Multiple-step Alternatives to Chromate Passivation

Craig V. Bishop & Dr. Gary Loar, McGean-Rohco, Cleveland, OH

One of the many advantages that hexavalent-chrome-based passivation methods enjoy is that they can be applied in a single step following cleaning or plating. Attempts to eliminate hexavalent chromium have been hampered by the self-imposed constraint of matching this single-step advantage. In this paper, we will explore how a multiple-step paradigm can be used to meet all the of the advantages of hexavalent chromium based on passivation.

For more information, contact:
Craig Bishop
McGean-Rohco, Inc.
2910 Harvard Ave.
Cleveland, OH 44105
Phone: 216/441-4900 Ext. 5
FAX: 216/441-1377
e-mail: kreg001@ameritech.net

Multiple Step Alternatives to Chromate Passivation

Craig V. Bishop
Gary W. Loar*
McGean-Rohco, Inc., Cleveland, OH
CeeBee Division, McGean-Rohco, Downey, CA

There are many perceived advantages with hexavalent chrome based passivation methods. Table one lists a number of them. However, hexavalent chromium is highly regulated and considered both a health risk and a pollutant. Consequently, finding a substitute for hexavalent chromium based passivates is an ongoing effort by individuals, companies, and government laboratories.

Various methods have been tried. One method is to analyze the structure of the passivation film and attempt to find analogous structures using non-chrome or non hexavalent chromium species. This technique has had some success. Trivalent chromium based passivates have been commercialized for zinc[i,ii,iii,iv] and zinc alloy treatment. Depth profiling of these films, using Auger Electron Spectroscopy and x-ray photoelectron spectroscopy[v], demonstrates many analogous features, such as olation polymerization[vi], in common with films obtained from hexavalent chromium based solutions. Based upon Pourbaix diagrams and other considerations it is likely that films based upon molybdenum, titanium, aluminum, and similar salts can also be considered analogous to the structure of hexavalent based chromium derived films.

Table 1

	Desirable Characteristics of Hexavalent Chromium Based Passivates:
1	Passivates the surface (prevents oxide formation)
2	Provides a color to the surface
3	Slows corrosion in prototypic tests such as salt spray, roof top exposure, beach exposure, etc.
4	Aids in providing adhesion to organic coatings
5	Conductive (not a great dielectric)
6	Thin Coating
7	Flexible Coating
8	'Primes' the surface to enable paints to easily spread and bond (coupling)
9	Helps prevent 'creep' in paint corrosion tests
10	Enhances paint adhesion
11	Easily applied, usually at room temperature, in a single immersion step
12	Not flammable
13	Stable solution
14	Durable - Can be handled roughly (eg. rubbed against each other)
15	Resilient - Can recover from scratches (self repairs)
16	Can rehydrate after being heated
17	Coatings are easily applied to recesses
18	Adequate lubrication for inserting and removing nuts and bolts automatically
19	Easily Stripped
20	Generally applied in a single tank or spray
21	Often does not require specific substrate alloy
22	Inexpensive

Another method to find a substitute for hexavalent chromium based passivates is to obtain homologous performance characteristics compared with hexavalent chromium based passivation treatments. For example, organic films such as polyacrylate, emulsified oil, micro-dispersed olefin or paraffin can provide a measure of corrosion protection but haven't a structure similar to the film from hexavalent chromium solutions. Metal-organic coupling agents such as silanes, titanates, organo chromium complexes and so forth can aid adhesion to subsequent layers of paint and have distinctive structures of their own. Zirconium, cerium, phosphates[vii], and a wide variety of metal oxides and salts can be used to make films which have colors similar to conventional chromates. Soluble or dispersed silicate has often been used to provide corrosion protection.

All of the above technologies have had some measure of success, yet, despite these efforts in finding analogues and homologues the search for a commercially successful non-chrome passivation treatment has been, by in large, unsuccessful. That is, one or more of the desirable characteristics of table one have been achieved by each technology. But, other desirable characteristics have not been achieved.

While the search for hexavalent chromium alternatives has progressed so has the technology of hexavalent chromium passivates. Especially those applied to zinc alloys. Modest amounts of iron in a zinc electrodeposit have greatly improved the salt spray protection of essentially conventional hexavalent chromates. Modified chromates, such as silver free black chromates, have been developed which take advantage of zinc-nickel alloy deposits and dramatically improve salt spray corrosion.

In addition to new formulations, different application methods have been commercially accepted. For example, it is not uncommon in Asia or Europe to passivate zinc or zinc alloy plated parts in baskets, off line, or on separate lines using multiple steps such as an activator, a chromating solution, a seal, then dry and package or apply a subsequent coating such as an oil to improve lubricity or an organic or silicate film to further improve corrosion protection after heat exposure or prevent worker exposure to hexavalent chromium.

If the multiple step approach with hexavalent chromium based passivates has achieved some measure of commercial success then can a multiple step approach be successfully applied to non hexavalent chrome based passivates? In other words, the 'desirable characteristic' of a single dip or spray no longer needs to be rigidly applied as a criteria for an acceptable non hexavalent chromium passivate.

Recent work in our laboratory has attempted to use a multiple step technique to duplicate hexavalent chromium based passivation performance. If each step results in a separate thin layer then we believe that there are three 'essential' layers to produce successful coatings on zinc or zinc alloys. These essential layers are an adhesion/color layer, a 'binder' layer, and a 'protective' layer. Additional layering may be necessary depending upon the final application of the part.

The bottom 'adhesion/color' layer must be adherent to the substrate and possibly produce color by adsorption or by thin film interference. Solutions which produce adherent films analogous to hexavalent chrome coatings such as those based upon trivalent chrome, aluminum, molybdenum, cerium, zirconium and titanium salts, often have 'color', and do not prevent adhesion, and often promote adhesion, of subsequent layers.

The center layer is designed to bind the first layer with a subsequent layer and utilizes a coupling agent[viii] such as a chrome coordination complex, orthosilicate, silane, titanate, or zirco-aluminate. The minimum requirement of this layer is that it can form an adhesive bond to both the underlying substrate adhering layer and the next layer. It is also desirable that the coupling agent be stable in aqueous solution so that it can be applied easily and that it also form a film which, after drying, is ultimately hydrophobic.

The next layer is designed to provide physical and chemical protection. If a thick coating is acceptable traditional 'top coats' such as acrylates, lacquers and paints may be applied. If the total thickness of the finish should not exceed that of a conventional chromate then micro dispersed colloidal nano-particles[ix] such as, gold, silicates, titanium dioxide, etc. have been found to be useful. Nano-particles can form very well ordered arrays on a properly prepared surface. These well ordered arrays are capable of providing corrosion protection and, when disturbed, in some cases, can re-order (e.g. repair) themselves. The thickness's of coatings using nano-particles are comparable to conventional hexavalent chrome based iridescent or 'olive drab' coatings based upon argon ion sputtering. Conductivity of the coatings can be controlled by the chemicals used to disperse the nano particle colloid.

The application of well ordered nano-particles seems to be facilitated if the preceding 'binder' is first dried (dry-wet processing). We have found that immersing 'wet' parts into solutions of nano-particles (wet-wet) often makes the nano-particles clump and provides non-uniform corrosion protection. However, if the binder is first dried, then the parts are immersed into solutions containing nano-particles, the resulting coating is well ordered and uniform. It is likely that this phenomena can be explained by the recently 'rediscovered' observation that entropy can drive solutions of particles to produce well ordered particles on a surface[x,xi]. Table two illustrates how salt spray performance can be dramatically effected by multiple step coatings on zinc and zinc alloy.

The performance benefit of dry-wet processing adds another level of complexity to multiple layers and since drying does not add a layer we refer to the entire process as multiple step. Compared to single dip, rinse, and dry chromating of zinc the sequence of steps seems cumbersome, impractical, and possibly prohibitive. However, we have seen many commercial examples of dry-wet processing of zinc parts prior to the application of hexavalent chrome passivates after plating and prior to the application of an oil or wax after chromating.

After the application of these three layers optional layering can still occur if desired. For example, additional colorants can be adsorbed by the coating. Or, polyethylene or polyolefin 'waxes' can be applied to control the lubricity of the final product. Of course, painting, powder coating, and e-coat finishes can also be applied.

We conclude that the multiple step application of sequential layers from non hexavalent chrome containing solutions can provide coatings that can match the majority of the desirable characteristics of hexavalent chrome based passivates.

Table 2 Examples of Variation in Salt Spray Performance With Treatment Steps

Treatment Sequence	Appearance	Salt Spray Resistance (5% WC)
Zinc, Colorant A	Black	< 2 hr
Zinc, Colorant A, Binder A, nano-particle A	Black	48 hrs.
Zinc, Colorant A, Binder A, dry, nano-particle A	Black	216 hrs.
Zinc nickel (14%), Colorant B	iridescent	240 hrs.
Zinc nickel (14%), Colorant B, Binder A, nano-particle A	iridescent	240 hrs.
Zinc nickel (14%), Colorant B, Binder A, dry, nano-particle A	iridescent	>1500 hrs.

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