Conversion Coatings For Magnesium and its Alloys

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For over fifty years chromium based conversion coating systems have been the conversion coating of choice to prepare magnesium and magnesium alloy surfaces to accept applied organic coatings and provide for secondary corrosion resistance. Chromate is now listed as a known carcinogen and is being phased out as a conversion coating material. European EU End –of - Life – Vehicles Directives specify that vehicles entering the market place as of July 6, 2007 may not contain any hexavalent chromium compounds. This paper presents an environmentally acceptable alternative with equivalent or better paint adhesion and corrosion resistant properties.

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INTRODUCTION

The term "conversion coating", as used in the metal finishing industry, refers to the conversion of a metal's surface into a surface that will more easily accept applied coatings and / or provide for a more corrosion resistant surface[1] . They are rather thin (generally not over 6000 nm thick), quickly and easily formed, easily scratched and, if used to enhance paint adhesion, are generally coated shortly after being formed to prevent degradation of the adhesive properties of the conversion coating. Magnesium and its alloys did not come into wide spread use until the second world war and their use has expanded greatly since then.

Conversion coatings for magnesium and its alloys, in common use, are based upon: (1) the formation of a film of chromium hydroxides and / or oxides; (2) the formation of a film of precipitated heavy metal phosphates; or oxides; (3) the use of various synthetic polymers, with or without heavy metal phosphates or oxides; (4) the formation of various manganese oxide – metal oxide films by use of permanganates.

CLEANING AND DEOXIDATION

In any metal finishing process (painting, conversion coating, anodizing, etc.) the most important part of the process is the cleaning (removal of surface oils and loose dirt) of the metal surfaces. In general, alkaline cleaners will do the best job. When used on magnesium their PH should not exceed 10 as highly alkaline cleaning solutions will stain magnesium surfaces (heavy film of magnesium hydroxide) and leave difficult to remove alloyed elements. Deoxidation is the removal of oxides and other inorganics that would otherwise interfere with further processing of the metal without significant attack upon the metal surface[3]. Magnesium and its alloys are very reactive toward mineral acids and as such deoxidation is generally carried out by use of rather dilute solutions or with mild organic acids such as acetic, citric or glycolic acid. Various chromic acid solutions may also be used as the chromic acid will inhibit attack upon the magnesium, but the use of these solutions presents significant environmental problems[2]. Excessive etching of magnesium surfaces will leave more inorganic oxides then it will remove and actually be harmful to any further metal processing.

CHROMATE BASED CONVERSION COATINGS

For all conversion coating processes the hexavelent chromium process of producing a film of mixed metal oxides, chromium oxides and chromium hydroxides is used as a "yardstick" against which all other conversion coatings are measured. Were it not for the issue of toxicity; their continued use would not be an issue. The conversion coating film is formed by the reduction of the hexavalent chromium to a jell like mixture that, when dry, initially has a rigid open porous structure that allows for the application of organic coatings. After about eight hours, these coatings have strong tendency to become soft and powder like in consistency and much more difficult to paint. For this reason, it is generally recommended that they be painted shortly after being conversion coated [8]. It is assumed that traces of hexavalent chromium left in the coating will “self seal” any breaks that may occur in the coating although this continues to be an issue of some debate among researchers. These traces of hexavalent chromium compounds are also responsible for the various shades of yellow to gold color that occur in the coatings. This color is a very useful feature in that it provides for a very quick and easy way to determine if, in fact, the coating has properly formed and the relative thickness and corrosion resistance of the conversion coating in question. A clear chrome conversion coating is used when a bare minimum of corrosion resistance is necessary and a conductive surface is required. These coatings are about 100 to 120 nm. thick and about 20 mg. per square foot in mass. An iridescent to light yellow coating is used as a paint base and is about 300 nm. thick with a mass of 50 to 60 mg. per square foot. A yellow to gold coating is necessary for maximum corrosion resistance and has a thickness of about 500 to 600 nm. with a mass of about 80 to 100 mg. per square foot. The coating compositions must be maintained at a PH of 1.2 to 1.9 and are known as simple chrome – fluoride or accelerated chrome fluoride compositions. The chrome – fluoride baths contain about three to four grams per liter of chromic acid, three to five grams per liter grams of sodium dichromate and about one gram per liter sodium fluoride. The accelerated baths will contain about two to five grams of potassium ferricyanide. One major drawback, to the use of these coatings, is the fact that they decompose when heated above 160 degrees F, due to the loss of water of hydration which holds their polymeric network together. In the case of magnesium this does not result in any significant loss of corrosion resistance[9], but the bare salt spray (see:“ ASTM B117” document) corrosion resistance of chromate conversion coated magnesium is quite small to begin with and there are no specified bare salt spray corrosion tests for magnesium. Heated chromate conversion coated magnesium parts will show increased paint adhesion as the coating reverts to one of simple magnesium and chrome oxides. Over the years many attempts have been made to duplicate the coating formed by hexavalent chromium conversion coatings using trivalent chromium compounds in place of the hexavalent chromium compounds. None of them has been successful without first producing hexavalent chromium by the oxidation of the trivalent chromium during the course of the reaction; as such, traces of hexavalent chromium compounds are always found on trivalent chromium treated magnesium surfaces.

HEAVY METAL PHOSPHATES AND OXIDES

The use of various heavy metal phosphates (iron, zinc, manganese, chromium, etc.) is the oldest of the conversion coating methods in use, and generally provides the best possible surface for paint adhesion. Magnesium is an exception to the rule. Phosphating of magnesium and its alloys is of little commercial application as the coatings are generally soft and powdery. The solutions are very quickly depleted and the corrosion resistance of the coatings is quite poor[3]. The best success has been with manganese based phosphating solutions[4]. A typical manganese phosphate solution would contain the following:[5]

Manganese dihydrogen phosphate:	80 grams per liter
Manganese silicofluoride:	500 grams per liter
Potassium fluoride:	40 grams per liter

Magnesium and its alloys may be anodized in much the same way that aluminum is to produce high porosity coatings in both alkaline and acid solutions. The hardness and / or porosity of the alkaline generated coatings may be improved upon by the addition of borates, silicates, fluorides and various organic acids [6]. A typical solution would contain:

Sodium hydroxide:	240 grams per liter
Ethylene glycol:	70 grams per liter
Oxalic acid:	25 grams per liter

The coatings consist of almost all magnesium hydroxide and are primarily used to increase the paint adhesion properties of the magnesium. Under acid conditions the solution generally used consist of [7]:

Ammonium bifluoride:	200 grams per liter
Sodium dichromate:	60 grams per liter
Phosphoric acid:	60 ml. per liter

Under these conditions, the composition of the coating consist of manganese phosphates, manganese fluorides and various chromium oxides. The coating is quite porous and like the corresponding alkaline generated coating gives very little corrosion protection by itself. The acid generated coating will stand up to heating without loss of paint adhesion properties and the hardness of the coating is quite similar to that of anodized aluminum coatings, but decreases with the thickness of the coating.

SYNTHETIC POLYMERS

Synthetic organic polymers were developed in the early 1970's in an effort to improve the adhesion characteristics of water based painting systems. In this application they work well and will also provide a degree of corrosion protection due to high humidity conditions when used on aluminum and / or aluminum alloys. Unless mixed with hexavalent chromium compounds, they provide no salt – spray protection. They are very effective wetting agents which allows for a "water break – free" surface to form over soiled area's. This often results in paint adhesion failures requiring expensive stripping and repainting.

They have a chemical structure quite similar to that of tannic acid which was used to improve corrosion resistance and paint adhesion on steel and zinc in the late 19th and early 20th century. Tannic acid is a polyphenolic compound with a backbone consisting of various simple sugars. Like tannic acid these polymers will only work effectively at certain precise concentration and PH levels. As such they require constant monitoring. As a general rule, they will decompose at about 330 degrees F leaving a brown stain; and, as a result they do not work well in many powder coating applications. Synthetic organic polymers are quite often used in conjunction with zirconium, titanium, or hafnium compounds to increase paint adhesion but do not work well on magnesium or its alloys as they are not able to form a good enough barrier to keep out moisture and / or salt and prevent oxidation of the magnesium. On average, the coatings are about 10nm thick with a mass of about 10 to 12 mg per square foot when used with one of the heavy metals mentioned above. Due to the small amount of material present, it is very difficult to determine the uniformity or the actual amount of material present without the use of expensive laboratory equipment.

Since the late 19th century various polymeric networks of metal oxides and silicon oxides have been used to prepare ceramic or glass surfaces to accept paints[10]. This process has been studied extensively for the preparation of metal surfaces to accept paint since the 1970's, when a low temperature process was developed to produce inorganic gels of various transition metal alkoxides and silicon alkoxides. This is refered to as the "sol-gel" process as a colloidal suspension ("sol") is first formed and then caused to undergo gelation ("gel") to form a unique inorganic network of transition metal oxides and silicon oxides[11] If prepared properly a particular "sol-gel" is able to provide excellent paint adhesion and in some cases excellent corrosion resistance to various non magnesium metal alloys[12]. As in the case of the polymers modeled after tannic acid, the surface conditions required of the metal being processed and the conditions necessary for the proper formation of the "sol-gel" in question are extreme relative to what may be done in the average industrial metal working facility. The films are quite thin (50 to 100 nm), clear and very difficult to detect without the use of sophisticated laboratory equipment not generally available to the average metal finishing facility. If not applied properly, you will have paint adhesion and / or corrosion problems. Various attempts have been made to attach silanes directly to the surface of magnesium alloys, but once again the processing is quite involved, the films (50 to 100 nm) are quite thin and detecting them is a very difficult process for the average metal finishing facility. If not attached properly to the metal's surface, you run the risk of expensive repainting procedures or corrosion failures.

The exposure of magnesium, or its alloys, to solutions of cerium, lanthanum or yttrium chlorides will produce a film of the corresponding rare earth metal oxide and / or hydroxide on the metal's surface, in the form of an inorganic polymer, but the film has a much higher content of magnesium hydroxide and has very poor paint adhesion and / or corrosion resistant properties associated with it. The rare earth salts used are, indeed, quite rare and as a result, rather expensive. The coatings may be clear (about 30 mg. / square foot and 100 nm) or have a characteristic yellow color to them (about 60 mg. / square foot and 300 nm) that allows for a visual determination of the presence of an acceptable coating. These coatings may be sealed with various organic polymers to improve their corrosion resistance and / or paint adhesion characteristics, but very little improvement results.

Cobalt compounds, which have been complexed with ammonia, will generate a barrier film of various cobalt oxides and / or hydroxides on a clean magnesium or magnesium alloy surface. This film is a polymeric barrier type of coating, held together by water of hydration and due the reactivity of the magnesium contains a much greater magnesium hydroxide content. This serves to destroy any paint adhesion or corrosion resistance associated with this type of coating. Thin films (25 mg / square foot and about 120 nm) are clear, and thicker films (up to 250 mg / square foot and 600 nm) are yellow in color. The solutions used are quite concentrated with cobalt which is expensive and a heavy metal subject to being removed from the work place due to environmental considerations.

PERMANGANATES

There is a great deal of similarity between the third row transition elements, in terms of their chemical and physical characteristics, until you reach iron. Thus the conversion coatings produced by hexavalent chromium compounds are, as expected, quite similar to the one's produced by the heptavalent manganese found in permanganate compounds, as shown by studies at Oxford university[13]. As in the case of hexavalent chromium compounds, the heptavalent manganese produced conversion coating contains a mix of various manganese (in place of chromium) and other metal oxides of various oxidation states. The higher oxidation state manganese oxides are reduced to a lower oxidation state, as necessary, in order to prevent oxidation of the magnesium, just as higher oxidation state chromium oxides are reduced in the hexavalent conversion coating system. The paint adhesion characteristics of the heptavalent manganese based system is as good as, or better than, the hexavalent chromium bases system (see table one) and will pass "Boeing Aircraft" company specification "DMS 1786L" for corrosion resistance and paint adhesion of magnesium alloys. The heptavalent manganese based system gives a gold - brown colored (about 0.5 mg / square foot and about 20 nm) finish to the magnesium which is quite similar to that of the hexavalent chromium based systems. It is very easy to strip and apply another conversion coating if the coating has not properly formed. A cold applied version (non dip tank) of the conversion coating, which reacts in a few seconds, is available for doing large structures, assuming the surface has been properly cleaned, to give a uniform an even yellow – gold color. A clear (about 0.1 mg / square foot and 10 nm) version is available with an easy to use test solution to confirm that the conversion has properly and uniformly 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[14]. Elemental manganese and / or soluble manganese divalent compounds, starting with heptavalent manganese, are very difficult to generate, and as such are not produced when permanganate is introduced to a potable water system under normal conditions (absence of any strong reducing agents) . Insoluble and very stable reduced manganese oxides are all that are normally produced when permanganates enter a potable water system which is why they are used in potable water systems.

RESULTS AND DISCUSSION

The primary function of any conversion coating is to provide for a corrosion resistant surface as insurance against any breaks in the secondary coating. By far, the greatest degree of success, in this regard, has been the hexavalent chromium based conversion coating systems. Any attempt to duplicate this degree of success must, of necessity, be based upon a process that matches, as closely as possible, to the hexavalent chromium based system. Of the approaches taken, only the permanganate based conversion coating system approaches the results shown by hexavalent chromium in actual test results and in theory. The permanganate based system allows for the use of powder coating and non – powder coating based coating systems and is the only heavy metal based system that may be disposed of with no environmental concerns.

CONCLUSION

Hexavalent chromium based conversion coating systems have been use for over sixty years because they have provided such excellent corrosion resistance and paint adhesion characteristics when used with magnesium and its alloys. Any replacement that expects to 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 magnesium 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.

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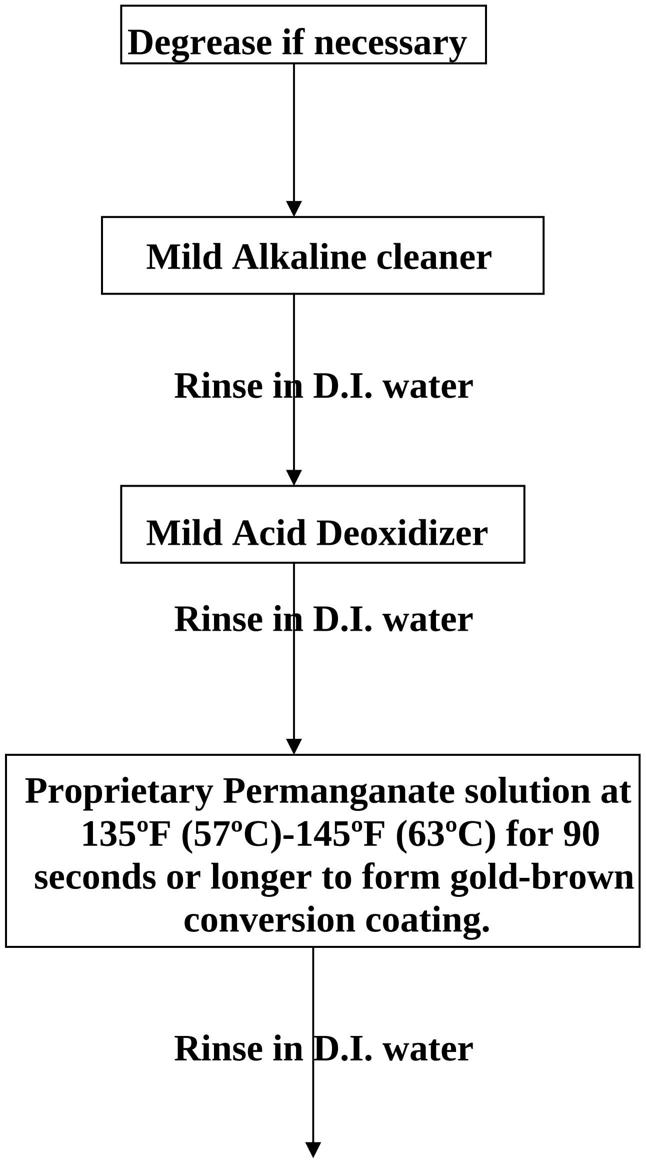
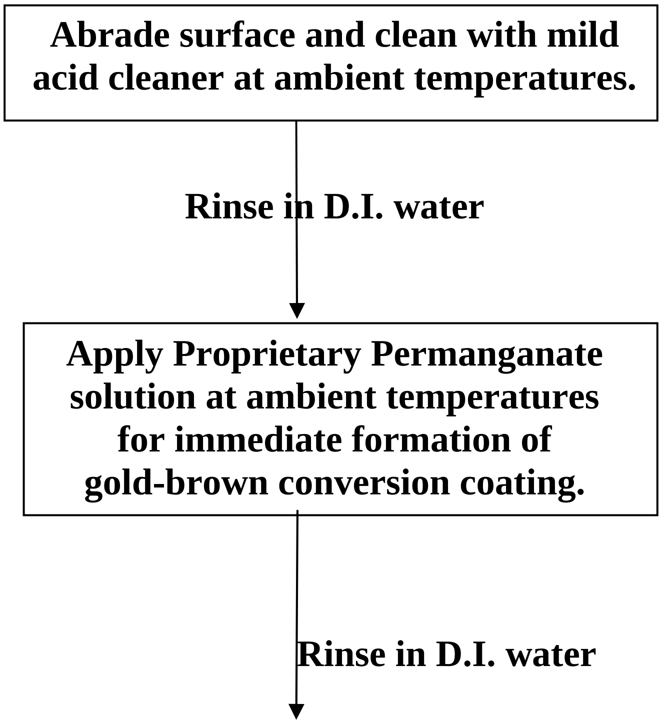
Continuous Processing of Magnesium Parts



In Service Repair of Magnesium Parts



Abrade surface and clean with mild acid cleaner at ambient temperatures.

Rinse in D.I. water

Apply Proprietary Permanganate solution at ambient temperatures for immediate formation of gold-brown conversion coating.

Rinse in D.I. water

Table 1: Paint adhesion and corrosion resistance After 200 hour neutral salt spray test (ASTM B117) Boeing Specification DMS 1786L

Alloy	Adhesion and Corrosion resistance
Z 312 B Alloy, water based primer	No loss of adhesion, no blisters or corrosion
Z 312 B Alloy, solvent based primer	No loss of adhesion, no blisters or corrosion
Z 312 B Alloy, Primer and Topcoat of Mil-C-83286 Gloss White	No loss of adhesion, no blisters or corrosion