Non-Hexavalent Chrome Passivation Technologies for Zinc and Zinc Alloys

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A variety of technologies have been employed, with varying degrees of commercial acceptance, in an effort to eliminate hexavalent chromium as a passivating species. Trivalent chromium compounds, organic films, non-metal oxides, organometallics, and non-chrome metal ions have all been proposed as alternatives to hexavalent chromium. A summary of these technologies, including their benefits and liabilities, will be presented as well as a discussion of possible synergies between hitherto competing technologies.

Hexavalent chromium based passivates (HCP's) exhibit a number of desirable characteristics (table 1). However, the health and environmental issues associated with hexavalent chromium argue for the replacement of HCP's[i,ii] There have been several technologies, which have been employed in attempting to replace HCP's. The authors classify the HCP alternative technologies into five categories: trivalent chromium based (CrIII), organic coating based, non-metal oxide based (oxide), organometallic based (OM), and non-chrome metal ion based (M^x). Many of the alternative technologies are used in complementary fashion either by sequential application or by mixing.

When examined by scanning electron microscope (SEM) HCP's generally have a cracked appearance if colored which clear HCP coatings lack. The presence of cracks indicates a thicker coating. The composition of HCP is

	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

Table 1 Desirable characteristics of HCP's

accepted as being based upon a trivalent chromium olation polymer[iii].

Of the HCP alternatives it is likely that the most popular alternatives have been CrIII based. The CrIII alternative was first described in the 1950's and gained commercial acceptance in the mid to late 1970's when non-cyanide alkaline zinc plating often exhibited dark spots after application of conventional clear HCP. CrIII based passivates did not 'spot' the work. The CrIII clear passivates of the 70's came in three varieties: peroxide augmented, non peroxide, and blended with metal ions such as cobalt ion, and rare earth ions (eg. cerium). These CrIII based alternatives were limited to 'clear' or 'blue' coatings on zinc and SEM demonstrated that the morphology was not 'cracked'. Recently iridescent and black CrIII alternatives were introduced into the market for use with zinc nickel (ZnNi) alloy followed quickly by other CrIII based coatings that produce pale colors on zinc and zinc iron alloys. These new coatings have SEM crack patterns from which increased thickness can be implied. The peroxide augmented CrIII alternatives are now seldom used with zinc but research into the use of peroxide augmented CrIII continues as an HCP alternative for aluminum alloys.

Perhaps as popular as CrIII HCP alternatives are organic coatings used as a final coating in a sequence of steps or combined with metalloid oxides such as silicates. For architectural metals such as aluminum or colored steels organic coatings from aqueous solutions are very popular. With electroplated parts, in some cases when leaching of hexavalent chromium is a concern, organic coatings are applied to HCP or combined with HCP. In which case excellent corrosion protection is achieved and leaching is claimed to be minimized. Most organic films are polyacrylate based however polyethylene waxes and solubilized oils are not uncommon coating constituents. Many claims have been made suggesting the use of various surfactant and surfactant combinations as non-HCP coatings however the commercial acceptance of these inventions has not been forthcoming. Stability of the organic coatings is often a concern as acids or plating solutions dragged into an organic solution can cause precipitation. The continuity of the film is important if good corrosion protection is desired but often, increasing the coating weight of the film so as to ensure continuity causes other problems such as 'sagging', dimpling, or thread tolerance loss. Continuous organic films are typically insulators and difficult to use if electrical conductivity must be assured.

The use of silicate with HCP is as time honored as leaching with carbonate or caustic. Silicate and other non-metal oxides such as phosphate have been applied directly to zinc, or HCP, or non-HCP for quite some time. Silicate coatings have been applied as topcoats since the mid-80's from alkaline solutions. The insoluble sodium silicate is glass like and can provide an effective barrier coating. However, silicates applied from aqueous solution can eventually be dissolved by aqueous solution and their protection is of limited duration. In order to improve the barrier provided by silicates many attempts at preparing silicate coatings using sol gel technology have been tried. The principal drawback to these technologies has been the stability of aqueous solutions. The sol 'gels' too quickly.

Recently sol gels employing the non-chrome metal oxide of zirconium and silicate from silane have been receiving interest as HCP alternatives[iv].

Organometallic based HCP alternatives are primarily based upon silanes although titanates, partially polymerized silanes, and organo-zirconates are also being taught. Silanes as adhesion promoters have a long history in the paint, rubber, and fiberglass industries[v]. Silanes are often di-functional with one end of the molecule having an affinity for an oxide surface and the other end of the molecule customized for bonding to a subsequent layer. For the past decade we have been recommending silane from aqueous solution as a multilayer bonding method in printed wiring board fabrication. In the early 90's we attempted to introduce silane from solvents as an alternative to HCP but the objections to a solvent could not be overcome at that time. Recently aqueous silanes have been proposed as an alternative to HCP[vi]. There are relatively few silanes that are stable in aqueous solutions for more than a few hours as the silane converts to siloxane then polymerizes. This polymerization of silane is one of the principal reactions involved in sol gel coating schemes. The cost of silane is significant.

Following the commercialization of CrIII in the late 70's there was a great deal of activity in proposing non-chrome metal ions as HCP alternatives. The coloring of zinc achieved with acidic aluminum, titanium, molybdenum, rare earth, and cobalt salts is dramatic.

	CrIII	**Organic**	**Oxide**	**Organo-metallic**	**M^x**
1	5 with zinc, 8 with ZnNi alloy	6-8 if thick	3	2	2
2	7-9	7	1	1	10
3	5 with zinc, 10 with ZnNi alloy	8-10 if thick	5	2	2-3
4	6	6	6 (SiOx), 10+(POx)	10+	5
5	10	0 if thick	0-5	8	10
6	10	0	3	10	10
7	8	10	4	10	8
8	8	6	3	8	6 est.
9	6	5	10	10	6 est.
10	7	7	10	10	8 est.
11	10	7	10	5	10
12	10	5 (concentrate)	10	5 (concentrate)	10
13	10	7	9	2	10
14	8	9 if thick	7	3	6
15	2	7	0	0	2
16	7	7	3	6	6
17	10	5	8	10	10
18	8	4	8	3	8
19	9	2	4	3	9
20	10	5	5	10	10
21	5	10	10	5	5
22	9	7	8	2	7
sum	165-169	123-127	126-135	123+	143-144 est.

Table 2 Comparison of HCP alternatives vs. desirable characteristics of table 1 (1-10 score).

The ease of application was similar to that of HCP.

But, the corrosion protection was not comparable to HCP nor even the modest corrosion protection of clear CrIII based passivates. Recently the use of cobalt salts with zinc and zinc alloys have achieved better corrosion results and zirconium treatments of aluminum have also enjoyed some improved performance. Commercial acceptance however has been non-committal.

We can subjectively compare the HCP alternatives to the desirable characteristics of HCP in a table and summarize the estimated benefits (table 2). When we do so we conclude that CrIII compares 75% favorably to HCP. Organic alternatives about 57%. Oxides about 59%. Organometallics about 56%. And, non-chrome metal ions about 65%. In terms of corrosion protection criteria (1,3,14,15,16) only CrIII (with ZnNi alloy) and organic films approach the performance of HCP. For appearance CrIII with ZnNi and non-chrome metal ions have the upper hand. For use as a primer organometallics are superior.

In a perfect world there would be a single dip alternative to HCP which matched all the desirable characteristics of HCP. Of the candidates CrIII and non-chrome metal ions have come closest. To date, however, they have failed to completely match HCP.

For these reasons more and more vendors are either using alloys with alternative HCP and/or combining alternative technologies by mixing them into composite solutions or suggesting that the alternatives be applied sequentially. These hybrid technologies often provide synergies that can nearly duplicate all the desirable characteristics of HCP.

Passivation of zinc nickel alloy by trivalent chromium[vii,viii] can provide iridescent colored coatings that easily outperform HCP on zinc although not quite match HCP on zinc nickel. Black CrIII coatings on zinc nickel are possible[ix] but not yet commercially perfected. The disadvantages of this hybrid process are the color of the coating is different than normal HCP and the CrIII solution must be heated. Commitment to this process from manufacturers already specifying zinc nickel should be forthcoming. However, some countries and manufacturers are moving toward regulation of nickel and possibly toward a total ban on chrome. These last two uncertainties make commitment to a CrIII Zn/Ni process difficult for all but the largest specifying organizations. Despite the tremendous longevity and corrosion benefits of Zn/Ni alloy and the fact that CrIII can eliminate hexavalent chromium in some cases CrIII coating with Zn/Ni is being viewed as an interim step to a ‘nickel free’ ‘chrome free’ process. Cost benefit analysis should be performed before such judgement is rendered permanent.

Mixtures of HCP with organic and/or oxides, especially silicates, or non-chrome metals have been used for nearly thirty years. These processes can greatly extend HCP corrosion protection and some claims have been made which argue that hexavalent chrome becomes immobilized (won’t leach out) with these technologies. Analogous mixes with non HCP alternatives such as CrIII and organometallics have not produced similar performance benefits.

For quite some time organic coatings have been applied after HCP. The organic films may improve appearance, corrosion protection or lubricity. In some applications parts are processed through HCP, dried, then dipped in organic solutions, then redried in order to prevent the decomposition of the organic solution.

Such a wet dry wet dry process sequence can also be employed with HCP alternatives. For example treatment with a non-chrome metal ion can provide a color which closely matches traditional HCP. Then applying an organic film or an oxide will preserve the color and improve corrosion protection. Recently, our laboratory has been testing a sequence consisting of metal ion colorization, application of an organo metallic, and application of an oxide to achieve salt spray results rivaling those of conventional HCP on zinc and surpassing conventional HCP on zinc if applied to zinc alloy.

	CrIII with Zn/Ni	Mixture	Multiple Steps
color	9	3	9
corrosion	10+	7	7
handling	10	8	4
paintable	9	3	6
Sum (40 max.)	39+	21	26
Cr free	0	10	10
Ni free	0	10	10
Sum (60 max)	39+	41	46

Table 3 Comparison of hybrid technologies with HCP (score 1-10).

Our goal has been to make the process cost effective and eliminate intermediate drying steps.

In table 3 we compare some of the ‘hybrid’ processes with conventional HCP on zinc. If the criteria of chrome free and nickel free are not considered CrIII treatment on ZnNi nearly matches the performance of HCP on zinc. It is only if the additional criteria anticipating ban on nickel and all chromium are factored in that hybrid mixtures and multiple step sequences become marginally better candidates for HCP alternatives than treatment of ZnNi with trivalent chromium. As ZnNi continues to gain adherents in Europe, Asia and eventually North America and issues such as ductility, efficiency, and control are resolved a commensurate increase in CrIII alternatives can be expected provided a total ban on chromium is not promulgated.

Should nickel and chromium become banned the most likely HCP alternative will be a hybrid process. The best current candidate involves multiple application steps although mixtures of technologies cannot be ruled out at this time.

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[i] General Motors GMW3059 forbids the use of hexavalent chromium as a topcoat after Jan. 1, 2003.

[ii] European End of Life Vehicle Requirement ‘will prevent the disposal of cars containing more than 3 grams of hexavalent chromium … after Jan. 1, 2003’

[iii] Von C.V. Bishop, D.M. Burdt, K.R. Romer. "Eine mogliche Struktur verschiedene Chromatierungsschichten aur electrolytisch abgeschieden

Zinkuberzugen" (Possible Structures of Various Chromate Coatings on Zinc Electroplate)"Galvanotechnik•, 71, 1199, (1980)

[iv] Blohowiak et al. "Sol-Gel Coated Metal", USP 5939197

[v] Edwin P. Plueddemann "Silane Coupling Agents 2nd ed.", Plenum Press, New York, 1991.

[vi] van Ooij and Yuan "Method of Preventing Corrosion of Metal Sheet Using Vinyl Silanes" USP 5759629.

[vii] Craig V. Bishop "Iridescent Chromium Coatings and Method", USP's 5393354 and 5407749

[viii] Patricia Preikschat et al. "Chromate Free Conversion Layer and Process for Producing the Same", WO 97/40208

[ix] Bishop and Thomay "Black Chromium Containing Conversion Coatings on Zinc-Nickel and Zinc-Iron Alloys", USP 5415702