

## HYBRID MANGANATE-BASED CONVERSION COATING ON ALUMINIUM

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### ABSTRACT

This investigation describes hybrid conversion coatings and efforts at reducing the environmental foot prints of chromates. Initial modification of chromate coating solution with tannins/glycerol was patented with number NG/P/2013/755, 2014. The usual mud cracking pattern characteristics of chromate conversion coatings (CCCs) and improved ability to release inhibitors to corroding sites was achieved. Optical microscopy and corrosion tests in high humidity environment showed that the replacement of chromate/tannin with manganate/tannin and or glycerol has improved paint adhesion and corrosion resistance on aluminium substrates.

**Keywords:** Aluminium, manganate/tannin/glycerol, adhesion, corrosion.

### INTRODUCTION AND LITERATURE REVIEW

It is usual practice to apply conversion coatings on aluminium and its alloys prior to paint applications. Such coatings can be developed by electrochemical reactions of the substrate with an electrolyte in a natural immersion procedure at ambient temperatures. The conversion coating procedure normally replaces the air-formed film on the substrate with a strongly adherent coating which restricts the metal from the environment and also provides a good keying surface for subsequently applied paints. Various authors (Tedim et al 2014),(Osborne 2001), (Chen, Li, & Cai 2011), (Oki & Charles 2009), (Oki, Oki & Charles 2012), (Oki 2014), (Oki 2013) have shown that both macroscopic and microscopic features developed on the substrate are important in achievement of improved adhesion capabilities of the coating in addition to secondary bonds which may be formed with the constituents of the paint (Asami et al 1987). Although the chromate conversion coating has been in use for decades with admirable good adhesion and corrosion resistance imparted on treated surfaces, concerns about toxicity and problems associated with effluent disposal of Cr (VI) has resulted in a wide and vigorous search for non-carcinogenic and environment-friendly substitutes for chromates in conversion coating formulations and processes. Efforts by researchers have resulted in conversion coating formulations made up of Vanadates, Cerium (Lin et al 2012), Siloxanes etc, which for the most parts provide good adhesion capabilities but with corrosion resistance properties which are inferior to those of chromates. In order to reduce the environmental impact of chromates other researchers (Oki 2014) have formulated fast drying chromate containing solutions and processes which reduced the environmental foot prints of chromate by eliminating process steps which result in copious amounts of effluents laden with Cr<sup>6+</sup> species.

The present investigation, takes a preliminary look at Manganate containing conversion coating formulation with the aim to ascertain its paint adhesion and corrosion resistance capabilities under high humidity and above ambient temperatures.

## METHODOLOGY

### Materials

99.99% aluminium with nominal impurities of 0.004wt% Fe, 0.002 wt% Cu, and 0.003 wt% Si was made into electrodes measuring 10mm × 10mm × 1 mm. The chemicals employed in this investigation are laboratory grade reagents from BDH Chemicals, UK. The conversion coating formulation was made up with the followings; 3g/l, KMnO<sub>4</sub>, 5ml/l fluorosilicic acid, 5ml/l tannin/glycerol and the solution was made up to 1000ml with double distilled water.

### Methods

The aluminium electrodes were etched in 10% NaOH solution for 3mins, rinsed in running double distilled water and thereafter desmutted in 50% HNO<sub>3</sub> for 2mins, rinsed in double distilled water and in acetone, dried in air for 10 minutes prior to being stored in desiccators. Triplicate immersion periods at 30° C, ranging from 1 minute to 5 minutes were performed in the manganate conversion coating solution. After each immersion period, the specimen was rinsed in double distilled water, dried under the fan for 10 minutes prior to storing in desiccators. These specimens were viewed under metallographic microscope. Similarly treated aluminium electrodes for 3 minutes were subsequently coated with lacquer, dried for 24 hours and exposed to relative high humidity at right angles to the roof of the humidity chamber with the aid of Perspex for 450 hours. Similarly exposed specimens are, cleaned aluminium electrodes with and without lacquer coating as well as manganate coated specimens without top coatings of lacquer to act as controls. Five specimens each for the various treatment procedures were exposed in the humidity cabinet. The relatively high humidity, 100%, was achieved by heating up water placed at the bottom of a cabinet which temperature was controlled at 40° C. After exposure in the cabinet, the specimens were dried for 24 hours after which the lacquer coated specimens were cross-hatched; to obtain 20 squares measuring 1mm<sup>2</sup> with ten centrally placed squares as area of interest. Adhesive tapes were applied firmly on the specimens after which the tapes were removed with a rapid motion against itself. The tape and metal sides of the specimens were examined under the microscope to ascertain the mode(s) of failure of the applied lacquer and the number of squares from which lacquer was removed was noted.

## RESULTS AND DISCUSSION

### General observation on the development of conversion coating

To the naked eye, the specimens were covered with a brown coating irrespective of immersion time. This shows at face value that the air-formed film on the clean aluminium specimens has been replaced with a conversion coating which brown colouration grew increasingly intense with increase in treatment time.

### Optical microscopy of treated surfaces

The surface finish of cleaned aluminium specimens have been described fully elsewhere (Oki 1989). However, it is characteristic of such surface to be comprised of pits which are associated with inclusions in the metal which had been removed during etching and de-smutting procedures.



Fig. 1 Optical macrograph of aluminium specimen treated for 3mins in manganate conversion coating solution at 30°C.

As displayed in Fig. 1, which is the surface of aluminium specimen treated for, 3 minutes in the manganate conversion coating solution, the coating is comprised of light and dark coating materials which developed over the initially lustrous, shiny finish of etched and desmuted aluminium substrate. These two shades are related to the colour of the coating which is a mixture of green, purple and brown as observed under the optical microscope at magnification of about 700 times. The coating has developed over inclusions and pits that may have been present in the metal.

#### **Exposure to 100% relative humidity**

Irrespective of treatment procedure, to the naked eye, all lacquer coated specimens revealed whitish colourations after exposure in the humidity cabinet. This is related to moisture absorption by the lacquer during long interaction with moist and humid atmosphere in the cabinet. However, the bare aluminium specimen appeared dull grey with apparent film growth which indicates transformation of the air-formed film on the specimen to a more voluminous hydrated form of alumina. On the other hand, the conversion coated specimen, without a top coating of lacquer turned a lighter shade of brown after humidity exposure for 450 hours at 40°C. This indicates that the conversion coating is composed of leachable components. Examination under the optical microscope did not reveal any features apart from those described for the specimen prior to humidity exposure. However, for the untreated aluminium specimens, mounds of bulky corrosion products which can be associated with the transformation of the air-formed oxide skin on aluminium after prolonged interaction with hot humid environment in the cabinet. This is further witnessed in the 'bare' specimen with a top coating of lacquer under optical microscopy examination which revealed variously sized cell like features. These features are bulky corrosion products which formed on the surface of the metal and exerted pressure on the lacquer to give rise to such patterns.

#### **Adhesion of lacquer to treated and untreated surfaces**

The summary of the results of adhesion tests is displayed in Table 1 where it can be observed that from 5 separate adhesion tests performed on 'bare' aluminium specimens with a top coating of lacquer, only one of the reference squares retained a semblance of retention of some lacquer. Whereas, for the manganate conversion coated specimens, with top coating of lacquer, some of the squares failed with cohesive failure mode in the lacquer as revealed during optical microscopy examinations while adhesive failure at the interface of manganate/lacquer was observed for only one of the reference squares. The percentage

improvement in adhesion imparted by the manganate conversion coating was estimated to be about 88% in contrast to 2% calculated for the air-formed film on the 'bare' metal. This is expected since it has been shown by several authors (Thompson et al 2000), (Oki 2007), (Kendig & Buchheit 2003), (Fontinha et al 2013) that, the air-formed oxide skin on aluminium must be replaced with conversion coatings prior to paint application in order to obtain adherent paint/lacquer on aluminium.

Table 1: Percent adhesion improvement for manganate conversion coating.

Experiments	Number of squares from which lacquer was removed	
	'Bare' Aluminium	Manganate coated
1	10	1
2	10	0
3	10	3
4	9	0
5	10	2
Average number of failed squares	9.8	1.2
% Adhesion improvement	$\frac{10-9.8}{10} \times 100 = 2\%$	$\frac{10-1.2}{10} \times 100 = 88\%$



Figure 2: Optical macrograph of metal side of manganate coated specimen after adhesion test.

The failure path demonstrated by the manganate/lacquer which is mostly cohesive in the lacquer indicates that after protracted exposure in the humidity cabinet, the forces within the lacquer weakened such that for the most part the adhesion between the lacquer and the manganate coating was superior.

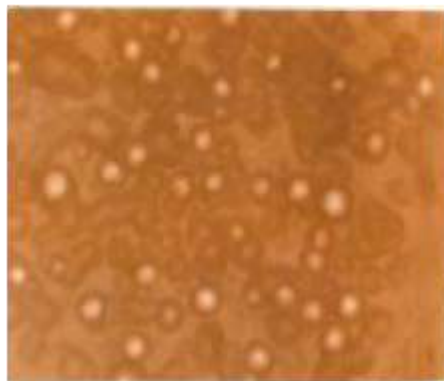


Figure: 3 optical macrograph of tape side for manganate coated specimen after adhesion test.

From Figs. 2 and 3, which are macrographs of the metal and tape sides for the manganate specimen after adhesion test, it can be observed that on the metal side, there are tufts of resin, whereas the left over resin on the tape side showed depression replica of the metal side. This confirms that the failure path was cohesive in the lacquer. The failure path for the 'bare' lacquer coated aluminium was adhesive and it occurred mostly at the lacquer/aluminium interface which indicates that the air-formed film on the aluminium substrate is a poor surface to receive paints. From Fig. 4, it can be observed that the metal surface, displayed at the top left hand side of the macrograph revealed only incipient pits developed during interaction with the hot humid environment in the cabinet. However an occasional let over resin, which appears darker than the rest of the surface is displayed at the bottom right hand corner of the figure.



Figure 4: Optical micrograph of metal side of 'bare' aluminium after adhesion test

Water from the humidity cabinet had gained entry to the interphase and displaced the bond between the substrate aluminium and lacquer. Whereas the manganate conversion coating had formed an inert barrier between the aluminium substrate and the environment in addition to providing a good keying surface to bond favourably with subsequently applied lacquer.

## CONCLUSIONS

There are leachable components in manganate conversion coatings which may act as corrosion inhibitors.

The manganate coating substantially protected the aluminium substrate from corrosion. The percentage improvement in adhesion capabilities imparted on aluminium substrate by manganate conversion coating is about 88%.

This is a preliminary investigation on manganate conversion coating; hence future studies will involve the use of SEM/TEM and Atomic forced microscopy to characterize the coating's morphology and composition. Electrochemical corrosion tests will also be performed on specimens carrying manganate conversion coating with reference to 'bare' substrates.

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