Chromate - Free Conversion Coatings For Aluminum

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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 cast and wrought aluminum alloys. All test data is presented in direct comparison to standard chrome - chromate conversion coatings on castings and wrought alloys. Hexavalent chromium used in in conversion coating systems is a known carcinogen. European EU End-of-Life-Vehicles Directives specified a limit of 2 grams of hexavalent chromium per vehicle entering the European after July 1, This conversion coating system will exceed these specifications.

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The term "conversion coating", as used in the metal finishing industry,[1] refers to the conversion of a metal's surface into a surface that will more easily accept applied coatings and offers corrosion resistance in the event that the secondary coating is breached. They are rather thin (not over 600 nm or 0.024 mil. on aluminum), quickly and easily formed, easily scratched and, if used to enhance paint adhesion, are coated shortly after being formed to prevent degradation of the conversion coating. By far the most successful conversion coating system used on aluminum has been that based on hexavalent chromium (generally known as chromate) and it is generally used as a "yardstick" against which all other conversion coating systems are measured. In the presence of aluminum the hexavalent chromium is reduced to various trivalent chromium compounds which form a soft jell like mixture that when dry, initially has an open porous structure that easily accepts applied organic coatings. After eight hours, these coatings lose their open porous structure due to the formation of an inorganic polymer that will not as easily accept applied organic coatings. For this reason it is generally recommended that they be painted shortly after being conversion coated [2]. It is this polymer that is primarily responsible for the excellent corrosion resistance shown by these conversion coating systems. Traces of hexavalent chromium left in the conversion coating give the conversion coating shades of yellow to dark brown color which serve as an easy reference to the relative coating mass or thickness of the coating and act to "self seal" the conversion coating by reacting with any open areas created by scratches in the finish. The major drawback to the use of these coatings is the fact that they will decompose when heated above 160 degrees [3] , due to the loss of water of hydration which holds the polymer together. This feature limits their use to non - power coating applications. Over the years many attempts have been made to duplicate the coating formed by chromate based conversion coatings systems by the use of trivalent chromium systems. In all cases hexavalent chromium is produced as a result of the chemistry used in these systems and traces of it are always found on the parts in question in unacceptable amounts.

This paper will show the advantages of using a permanganate - based conversion coating system in conjunction with, and without, the use of an organic seal to duplicate the inorganic polymer formed by the chromate based conversion coating system. Various paint adhesion and corrosion resistance studies will illustrate the advantages gained, in addition to the systems complete lack of toxicity.

PERMANGANATES

Going across the third row transition metals, from left to right, there is a great deal of similarity between the elements in terms of chemical and physical characteristics, until you reach iron. As a result the conversion coatings produced by hexavalent chromate compounds are, as expected, quite similar to those produced by the heptavalent permanganate compounds as shown by studies at Oxford university.[4]

As in the case of chromates, the permanganate generated conversion coating system contains a mixture of manganese (in place of chromium) and aluminum oxides. The higher oxidation state manganese oxides are reduced to a lower oxidation state, as necessary, in order to prevent the corrosion (oxidation) of the aluminum, just as the higher oxidation state chromium compounds (chromates) are reduced to various trivalent chromium compounds. The chromate based conversion coating system gives a protective inorganic polymer. The permanganate based system will not. This allows the permanganate based system to be used in powder coating applications (it is not affected by heat) and places no restrictions on when the conversion coating may be painted. The paint adhesion characteristics of the permanganate based system are as good as, or better then chromate based systems[5]. With the exception of high copper or zinc alloys (2024, 7075 aircraft alloys etc.), the corrosion characteristics are identical. In order to compensate for this deficiency, the heptavalent manganese based system may be used with a unique organic seal [6] that bonds to the permanganate generated conversion coating and allows for electrical conductivity (see Table 1). This system has shown corrosion resistance that exceeds all the requirements of "MIL-C-5541E" and its qualifying specification; "MIL-C-81706"(see Table 2)[7] . The permanganate based system gives a yellow -gold color that is almost equivalent to the color produced by the chromate based system and indicates that the conversion coating has properly formed. If the coating has not properly formed, it is quite easy to strip the coating off and reapply the conversion coating. A cold applied version of the conversion coating, which reacts in a few seconds, is available for the processing of large structures (aircraft). A clear version is also available with a "test" solution to confirm that the conversion coating has actually formed.

Permanganates have been used for over 80 years to treat potable water systems, and they are on the list of materials allowed in drinking water [8]. Permanganates will not generate water soluble manganese compounds under normal conditions (absence of any strong reducing agents) which is one reason why they are allowed in potable water systems.

CLEANING AND DEOXIDATION

In any metal processing procedure (anodizing, painting, conversion coating, etc.) the most important part of the process is proper cleaning and deoxidization of the metal. Cleaning is the removal of surface dirt and oil. As a general rule 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 elemental silicon or heavy metals. To prevent excessive etching silicates are usually added in amounts up to 500 ppm. Excessive amounts will hinder cleaning[9] and leave difficult to remove silica deposits.

Deoxidation is the removal of oxides and other inorganics that would hinder further processing of the aluminum without significent attack upon the metal [10]. To prevent excessive attack , deoxidizers generally contain an oxidizing agent to generate an oxide film on the surface of the metal. This allows the oxide to be dissolved by the deoxidizer as opposed to a direct attack upon the metal by the deoxidizer. Many of the deoxidizers now in use contain an iron (III) salt, such as ferric sulfate,coupled with hydrogen peroxide[11] , or anyone of a number of alternative oxidizers (chlorates, nitrates, persulfates, etc.). Iron based deoxidizers leave deposits of iron on the surface of the aluminum which creates galvanic corrosion. The other oxidizers mentioned are, in general, not good enough oxidizing agents to maintain an oxide film on the surface of the aluminum, or are considered to environmentally unfriendly. The best deoxidizers for aluminum are those based upon nitric acid (less then 20%) and hydrogen peroxide or bromate[12], as these are strong enough oxidizers to maintain an aluminum oxide film on the metal and quite environmentally friendly. Unlike other strong mineral acids, nitric acid will not attack the aluminum. Nitric acid of 20% or higher concentration will tend to maintain an oxide film on the metal rather then dissolve it. Castings present a special problem in that they generally contain large amounts of elemental silicon. As a result they will require a nitric acid / fluoride mixture to remove the silicon as silicon tetrafluoride. If you must use fluorides, keep the fluoride content less then 200 ppm to avoid excessive formation of an insoluble film of aluminum trifluoride.

CONVERSION COATING PROCESS

(See Treatment Process Flow Chart, Figure 1)

After proper cleaning and deoxidization of the aluminum, a simple one stage treatment in a propriety permanganate solution at 135 - 145 degrees F. for 90 seconds or longer will be sufficient for all but the more corrosion prone high copper or high zinc aluminum alloys. Assuming that the metal has been properly cleaned, the above process will produce a characteristic, uniform and even, yellow - gold conversion coating. A non - uniform film is indicative of improper cleaning. If necessary the coating may be stripped in a 1% hydrogen peroxide - 0.1% nitric acid solution and reprocessed or simply cleaned again and processed a second time. A clear conversion coating may be produced by treatment in the above solution for 15 seconds or less. A drop of a strong hydrogen peroxide (at least 20%) solution will cause the metal to effervesce if the coating has formed properly. Large structures (aircraft) or in service repair may be accomplished by the use of a two component cold applied mixture that is active for about eight hours. If the surface has been properly cleaned, the characteristic gold - yellow conversion coating begins to form in a few seconds. The conversion coating process is self limiting and will not continue beyond the formation of a thin uniform yellow - gold film. Once dried, there are no limits on when the metal may be painted or on the type of paint that may be used. In most cases adhesion and filiform corosion protection are excellent (see Tables 3 and 4). A unique set of organic seals are available for improved paint adhesion and / or corrosion resistance in the case of high copper or high zinc content alloys.

CORROSION STUDIES

Many studies have been performed on permanganate-based conversion coating systems[7] and the organic seals. Neutral salt-spray corrosion resistance studies, according to ASTM B-117, and filiform corrosion studies will be presented for the wrought alloys “2024 - T3”, “7075 - T6” and “6061 - T6”. These are among the more corrosion susceptible aluminum alloys. In addition they are widely used in military and aircraft applications that require strength and lightness.

ASTM standard “B-117” sets forth neutral (PH = 6.5 to 7.2) salt-spray testing specifications. Under these specifications the panels are suspended at from 15 to 30 degrees from the vertical, the solution contains about 5% sodium chloride, the temperature is maintained at 95 degrees Fahrenheit (+2 to -3 degrees Fahrenheit) and the spray is such that each 80 square cm. Of collecting area will collect 1.0 to 2.0 ml. per hour of salt spray solution. Military specification "MIL-C-81706" only differs in that it requires a 6 degree angle from the vertical. All tests were performed using a 6 degree angle from the vertical.

Filiform corrosion may be defined[13] as corrosion that occurs under under coatings on metal substrates characterized by a definite thread-like structure and directional growth. Thus, the term "dense", used in table three, refers to many thread like structures extending away from a scribed line on a metal surface while "few" refers to few thread like structures extending away from a scribed line. The number of millimeters (mm) refers to the distance away from the scribed line on the metal surface. At the start of the test, an "X" is scribed on the metal panels extending from each opposite corner of the panels. The filiform testing was performed in accordance with ASTM D 2803-93. Electrical conductivity and wet tape adhesion studies were performed according to "MIL-C-81706".

RESULTS AND DISCUSSION

The primary function of a conversion coating is to provide for a corrosion resistant surface as insurance against failures in the secondary coating. With the exception of chromate generated conversion coatings, the permanganate conversion coating system is the only system that provides for this type of protection while at the same time providing for excellent paint adhesion characteristics as shown by the data presented.

Permanganate generated conversion coating systems function as well as they do because of the similarity between the chemistry of chromium and that of manganese. Figure two shows the FTIR spectra of a potassium permanganate produced conversion coating followed by that of a dry in place chromate generated conversion coating. With the exception of the spectra created by the presence of silica, the spectra of both conversion coatings are very similar. In both cases there are traces of starting materials, evidence of hydroxyl groups, evidence of mixed metal oxides, reduction residue and the characteristic peaks due to the presence of aluminum oxides and hydroxides. The results of "TEM" studies show both coatings to have about the same density, uniformity and thickness. In both cases they are ideal for corrosion resistance and paint adhesion.

The only major difference between the conversion coatings is the ability of the chromate produced coating to form its own inorganic and hydrophobic polymer. The ability of this coating to exclude moisture and salt is the primary reason for its excellent corrosion resistance and also its "Achilles heel" in that this will not allow the chromate generated coatings to used in high temperature applications (powder coating) and places limits on when and how they may be painted by more conventional painting systems. To compensate for this deficiency the permanganate based system uses various unique organic seals that provide for electrical conductivity, if required, give excellent paint adhesion and corrosion resistance that exceeds that of the chromate generated systems.

CONCLUSION

While the precise mechanism by which chromate generated conversion coatings impart their paint Adhesion and corrosion resistance may never be known, an alternate system must involve the use of materials that have similar chemical and physical properties. Permanganates are by far the most closely related to chromates in this regard. Thus the manganese - aluminum oxide conversion coatings produced by the permanganate based conversion coating system, very closely matches the performance of chromate based systems.

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FIGURE 1

TREATMENT PROCESSES

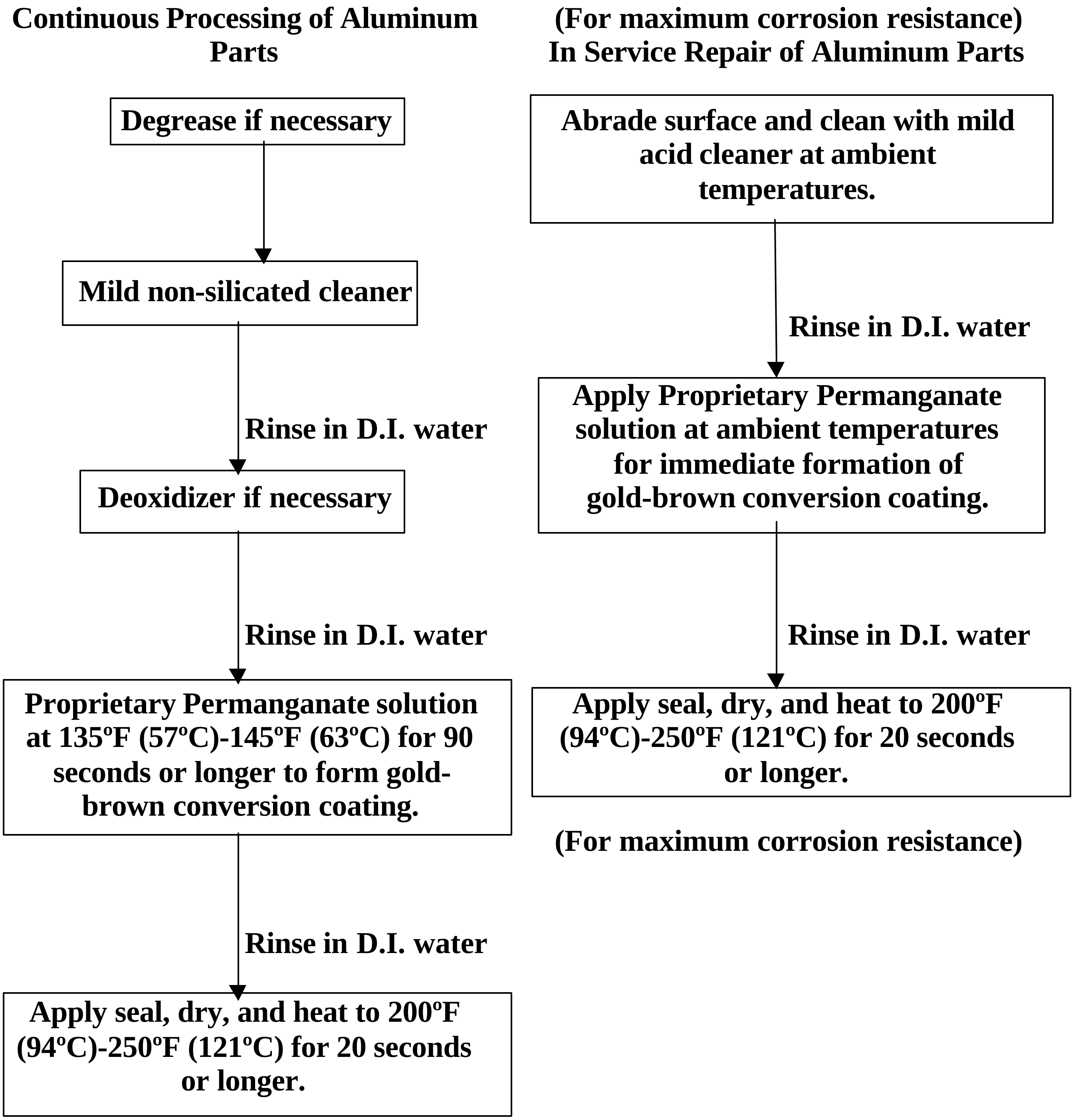

Table 1: Contact Electrical Resistance (microhms)

Panel #	Hours in Salt Spray	Reading 1	Reading 2	Reading 3	Reading 4	Reading 5	Average	Std. Dev.	*Limit*
1	168	4,000	5,000	6,000	5,000	6,000	5,000	1	<10,000
2	168	6,000	5,000	5,000	5,000	5,000	5,000	0	<10,000
9	0	4,000	3,000	4,000	5,000	5,000	4,000	1	<5,000
10	0	4,000	4,000	5,000	4,000	3,000	4,000	1	<5,000

Chatillon Load System, Model 2759-S, MDC #125319, Cal Exp.: 11 Nov. 1998 Valhalla Digital Micro-ohmmeter, Model 4300B, MDC #128382, Cal Exp.: 7 Jun. 2000

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

Table 4: 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