Chrome Free Conversion Coatings For Zinc and its Alloys

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For over sixty years chromium based conversion coating systems have been the conversion coating system of choice for zinc and its alloys. Chromate is now listed as a known carcinogen and as such is being phased out of the work place European "RoHS" (Restrictions of Hazardous Substances) directives will only allow for chromate being present to the extent of 0.1% in the conversion coating being used. This paper presents several environmentally acceptable alternatives with equivalent or better performance properties

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The expression "conversion coating", as used in the metal-finishing industry, refers to a chemical conversion of the surface of a metal to a surface that will more easily accept applied coatings and / or resist corrosion.[1] They are rather thin (not over 6000 nm on zinc), quickly and easily formed, easily scratched, and, if used to improve upon paint adhesion, they are coated shortly after being formed to prevent degradation of the conversion coating. Conversion coatings, of one kind or another, have been used on zinc and its alloys for over 100 years and there are a number of different processes available for use. The four primary types of conversion coatings available to the general public are: (1) the production of a film of mixed chromium and zinc hydroxides and / or oxides; (2) the generation of a film of heavy metal phosphates; (3) the use of various synthetic polymers with or without various heavy metal phosphates and / or oxides; and (4) the formation of various manganese oxide / zinc oxide films by the use of permanganates.

Cleaning and Deoxidation

In any metal processing procedure, the most important aspect of the entire process is the proper cleaning and deoxidation of the surface of the metal in question. Cleaning is the removal of surface oils and organic soil while deoxidation is the removal of unwanted metal oxides and / or other unwanted inorganic compounds which would interfere with the conversion coating process in question. Zinc is a rather reactive metal which easily forms dark deposits of oxides and / or hydroxides which are difficult to remove. Heavy organic deposits are removed by degreasing with a organic solvent while the lighter organic deposits are generally removed with a mild nonionic detergent.[2] The unwanted oxides are then generally removed by a strong alkaline cleaner, followed by the use of a mild mineral acid (generally about one percent nitric acid) to remove any alkaline residue. Electrodeposited zinc coatings are conversion coated immediately after the deposit has been applied and they have been rinsed in D.I. water. Hydrogen release annealing of zinc-plated articles should be done before conversion coating and just after the removal of the outer oxide coating with a brief (about 30 seconds) dip in a one percent nitric acid solution[3] (see Fig. 1).

Chromium Based Conversion Coatings

Chromium based conversion coating systems for zinc have been the most widely used as they give excellent corrosion resistance and paint adhesion. In addition the Coating weight, corrosion resistance and paint adhesion characteristics may generally be determined by a characteristic color imparted by the chromium compounds formed on the surface of the zinc or zinc alloy. Very light or colorless conversion coatings are produced by hexavalent chromium solutions with a PH of zero to 1.5 or trivalent chromium processes as the trivalent chromium is oxidized to the hexavalent form. They are widely used in the electronics industry to give

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[1] Definitions Committee, Federation of Societies for Coating Technology, p.177, Philadelphia; 1978.

[2] Spring, S., "Industrial Cleaning", p. 146, Prism Press, Melbourne; 1974.

[3] Biestek, T. and J. Weber, "Electrolytic and Chemical Conversion Coatings," p.72-73, Portcullis Press Ltd., Redhill, Surrey, U.K.; 1976.

protection against humid conditions but offer little salt spray protection. Colored hexavalent chromium based conversion coatings are produced by solutions with a PH of 1.0 to 3.5. These are generally considered to give the best overall corrosion protection, have poor electrical conductivity and have excellent paint adhesion properties. Heavy (40 milligrams per square foot or more) trivalent based systems will slowly become yellow in color as oxidation to the hexavalent form progresses. (see analytical report). All chromium based systems function by initially forming an open porous structure that will easily accept applied coatings. This initially open porous structure then forms a water based closed polymeric network that will not easily accept applied coatings about eight hours after application. These coatings will not stand up to temperatures above 160 degrees F.[4] This restricts the use of these coatings in power coating applications.

The closed polymeric structure of chromium based conversion coating systems is the primary reason for their excellent corrosion resistance and all other non chromium based systems attempt to duplicate this structure in order to obtain good corrosion resistance with various degrees of success.

Heavy Metal Phosphates

The use of various heavy metal phosphates (iron, manganese, chromium, etc.) is the oldest of the conversion coating methods I use on zinc and produces one of the best conversion coatings for painting applications with the exception of powder coating as these coatings will in general not stand up well to temperatures above 200 degrees F. Zinc phosphating solutions will, in almost every instance, contain zinc phosphate as the major component of the bath[5] in order to slow down the activity of the bath; and about 1.3 to 1.5 as much iron[6] to force the reaction. Coating thickness will average about 100 nm to 2000 nm, but may be as high as 6000 nm. The most difficult zinc alloys to phosphate are those containing aluminum as aluminum will slow down the rate of reaction. The fact that the baths contain iron means that iron deposits will show up in the finished parts and lead to galvanic corrosion, making a poorly corrosion resistant conversion coating even less corrosion resistant. All phosphating baths for zinc will result in some degree of pitting. Pits act to trap and hold moisture and unwanted heavy metal deposits (iron) and further decreases the corrosion resistance of the conversion coated surface. All zinc phosphate baths require a considerable amount of monitoring to keep the PH within a rather narrow range. In addition they have a high rate of chemical usage. Zinc phosphate baths are generally operated at 130 to 150 degrees F. and give coating of about 100 to 500 mg/square foot.

Synthetic Polymers

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[4] Wernick, S. and R. Pinner, "The Surface Treatment and Finishing of Aluminum and its Alloys" , p. 264,ASM International, Metals Park, Ohio, 1987.

[5] Biestek, T. and J. Weber, "Electrolytic and Chemical Conversion Coatings," p. 200, Portcullis Press Ltd.,Redhill, Surrey, U.K.; 1976.

[6] Biestek, T. and J. Weber, "Electrolytic and Chemical Conversion Coatings," p, 199, Portcullis Press Ltd.,Redhill, Surrey, U.K.; 1976.

Synthetic organic polymers, similar in composition to that of tannic acid, were first marketed in the early 1970's to improve upon the adhesion characteristics of water based paints. In this application they work quite well and provide some protection to high humidity conditions, but no salt spray protection unless blended with chromium compounds in the hexavalent form or designed to oxidize to the hexavalent form. They are very effective wetting agents and as a result will always show a "break-free" surface that may mask the fact that the parts in question are in point of fact not clean. This may well lead to paint failures and the expense of painting the parts over again. Like the tannic acids they are replacing, these compounds are only effective at certain precise PH and concentration levels; they are dependent upon having an extremely clean surface and the require constant monitoring to insure that they are working properly. As a general rule these compounds decompose at about 330 degrees F. leaving a light brown stain. As a result they will not work well in many power coating applications.

Synthetic polymers of this type are often used to improve upon the corrosion resistance of heavy metal phosphate based coatings[7]. Various acrylic based polymers are mixed with heavy metals such as zirconium or titanium to improve upon paint adhesion and corrosion resistance when used by themselves[8]. These polymers don't have the strength or the integrity of inorganic polymer systems such as those formed by chromium based systems. The extremely small coating of most of these systems make it very difficult to determine the uniformity or actual amount of material present on the coated surface in question.

Since the latter part of the 19th century various polymeric networks of metal oxides and silicon oxides have been used to generate ceramic or glass like surfaces to accept organic coatings[9]. Renewed interest in this process in the 1970's has resulted in a low temperature process to generate inorganic jells of a number of transition metal alkoxides, often refered to as the "Sol-jell" process. If prepared properly, a given "sol-jell" will provide for excellent paint adhesion and, in some cases, excellent corrosion resistance.[10] The surface conditions necessary to obtain the proper film are extreme and generally only obtainable under laboratory conditions.

Permanganates

Going across the third row transition metals, from left to right, there are a great number of similarities between the elements in terms of their respective chemical and physical characteristics, until you reach iron. Thus, the conversation coatings produced by chromium are, as expected, quite similar to the one's produced by heptavalent manganese compounds, in particular, permanganate[11]. Just as higher valence chromium compounds are reduced to lower valence chromium compounds, so to are the higher valence manganese compounds reduced to lower valence

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[7] Kulick, L. and K. I. Saad, U.S. Patent 3,975,214.

[8] Dollman, D.Y. et al., U.S. Patent 4,191,596

[9] Erinkers, C.J. and G. Scerer, "Sol-Gel Science," Academic Press, New York, 1990.

[10] Van Ooij, W.J. and T. Child, Corrosion, 54(2):26-35; 1998.

[11] Danilidis, I. et. al., "Manganese-Based conversion treatment," Dept. of Materials, Universsity of Oxford, U.K.; 1998.

manganese compounds with very similar properties to those of the chromium compounds. The lower valence manganese compounds are not as good as the corresponding chromium compounds in all respects, but they are quite good. The manganese based systems will withstand the high temperatures of power coating without any loss of corrosion resistance. In addition, the manganese based system will not allow zinc to form a difficult to paint over hydrophobic film of zinc oxides and / or hydroxides. By itself the manganese generated conversion coating over zinc will provide for as much paint adhesion and corrosion resistance as a thin chromium generated conversion coating and it is used in that application as a clear and / or a light gold conversion coating in automotive and electronic applications. The use of a secondary inorganic seal will allow the clear and / or gold generated conversion coating to meet all of the paint adhesion and corrosion requirements of the chromium generated system while still providing for excellent electrical conductivity. This permanganate based system does not require an excessively clean working surface and will actually assist in the cleaning process. The gold – brown color serves as a quick reference point as to the coating mass and as a check to the proper functioning of the conversion coating bath and / or the cleaning bath. Thus preventing the necessity for expensive reprocessing of parts.

Permanganates have been used for over 90 years to treat drinking water systems and are on the list of allowed materials in drinking water.[12] Elemental manganese and / or soluble low valence manganese compounds are very difficult to generate and as such are not generated when permanganate is introduced into drinking water systems under normal conditions.

Summary

The primary function of all conversion coating systems is to provide for a surface that accepts applied coatings and resists corrosion as insurance against any breaks in the applied coating. By far the greatest success in this regard has been achieved by the chromium based conversion coating systems, which have been in wide use for over 70 years. Any attempts to duplicate this success must, of necessity, be based upon a process that has its chemistry as closely as possible aligned with that of the chromium based systems. Of the approaches taken, only that of the permanganate based system approaches that of the chromium based system in all respects and it is the only heavy metal system with no environmental problems associated with its use.

Conclusion

Chromium based conversion coating systems have been in use for over 70 years because of their excellent paint adhesion and corrosion resistant properties when used on zinc surfaces. Any replacement system that expects to function the same must be designed to duplicate, as closely as possible, the chemical and physical properties of such a system. The manganese oxide, zinc oxide conversion coating produced by the permanganate based system is the most closely matched in terms of chemistry and performance.

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[12] "Drinking Water System Components, Component Materials and Treatment Additives in Accordance with ANS/NSF 60 and 61." Underwriters Laboratories, Inc.; 1997.

Analytical Report:

Sample: A cast zinc sample was conversion coated with a commercially available chromium plus three conversion coating process and then allowed to sit in a 100% humidity environment at 100 degrees F. for seven days. The sample was then analyzed for the presence of hexavalent chromium using x-ray photoelectron spectroscopy or "ESCA"

Analysis: The sample was directly mounted on a platen surface for chemical analysis using a "Phi Quantum 2000 XPS" system. In "XPS" or "ESCA" an x-ray beam is used to generate photoelectrons in the sample, which carry analytical data from the outermost 5 nm of the sample. This method is well suited for the analysis of surface chemistry on solid samples. A low energy ion beam was used to remove surface contamination from the sample. The "XPS" or "ESCA" spectra was processed to give quantitative results, using relative sensitive factors from standards. We also collected high resolution spectra to study the chemistry of the conversion coating.

Results: Analysis of the samples after cleaning most of the carbon from the samples was combined to give average results of :

Chromium: 17%, Zinc: 12%, Carbon 10%, Oxygen: 54%, Aluminum 6%, trace: Copper and Fluorine (less then 2%)

The high level of zinc on the surface presented a problem in that the Auger electron peaks occur at similar energies to the chromium 2p photoelectron peaks used for the analysis. The spectra were analyzed by peak fitting utilizing reference chromium spectra, and by fitting using synthetic peaks based on parameters measured on standards. Based upon the chromium "XPS" spectra, most of the chromium was in the plus three state. Because of overlapping zinc Auger peaks, it was difficult to determine to exact amount of chromium plus six present, but it was not more then 10% and not less then 7% of the total chromium present or 1.7% to 1.2% of the total mass of the conversion coating. This is about what one would expect from a standard hexavalent chromium generated conversion coating system. Current "RoHS" regulations will not allow for more then 0.1% hexavalent chromium in the applied conversion coating.

Table 1: Salt Spray (ASTM B117) and Stack Test on Hot Dip Galvanized Steel Panels

Pretreatment	Salt spray	Stack test
Standard chromate	48 hours	14 days
Non Chrome Replacement	150 hours	28 days

FIGURE 1

TREATMENT PROCESS

Continuous Processing of Zinc Parts

Degrease if necessary

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Mild alkaline cleaner

Rinse in D.I. water ↓

Deoxidizer

Rinse in D.I. water ↓

Proprietary Permanganate solution at 70°F (21°C)-145°F (63°C) for 10 seconds or longer to form clear to gold-brown conversion coating.

Rinse in D.I. water ↓

Apply inorganic seal and dry (For maximum corrosion resistance)