conversion coatings are continuous, and the surfaces of the specimens treated in the coating bath are composed of irregularly shaped and mud-cracked coating materials. The coatings, as revealed from energy dispersive spectroscopy (EDX) analyses in the SEM are composed essentially of aluminium, oxygen and manganese compounds which are likely to be hydrated. Accelerated corrosion tests in near neutral 3.5% sodium chloride solution and natural exposure tests revealed that the replacement of chromate with permanganate improved paint adhesion and corrosion resistance on aluminium substrates. Furthermore, the results indicated that the corrosion resistance of the permanganate-based conversion coating matched those from the traditional chromate coating bath, but for the corrosion resistance, after application of a top coat of lacquer, the former was adjudged better than the later.*

Keywords: Aluminium, permanganate, corrosion resistance, conversion coating, corrosion

1. INTRODUCTION

Aluminium and its alloys usually carry air-formed thin oxide layer with inherent corrosion resistance to mild environments despite having flawed regions. However, in some instances, such as in the aircraft and building industries, it is usually beneficial to replace the oxide layer with inert, more corrosion resistant conversion coatings. In the past few decades, chromate conversion coatings (CCCs) which impart superior corrosion resistance and improve paint adhesion on aluminium among other characteristics, have been the choice of the metal finishing industries. Chromates have been classified as carcinogens and efforts in finding their replacements in traditional metal pretreatment baths have received much attention in recent times. While some researchers have attempted to replace chromates with zirconium, vanadium, molybdenum, cerium and permanganate, others have tried the sol-gel route with siloxanol, alkoxysilane and aluminium doped sol-gel materials.[1–13] Most results obtained from these research works pointed to the direction of inferiority in corrosion resistances of these substitutes, whereas their paint adhesion characteristics have been described as good as those of chromates.

The mechanisms of formation of the coatings through the sol-gel route have been succinctly described by Osborne.[14] However, the mechanisms of chromate conversion coating formation in the presence of fluoride species in the coating bath is thought to involve the activation of aluminium surface prior to deposition of coating materials through reduction of Cr(VI) ions in solution to Cr(III) ions, and subsequent deposition of Cr(III) hydroxide/oxides as the major components of the coating. However, some aluminium and Cr(VI) compounds, probably hydrated, were incorporated in the coating as well.[15–17] The formation of conversion coatings on aluminium from permanganate solution probably follows similar routes as those of the chromate coatings since fluoride species in solution are known etchants of aluminium and manganese can exist in various oxidation states. Thus, in the presence of an activator like fluoride and a species that can exist in more than one oxidation state, the combination was thought to be ripe for formation of a conversion coating on aluminium. This is in agreement with the findings of Yoganandan et al. and Wang et al. that separately concluded that permanganate coatings are composed of metal-oxides, MnO_2, Mn_3O_4 and Mn_2O_3, etc., as detected by XRD and XPS, respectively.[8,18] They further suggested that the coatings have superior corrosion resistance to "bare" aluminium in 3.5% NaCl solution. With these at the background, the present investigation seeks to know the morphology of any coating formed on aluminium from the permanganate solution and examine its corrosion resistance with reference to a standard chromate coating employed in the aluminium coil coating industry.

2.   EXPERIMENTAL

2.1   Surface Preparation of Substrates

All chemicals used were of laboratory grade obtained from British Drug Houses Chemicals Ltd., Poole, UK. Samples of aluminium alloy 6000 series obtained from first Aluminium Plc, Nigeria were made out into spade-like electrodes with approximate dimensions of 30 mm × 20 mm × 10 mm. The specimens were cleaned in 10% NaOH solution for 5 min, rinsed in water prior to de-smutting in 50% w/w nitric acid solution for 5 min. After rinsing in water, the specimens were allowed to dry in air at room temperature.

2.2   Conversion Coating Formation

The conversion coating solution was prepared by mixing 4.0 g l^{-1} of potassium permanganate and 1 g l^{-1} of sodium fluoride in a 1 l flask. The pH of the coating solution was 7.92 as determined by JENWAY, Model 3505 pH Meter. Coating procedure was by dipping clean and drying pre-weighed aluminium specimens in 100 ml of coating solution for various times ranging from 30 s to 10 min. After each period of immersion, the specimens were rinsed in water and dried for about 30 min at room temperature prior to obtaining the weights of the coated specimens. The average changes in weights of five specimens individually treated for the various times employed to determine the rates of development of the coatings were recorded against time. Also, the progress of colour changes was monitored and recorded by photography. Similarly, a chromate conversion coating solution, prepared in the usual manner was employed to coat various aluminium specimens for various times with an average of five changes in coating weights and colours recorded against time.[19]

2.3   Coating Morphology and Composition

Five separate specimens treated for various times in both coating solutions were examined in scanning electron microscope (SEM), Phenom proX SEM, model MVE0224651193, operated at 15 KeV and their elemental compositions obtained from the energy-dispersive X-ray (EDX) attachment in the microscope. The coating development was likewise monitored through optical microscope of limited resolution.

2.4   Corrosion and Adhesion Tests

Five specimens coated for 180 s in the coating solutions were exposed to the tropical, savanna environment in Kwara State of Nigeria for about 500 h with five untreated aluminium specimens serving as control. The specimens were examined daily, and the progress of exposure test was monitored by visual inspection and optical microscopy. Specimens treated in the coating solutions for 180 s were further coated with a nitrocellulose lacquer by immersing the aluminium specimens as near vertical as possible in 100 ml of the lacquer for 60 s and withdrawn as immersed, allowed to dry for 24 h prior to further examination. Untreated aluminium specimens, specimens treated in the coating solutions, and those over coated with lacquer were cross-scratched prior to exposure to near neutral 3.5% NaCl solution for 168 h. After the exposure period and in accordance with Japanese industrial testing method, transparent cellophane adhesive tapes were firmly applied on each of the specimens.[20] The tapes were subsequently rapidly pulled from the substrates. The surfaces were examined to appraise the mode(s) of coating failure by optical microscopy and in the SEM with analyses performed in the EDX attachment of the SEM.

3.   RESULTS AND DISCUSSION

3.1   Coating Development

The coating growth pattern in both permanganate and chromate solutions are similar. The colours changed from metallic aluminium substrate progressively from light yellow to golden colouration after 3 min of treatment in both solutions. These are indicative of coating formation and development. The colour of the specimens changed to dark yellowish brown after 10 min of treatment which further showed that interactions between the already formed coating and the coating solutions were dynamic with formation of coating materials either by adsorption/absorption and reaction of coating solution materials with the substrate through pathways that may have developed within the coating.[19,20] The rates of coating development in both permanganate and chromate solutions are displayed in Figure 1 where it can be observed that the coatings developed rapidly initially with rates that decreased with time of immersion in the coating solutions. These were expected since the initially formed coating materials will restrict further interaction of the coating solution species with the substrate. These observations are also supported by the findings of Hughes et al. who observed increase in Mn content of PCC with time although the coating remained stunted at about 70 nm in thickness.[21]
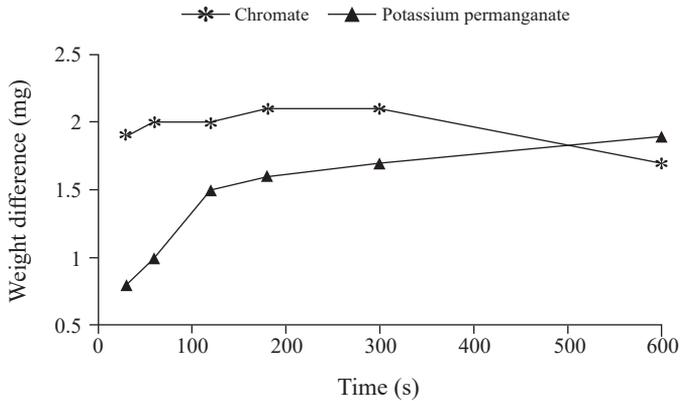
Figure 1: Weight change of aluminium specimens with time of immersion in permanganate and chromate conversion coating baths.

However, further development of the coating although at a slower rate might have continued with the formation of pathways within the coating.[17,22] The rate of development of the chromate coating was faster than for the permanganate which was expected as the chromate bath was acidic, and the permanganate was a near-neutral coating solution. The maximum weight attained in the chromate bath was about 2 mg whereas for the permanganate coating, it was about 1.8 mg. These were attained over a protracted treatment time of 600 s which was as a result of the reduction in the rate of change in weights of the coatings due to weathering occasioned by the aggressive coating baths.

3.2 Surface Morphology and Composition of Permanganate Conversion Coating

The development, morphology and corrosion resistance of CCCs on aluminium have been described by various authors as characterised by mud-cracked morphology and are presently considered to have superior corrosion resistance and improved paint adhesion over their contemporaries.[19–24] However, SEM examinations revealed that the morphologies of all specimens treated for various times in the permanganate solution appeared similar. A typical example is displayed in Figure 2 (a and b), where light and dark randomly shaped materials of various sizes can be observed in a matrix of cracked coating materials. Such micro-roughness at the coating/solution interface may contribute to colour changes in the coatings from light yellow to golden yellow colouration with increases in immersion times of the specimens. In addition, increases in coating thickness with the formation of coating materials as well as uptake in coating solution species as described elsewhere and by others may contribute to the gradual colour changes.[8,15,21,25]

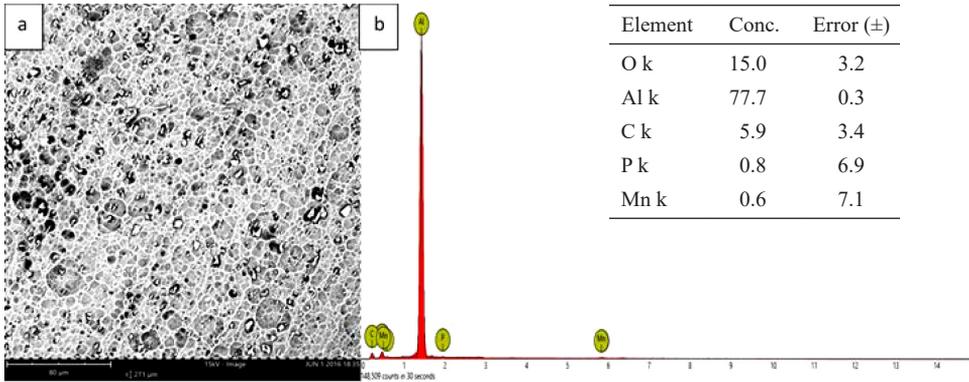| Element	Conc.	Error (±)
O k	15.0	3.2
Al k	77.7	0.3
C k	5.9	3.4
P k	0.8	6.9
Mn k	0.6	7.1

Figure 2:   SEM and EDX of the specimen treated for 180 s in permanganate conversion coating solution at 30°C.

The cracks may have developed as a result of shrinkage stresses normally observed in drying out gel-like materials. These coating features, which are characteristic of all specimens treated for 30 s to 600 s, may have developed in a manner that mapped the grain and sub-grain boundaries of the substrate aluminium as described by Oki and Charles.[22] It is generally known that grain boundaries are anodic to the interior of grains; also it has been shown by various authors that fluorides in conversion coating baths activate aluminium with the release of 3 electrons, thus:[26]

$$Al \quad \rightarrow \quad Al^{3+} \quad + \quad 3e^- \tag{1}$$

The electrons released in the anodic reaction (Equation 1) will be taken up in the cathodic half of the redox reaction which will predominantly take place within the grains and impurities in the substrate with the deposition of the coating materials when their solubility constants are attained. For the permanganate coating bath, at near-neutral pH regime, the most favourable cathodic reaction will be:

$$2H_2O \quad + \quad MnO_4^- \quad + \quad 3e^- \quad \rightarrow \quad MnO_2 \quad + \quad 4OH^- \tag{2}$$
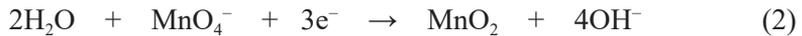
Thus, MnO_2 will form the bulk of the coating materials with aluminium oxides/hydroxides deposited along with it while MnO_4^- may be adsorbed/occluded within the growing coating materials.[27,28] The predicted mechanism of formation agreed with the elemental compositions obtained from EDX analysis displayed in Figure 2(b) and supported by the findings of Yoganandan et al. and Wang et al.[8,18]

Although most researchers agree with Equation 1, Thompson suggested that thinning of the oxide skin on aluminium occurs with formation of aluminium ions which are further re-oxidised to Al_2O_3 formed the basic anodic reaction.[23] The oxide layer, very much thinner than the original 2.5 nm as described separately by

Pokorny et al. and Thompson, allowed electron tunnelling for subsequent cathodic reactions to take place as described in Equation 2.[19,22,23]

The elemental compositions of the coating as revealed by the EDX analysis are Al, Mn, O and C. Although EDX does not give quantitative analysis of elements present in a given sample, it was observed that signals for the coating components increased in height as the time of treatment of specimens increased in the coating bath in a similar manner observed by various other authors.[15,19,21,25] The EDX yield for aluminium is large, however, this is a result of X-rays generated from the substrates as well as from within the coating. Other observed peaks must have been generated from within the coating/residual impulses from within the equipment. Higher yields for Mn, as depicted in Figure 3, were observed when spot analyses were performed on the white, randomly shaped materials with a population density of about 3×10^{10} m^{-2} on the surface of the coating displayed in Figure 2. These showed an enrichment of Mn at specific regions of the coating probably with iron inclusions as an intermetallic which are normally cathodic to the aluminium matrix.[29,30]

The compositional analysis obtained by other authors using various analytical tools agree with the findings in this investigation that permanganate conversion coating is essentially composed of MnO_2 and Al_2O_3 /(OH)$_3$ which are probably hydrated.[8,18,21]

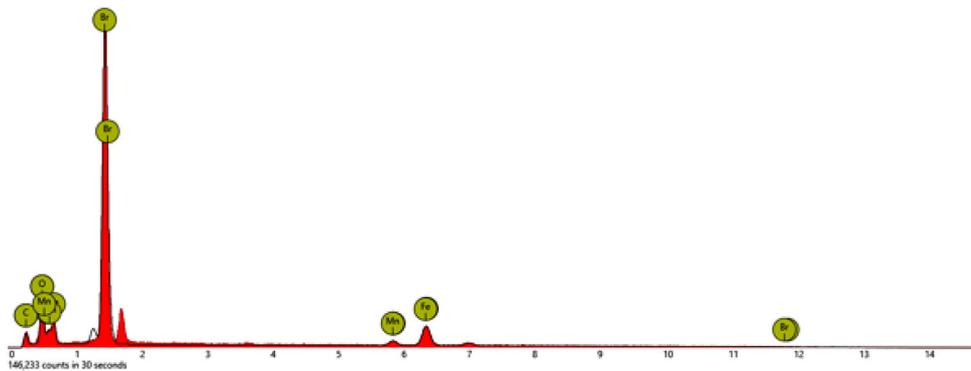Figure 3:   EDX spot analysis at light coloured coating materials on specimen treated for 180 s in permanganate coating bath at 30°C.

3.3   Corrosion and Adhesion

Conversion coated specimens, without a top coating of lacquer, during atmospheric exposure tests gradually faded in colour to a lighter shade of golden yellow whereas bare aluminium, similarly exposed developed mounds of corrosion

products, aluminium oxide/hydroxide were also observed on the lacquer coated bare aluminium specimens after the exposure time of 500 h (a representative micrograph is presented in Figure 4).
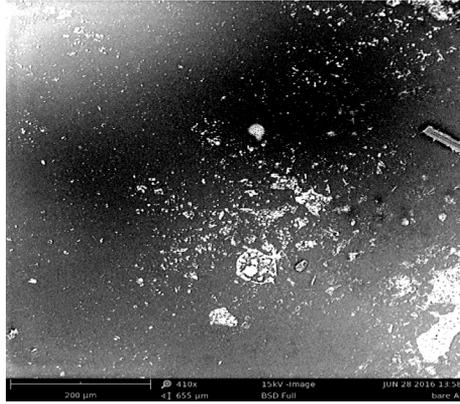

Figure 4:   Lacquer coated bare aluminium after exposure for 500 h in 3.5% sodium chloride solution.

The corrosion products were visible to the naked eyes under the top lacquer coating applied prior to atmospheric exposure. However, the specimens with conversion coatings and top coating of lacquer performed creditably well as revealed during optical microscopy examinations.

Figures 5 displays the optical photographs for chromate and permanganate conversion coated specimens with top coatings of lacquer after exposure for 168 h in near-neutral 3.5%.
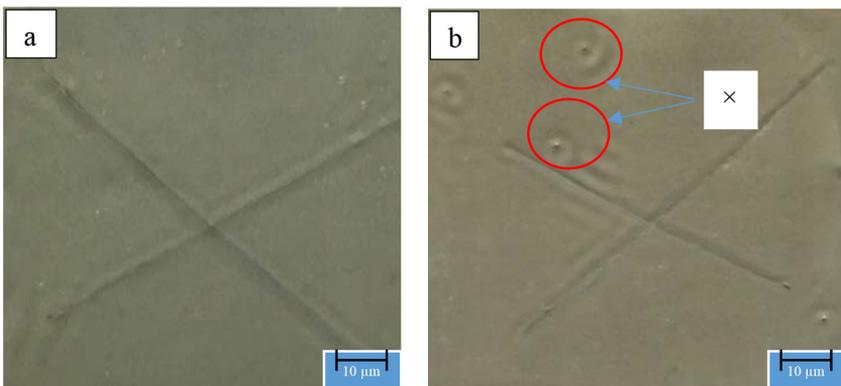

Figure 5:   Lacquer coated with (a) chromate and (b) permanganate conversion coated aluminium specimens after exposure for 168 h in 3.5% sodium chloride solution.

Sodium chloride solution where the superiority of the former over the latter can be vividly observed. The permanganate specimen showed some signs of pitting corrosion at various regions marked "X" in Figure 5(b), while the chromate portrayed a surface without any sign of corrosion. However, it is worthy of note that the untreated, lacquer coated counterpart showed paint delamination, whereas for the two conversion coated specimens, paint delamination was not observed and the lacquer was not peeled off after application of adhesion tests.[20] For those specimens without a top coating of lacquer but similarly treated in conversion coating baths prior to exposure in 3.5% sodium chloride solution, apart from gradual fading in colour, pitting corrosion was not observed on the specimens. It has been observed by other researchers that there are leachable Cr^{6+} species in chromate conversion coatings which serve as corrosion inhibitors at transiently exposed regions of aluminium substrate.[14,24,31] It is likely that leachable MnO_4^- species are present in the permanganate coating and these can be reduced at corroding sites of the substrate to plug any corrosion reaction in such regions as with the use of XPS, $KMnO_4$ as was detected in PCC by Yoganandan et al.[8] The specimen immersed in 3.5% NaCl but initially treated in permanganate coating solution carrying a top coating of lacquer was further examined with SEM. As displayed in Figure 6, there was no paint delamination and the lacquer did not peel off after the application of adhesive tests.[20]
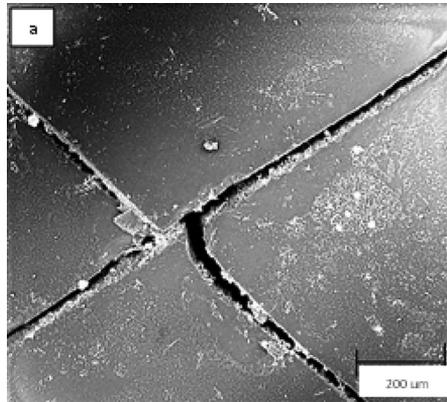

Figure 6:   SEM of permanganate treated aluminium specimen with a top coating of lacquer after exposure to 3.5% sodium chloride solution for 168 h.

4.   CONCLUSION

Improvement in corrosion resistance of aluminium alloy by permanganate-based conversion coating has been investigated. The results obtained within the detection limits of EDX revealed that the permanganate coating is composed of manganese,

aluminium and oxygen compounds, which were probably hydrated. The atmospheric corrosion protection and paint adhesion characteristics of the permanganate coating compared favourably well with those of chromate conversion coating. However, with the exposure of lacquer coated specimens to sodium chloride solution, pitting corrosion resistance of chromate conversion coating was found to be superior to those of permanganate-based conversion coating. They both performed better than bare aluminium alloy specimens.

5.   ACKNOWLEDGEMENTS

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