An RoHS Compliant Conversion Coating System For Aluminum And its Alloys

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ABSTRACT

This paper presents filiform, neutral salt - spray, electrical conductivity and paint adhesion data on a commercially available and environmentally friendly conversion coating coating system for all types of aluminum alloys. All test data is presented in direct comparison to standard chrome - chromate or hexavalent chromium conversion coatings systems. The hexavalent chromium used in conversion coating systems is a known carcinogen. The european RoHS directive will not allow for the presence of any hexavalent chromium on electrical and electronic equipment as of July 1, 2006. This conversion coating system will meet the requirements of that directive.

A “conversion coating” refers to the conversion of the surface of a metal into a surface that more easily accepts applied coatings (paints) and at the same time gives a certain degree of stand alone corrosion resistance. Aluminum forms a rather hard, corrosion resistant and paint accepting film of aluminum oxide and as a result, oxide coating generated conversion coatings have been used on aluminum since the 1920's. The oxide coatings discussed in this paper are less expensive then electrolytic generated coatings and because they are non crystalline in nature will have a much less of an ability to crack or break off then an anodized coating. In addition these coatings are quite environmentally friendly and will meet the requirements of the RoHS directives.

CLEANING AND DEOXIDATION

In any metal processing procedure (painting, conversion coating, anodizing, etc.) the most important part of the processing is the proper cleaning of the metal surfaces prior to processing. In general, alkaline cleaners do the best job. When used on aluminum they should be non–etching, as etching will leave difficult to remove alloyed elements, such as, heavy metals or elemental silicon and will pit the metal's surface. To prevent excessive etching, various inhibitors are often added to the alkaline cleaners. If added they should be present in small amoumts (generally less then 500 ppm) as excessive amounts will hinder cleaning and may leave difficult to remove chemical residue.[1]

Deoxidation is the removal of oxides and other inorganics, such as silicon, that would otherwise interfere with further processing of the aluminum without significant attack upon the aluminum surface[2] . To prevent excessive attack, deoxidizers generally contain an oxidizing agent designed to maintain a thin film of oxide on the metal's surface. This allows for the oxide to be removed rather then having a direct attack on the metal by the deoxidizer. Many of the deoxidizers now in use will use an iron (III) salt, such as ferric sulfate coupled with hydrogen peroxide[3], or any one of a number of other oxidizers (chlorates, nitrates, persulfates, etc.). Iron based deoxidizers leave deposits of iron on the surface of the aluminum which encourages galavanic corrosion, as you now have two dissimilar metals in direct contact with each other. The other oxidizers mentioned are, in general, not strong enough oxidizing agents to maintain a good oxide film on the metal, or have toxicity problems associated with them. The best deoxidizers for aluminum are those based on nitric acid coupled with another oxidizer, such as, hydrogen peroxide or sodium bromate, 4as bromates are strong enough oxidizing agents (when used with nitric acid) and quite environmentally friendly. Unlike other acids, nitric acid will dissolve aluminum oxide, but has very little effect upon aluminum itself.

With high silicon content alloys, it is very difficult to avoid the use of fluorides in spite of their toxicity. If you must use fluorides, keep the fluoride level low (generally not more then 200 ppm), as excessive amounts of fluorides will leave a white deposit of insoluble aluminum fluoride on the metal's surface and will pit the metal, as will the use of acids other then nitric and/or the use of heavy metals such as iron. For years chromic acid and / or chromates were used in deoxidizers in conjunction with nitric acid, and were generally considered the best deoxidizers on the market. In addition to the toxicity issue, associated with the use of hexavalent chromium, these deoxidizers always leave a thin deposits of chromium oxides on the metal's surface which will not allow for the subsequent use of a non hexavalent chromium conversion coating system free of all hexavalent chromium.

CONVERSION COATING AND CONVERSION COATING PROCESS

The first stage of the process is the formation of a hydrated aluminum oxide film by the use of boiling deionized ("D. I.") or otherwise purified water (reverse osmosis). The aluminum begins to react within 10 to 15 seconds and completes the formation of a 250 to 300 nm thick (about 0.00001 inch), soft, bluish – gray , coating of hydrated aluminum oxide in about five minutes (see figure 1).

The second stage of the process involves treatment of the aluminum in a proprietary aluminum salt solution at about 200 degrees F for at least one minute to decrease the hydration of the aluminum oxide film and remove unwanted inorganics (smut). At this point the aluminum is metallic in color and has a well defined structure (see figure 2).

The third step involves treatment in a proprietary potassium permanganate solution at 130 to 140 degrees F for three minutes to give a manganese oxide – aluminum oxide coating of about 300 to 400 nm thick with a very well defined structure (see figure 3). The metal itself will have a clear to light gold and iridescent finish. The coating is quite hard and scratch resistant, will withstand temperatures up to the melting point of the aluminum and will not degrade over time. The already excellent corrosion resistance and paint adhesion may be still further improved by use of one of several secondary seals available for that purpose. The secondary seals are non toxic, environmentally friendly and water based products applied at ambient temperature and allowed to air dry. Potassium permanganate is on the list on materials allowed in potable drinking water[5] and has been used for over eighty years in the treatment of potable drinking water systems. Potassium permanganate will leave no heavy metal residues in your rinse water.

PAINT ADHESION AND CORROSION RESISTANCE

Numerous paint adhesion and corrosion studies have been performed on bare and painted aluminum alloys conversion coated by this process[6,7]. Bare salt spray corrosion resistance according to ASTM B –117 , filiform corrosion resistance studies and paint adhesion studies are presented in Tables I, II, and III. In all cases the coating is shown to meet or exceed the required standards of the tests. Independent tests on high solids heat resistant paints have shown performance values that exceeds that shown by chromic acid anodizing in paint adhesion and corrosion resistance characteristics. In many cases these coatings are used to bond high flurocarbon containing coatings to aluminum surfaces with great success.

CONCLUSION

Hexavalent chromium based conversion coating systems have been use for over sixty years to generate aluminum oxide based conversion coating systems because of their excellent paint adhesion characteristics and corrosion resistant properties when used with aluminum and its alloys. Any replacement that expects function as well, must be designed to duplicate its characteristics as closely as possible. The manganese oxides produced by the heptavalent manganese based system are by far the most closely related to the chromium oxides and hydroxides in terms of their respective chemistries. Thus, the aluminum oxide – manganese oxide film, as produced by the heptavalent manganese conversion coating system, is the most closely matched in terms of performance and actual chemistry.

REFERENCES

1. Spring, S., "Industrial Cleaning", Prism Press, Melbourne, 1974, p. 20.

2. Spring, S., "Industrial Cleaning", Prism Press, Melbourne, 1974, p. 145.

3. Anchem Products, Inc., British Pat. # 1,368,230 (1974).

4. United States Patent # 4,883,541.

5. "Drinking Water System Components, Component Materials and Treatment Additives in Accordance with ANSI/NSF 60 and 61", Underwriters Laboratories, Inc., 1997.

6. Stephen J. Spadafora, "Naval Air Warfare Center Aircraft Division Warminster", Warminster, PA., Report #NADC-92077-60.

7. Jang, Elwin and Meininger, John, "Enviromental Compliant Chemical Conversion Coating", AF Contract: FO 4699-98-D-0004,1 AR.

Table 1: Wet Adhesion, Primer and Topcoat (Mil-C-81706) 2024-T3, 7075-T6, and 6061-T6

	Adhesion
Mil-P-85582B Primer Only (water Based)	No loss of Adhesion
Mil-P-23377G Primer Only	No loss of adhesion
Mil-P-23377G Primer and Topcoat of Mil-C-83286 Gloss White	No loss of adhesion

Table 2: 5% Neutral Salt-Spray (Mil-C-81706) Unpainted Panels

Alloy	Pretreatment	168 Hours	336 Hours
2024-T3	Chromate	No Surface Corrosion	No Surface Corrosion
7075-T6	Chromate	No Surface Corrosion	No Surface Corrosion
6061-T6	Chromate	No Surface Corrosion	No Surface Corrosion
2024-T3	Permanganate w/seal	No surface corrosion	No surface corrosion
7075-T6	Permanganate w/seal	No surface corrosion	No surface corrosion
6061-T6	Permanganate w/seal	No surface corrosion	No surface corrosion

Table 3: Typical Filiform Results on "2024-T3" Clad and Bare (ASTM D 2803-93) –1008 hours

	Deoxidized Only	Chrome-Chromate	Permanganate w/seal
Mil-P-855828B Primer Only (water based)	None	None	None
Mil-P-23377G Primer Only	Few, 5-7mm	Few, 2-4mm	Very Few, 2-4mm
Mil-P-23377G Primer Only	Few, 3-6mm	Few, 2-3mm	Few, 2mm

Figure 1:

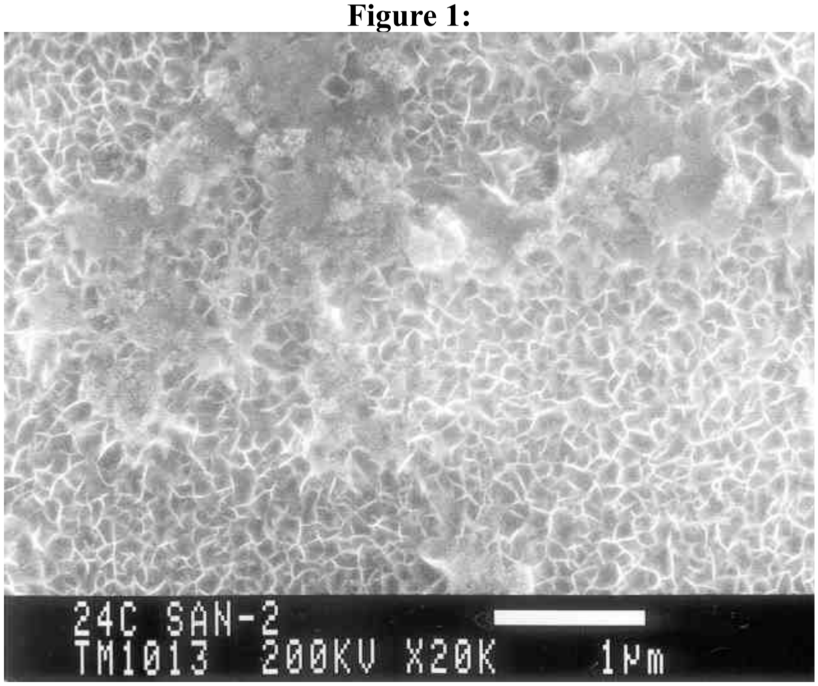

Figure 2:

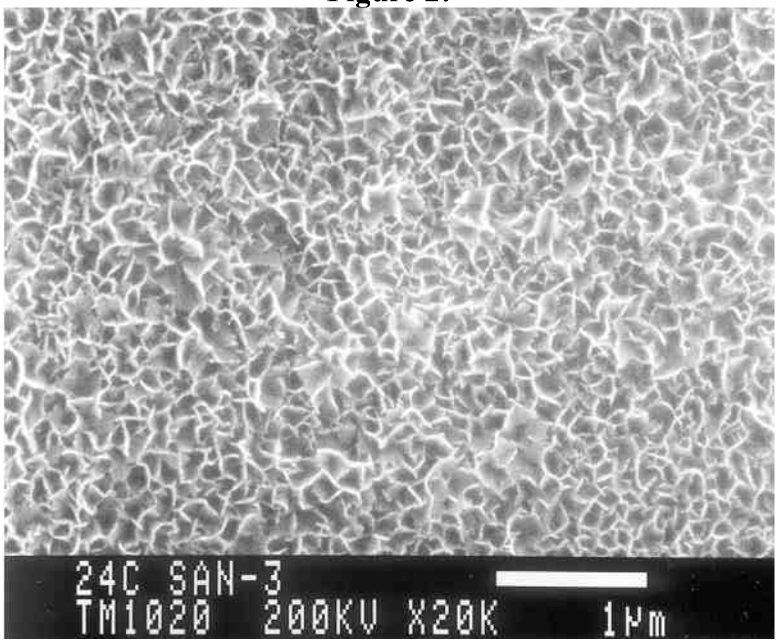

Figure 3: