Corrosion Performance of Environmentally Acceptable Alternatives to Chromium Coatings

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Coatings and surface modifications represent an approach to implementing alternatives to environmentally unacceptable chromium coatings. Suitable replacements must exhibit the desired combination of properties, such as appearance, wear and corrosion resistance, and hardness without adversely affecting the substrate materials. Corrosion resistance is a key parameter for evaluating candidate alternatives. The corrosion performance of coatings and surface modifications, applied by a variety of wet and dry methods, is reviewed for some of the candidates under consideration for use in industry and the military industrial base. Some electroless nickel and HVOF thermal spray inorganic coatings show promise as replacements for chromium.

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Introduction

Because there are health risks and environmental problems associated with the use of chromium, the U.S. Environmental Protection Agency (EPA) included it on their list of 17 high priority chemicals for voluntary reduction by industry. Consequently, in the manufacturing sector there has been an extensive search for alternatives to provide acceptable decorative finishes or functional coatings with properties, such as corrosion resistance and wear resistance, at a reasonable cost. However, no single replacement has been found that is suitable for all end use applications. Replacements ranging from vacuum deposited coatings to thermal spray coatings to alternative electroless and electrolytically deposited alloys have been proposed and evaluated. Some of these alternatives are being used commercially.

References (1) through (6) summarize some of the recent and ongoing work in this area and baseline properties for chromium coatings. The purpose of this paper is to bring together the available data on the corrosion resistance of these alternative coatings so that more informed decisions may be made about which to use for a given application.

Types of Corrosion Tests

There are several ways to categorize corrosion testing; e.g., low temperature *versus* high temperature, wet *versus* dry, atmospheric *versus* immersion, industrial *versus* marine, and so on. For the purposes of this paper, three general types of test were used to obtain the majority of the published corrosion data; namely, atmospheric or simulated exposure, chemical immersion, and electrochemical polarization techniques.

Much of the reported corrosion data is obtained from an exposure to salt fog (salt spray) using the ASTM B 117 testing method. While this test does not provide data that correlate well with actual use, it is widely accepted as a means for screening and comparing materials, coatings, and surface modifications. A much more realistic test involves cyclic conditions of exposure to the corrosive environment(s) (e.g., temperature, humidity, and so on) in GM 9540P, "Accelerated Corrosion Test"). However, only limited data exist in the literature on the results of such testing.

For some applications, resistance to specific chemicals is important. These range from acidic and alkaline solutions in food processing and paper making, to hydraulic fluids in aircraft. Coatings for these applications are evaluated in part by simple immersion tests. For other applications, high temperature oxidation or sulfidation resistance may be important. Coatings for these applications are evaluated by exposure tests at anticipated operating temperatures.

Fundamental information about the corrosion processes occurring, or the likelihood that corrosion may occur in given environments under specified conditions, can be obtained from electrochemical polarization and impedance measurement techniques. Parameters such as corrosion potential (voltage), corrosion current, passivation current, passive - active - transpassive transition potentials, and real and imaginary impedance, are used by corrosion engineers to interpret corrosion behavior. It is beyond the scope of this paper to discuss these tests and their interpretation. References (7) and (8) provide some helpful background information on this topic.

Alternative Coatings - Overview

Table I summarizes the types of coating and surface modifications that have been investigated and reported as possible replacements for conventional, electroplated chromium coatings using an arbitrary classification (i.e., metallic, inorganic, and non-metallic). These coatings are said to have a less adverse impact on the environment because of the reduction in use, or elimination of chromium.

References (1) through (6) provide some general details about these coatings or modifications, how they were applied, and their mechanical properties. Subsequent sections of this paper provide a discussion of the published corrosion test results for some of these chromium alternatives.

The Federal Specification for "Chromium (Electrodeposited)", QQ-C-320B does not contain requirements for corrosion resistance for either Class 1 ("decorative") or Class 2 ("hard") coatings. Typically, with a nickel under-coating on ferrous substrates, electroplated hard chromium deposits should not exhibit signs of red rust after 96 hours of salt fog exposure in the ASTM B 117 test.

Table 1. Possible Alternatives to Cadmium and Chromium Coatings

Category	Chromium Alternatives**
◆ Chromium-based Coatings*	• Cr(III) ("trivalent chromium") • Cr_2C_3 Compounds • CrN Compounds • Cr-Ni Alloys • Cr-Si Alloys
◆ Cobalt-based Coatings	• Co-W Alloys • Co-Mo-Cr-Si Alloys
◆ Nickel-based Coatings	• Electroless Ni (with P, B, W) • Ni • Ni-Co+ZrO_2 Composites • Ni-Cr-Mo Alloys* • Ni-CrO_3 Composites* • Ni-Mo Alloys • Ni-P+SiC Composites • Ni+PTFE Composites • Ni-SiC Composites • Ni-Si_3N_4 Composites • Ni-W Alloys • Ni-W-B Alloys • Ni-W-Cr-Si-B Alloys* • Ni-W-SiC Composites • Ni+WC Composites
◆ Tin-based Coatings	• Sn-Co Alloys • Sn-Ni Alloys
◆ Miscellaneous Inorganic Coatings	• Al_2O_3-TiO_2 Mixtures • *Fe-Cr-Mo Alloys** • TiN Compounds • WC-Co Mixtures • WC-Co-Cr Mixtures*
◆ Non-metallic Coatings	• Nylon-based Polymers • SiO_2 Polymers

* *Lower exposure to hazardous material (e.g., Cr^{6+}).*

** *Deposited by variety of techniques.*

It should be pointed out that thin chromium coatings are usually employed for their aesthetic (decorative) qualities, while thick coatings are employed for their engineering properties, such as wear and abrasion resistance, and are used to restore worn surfaces. Chromium is a relatively inert metal and provides protection from the environment through a barrier mechanism. However, electrodeposited coatings tend to be microporous or microcracked, offering little protection to the substrate material in aggressive environments unless a corrosion-resistant undercoating (such as nickel) is used. As a result, some of the chromium alternatives proposed incorporate an under-coating, or consist of layered structures to provide good corrosion resistance.

Chromium-Based Alternatives

While the search for acceptable alternatives is underway, it has been proposed that chromium or chromium-containing coatings, deposited by other than electrolytic methods, would present less of a health and safety risk by avoiding exposure to hexavalent chromium [Cr(VI)] compounds. Also, there are serious proponents for using chromium coatings electro-deposited from baths formulated with trivalent chromium [Cr(III)] salts, and not hexavalent salts.

The regulations governing the use and disposal of chromium metal and trivalent salts are less restrictive than those for hexavalent salts, so some surface finishers requiring coatings with equivalent properties to electroplated hard chromium (EHC) have chosen to use "chromium-based" alternatives. The corrosion resistance of some of these coatings is described in this section.

Trivalent chromium, electrodeposited coatings, in particular, are discussed in References (2) and (3). As for most EHC coatings, typically one or more nickel "barrier" layers are deposited followed by the Cr(III) coating. These multilayer coatings have been said[1,2] to exhibit comparable corrosion resistance to EHC coatings when evaluated using the ASTM B 117 Salt Fog Test or the CASS Test (ASTM B 368, Copper Accelerated Salt Spray). However, when subjected to the Corrodkote Test (ASTM B 380, service condition #4) for equivalent nickel and chromium coating thicknesses, the trivalent chromium performed better than the baseline, electroplated hard chromium coating[3]. These test results are summarized in Table 2 below.

For functional (engineering) applications, pulsed current plating has been tried to obtain better, thicker, trivalent chromium coatings. To date the results of corrosion testing of these coatings have not been very promising. Reference (9) provides some data from an ASTM B 117 test on shock absorber rods. For (cathodic) duty cycles of 80 % and higher, the pulse plated deposits exhibited fewer and smaller corrosion pits than the equivalent direct current plated coatings. However, after 48 hours, these surfaces exhibited "spots of corrosion" covering 8 % to 15 % of the exposed area. After the coatings received a surface pretreatment ("microstoning") to reduce porosity and close micro-cracks, the corrosion related performance was improved, but still could not meet the 96-hour arbitrary exposure set for EHC.

Electroplating is a "wet" process, usually carried out in aqueous solutions. As an alternative, cathodic arc sputtering - a "dry" process - has been investigated for depositing thin, dense chromium films[10]. An alternating immersion test, carried out over a period of 24 hours in a 4 % sodium chloride solution, demonstrated that this type of coating performed as well as the traditional EHC coating. In this test, the specimens were dipped in the salt solution once every second.

Chromium with nickel or silicon has beer diffused into the surfaces of ferrous materials t improve their corrosion resistance. A proprietar laser alloying technique[11] or a more traditional, co diffusion technique[12] were used, respectively. Th former technique had as its objective providing stainless steel type composition on the surface of 1010 steel. The open circuit potentials in chloride environment (3.5 % NaCl) were mor positive for the treated steel, and the linea polarization resistance values were an order o magnitude greater than those for the untreated 101 steel specimens. Instantaneous corrosion rates, as function of time, were calculated from the linea polarization resistance measurements. The rate were considerably lower for the alloyed surfaces as indicated in Table 3 below. Based on ASTM D 714 ratings, the laser treated specimens wer acceptable ("passed") after testing for 90 days[11].

The co-diffusion coated, 1018 steel i being used successfully in the petrochemica industry. The high chromium content (about 30-4 weight percent) and silicon content (about 1.5-2.5 weight percent) is said to resist "..most aqueou environments ...even sour, acidic, and heavy crudes". Tests in simulated, downhole wel conditions yielded corrosion rates of only 25 to 3 µm/yr (about 1.0 to 1.3 mils/yr). These chromium containing diffusion coatings also are said t provide excellent resistance to high-temperatur oxidation, sulfidation, and halide attack, such as i found in boilers, heat exchangers, and incinerator in the power generation and chemical industries[12].

Cobalt-Based Alternatives

Alloy coatings containing nickel, tin, anc cobalt have received considerable attention a substitutes for EHC coatings. Only limited data exist for cobalt-based alternatives. References (5) and (13) describe the properties of an electro-deposited alloy coating that was nanocrystalline o fine grained (crystal sizes of 90-150 Å) depending on the deposition parameters used. Nevertheless all coatings were found to display simila properties. In adhesion tests, all coatings adhere well to the carbon steel or mild steel substrate when exposed to temperatures up to 400 °C Cracks in the coating became evident at 500 °C and the Co-W coating peeled at 600 °C, making this coating unsuitable for high temperatur applications. In comparison, the chromium-coate specimen continued to adhere to the substrates.

Table 2. Comparison of Corrosion Data for Cr(VI) and Cr(III) Decorative Coatings

ASTM Test*	Average Thickness, µm				Rating** After Hours Shown		
	Nickel*		Chromium				
	Semi	Bright	(VI)	(III)	16	32	96
B 368	23	7.5	0.3	- -	10/9.7	10/8	8.8/6.7
	23	7.5	- -	0.3	10/9	10/8	10/6
	23	7.5	- -	0.9	10/9	10/8	10/6
					22	**44**	**132**
B 380	23	7.5	0.3	- -	10/8	10/8	7.5/5.7
	23	7.5	- -	0.3	10/9	10/8	10/7
	23	7.5	- -	0.9	10/10	10/10	10/6

** Barrier layers applied under the chromium electrodeposits.*

*** B 368 = CASS Test; B 380 = Corrodkote Test: 10 = Best (no discernible corrosion); 1 = Worst.*

Table 3. Corrosion Rates of Bare and Laser Surface-Alloyed 1010 Steel

Specimen	Rate, µm/yr after Exposure to 3.5% NaCl Solution					
	10 Days	20 Days	30 Days	40 Days	50 Days	60 Days
Bare 1010 Steel	163	185	188	168	218	163
1010/Cr+Ni	2.5	5.1	5.1	7.6	7.6	2.5

Source: Reference (11). Values are approximate: 1 mil = 0.001 inch or 25.4 µm.

The as-plated Co-W coatings were about 1.4 to 1.5 times softer than the EHC-coated, baseline specimens[13]. Comparisons were made of corrosion rate using data obtained from potentiodynamic polarization as well as electrochemical impedance spectroscopy (EIS) tests. Specimens that were heat treated at 500 °C exhibited corrosion rates that were 1.6 to 2.0 times less than the EHC controls. This improvement in corrosion resistance was attributed to the surface oxide layer formed during annealing. Salt fog tests showed that both the Co-W alloy coatings (heat treated at 500 °C) and the hard chromium coatings behaved similarly. That is, they displayed only small pits after 60 hours exposure[13].

Nickel-Based Alternatives

Nickel, and nickel alloy or composite coatings, typically are deposited by electrolytic (electroplating) or electroless techniques. Electroplated nickel coatings exhibit relatively good corrosion resistance, especially in alkaline environments, but tarnish easily in sulfur-containing atmospheres. They do not perform as well in marine, environments. Like chromium, protection is provided by the formation of a physical barrier between the substrate and the environment. Consequently, dense, defect free nickel coatings provide the best protection.

Similarly, electroless nickel (EN) coatings containing phosphorus (Ni-P) or small amounts of boron (Ni-B) to provide desirable properties, also provide a barrier to the environment. Ni-P or Ni-B coatings are often used under thin PVD or CVD coatings, such as chromium or titanium nitrides, to increase their corrosion resistance. Electroless Ni-P coatings are usually categorized as "low P", "medium P", or "high P". Each category exhibits a different range of properties that makes those coatings best suited for specific applications. In general, greater aqueous corrosion resistance is exhibited by coatings with higher phosphorus contents; however, good corrosion resistance is exhibited by low P deposits in alkaline solutions.

Electroless Deposited Coatings

According to Reference (2), electroless nickel (Ni-P) coatings, about 8 µm thick, in the as-deposited condition, exhibit resistance to salt fog exposure of 50 hours, or longer, depending on the heat treatment that the coatings had received. In comparison, the time to red rust for a chromated, electroless, high P nickel coating on steel is about 1,000 hours. Unfortunately, (di)chromating reintroduces Cr(VI) into the processing chemicals, and these have to be treated as hazardous materials.

Some data are available for chemical immersion tests in a wide range of acids using a high-phosphorus (11%), electroless nickel coating as a control. The test data for the latter are summarized later in Table 7. Other data[6] for a low P coating show that, although it exhibits good resistance to oils, greases, and hydraulic fluids, it is attacked by nitric acid and sulfuric acid-hydrogen peroxide mixtures.

As stated earlier, the resistance to salt fog exposure generally improves as the phosphorus content increases in the deposited coating. Data for a wide range of commercially available, EN coatings are contained in Reference (6). While the results vary depending on bath chemistry, deposit thickness, and post-treatments, the data summarized in Table 4 provide a general guideline. The medium P and high P coatings provide good corrosion resistance; however, the hardness of many of these coatings does not match that of EHC, and some of these coatings may have been chromated.

Table 4. Guidelines for the Corrosion Resistance of EN Coatings

Type of EN Coating	Hours (Days) to Red Rust*
Low P	> 96 (4)
Medium P	>240 (10)
High P	> 1,008 (42)

** Source Reference (6). ASTM B 117 Salt Fog Test.*

A proprietary, electroless nickel-phosphorous (ENP) bath has been developed that utilizes operating conditions similar to that of a standard electroless nickel plating bath. However, this new plating bath contains only 5 g/l of nickel and is operated at a neutral pH of 7. Because the hardness and wearability has been improved over conventional EN deposits, this ENP coating has been used as a chromium replacement. Corrosion studies were performed on 38 μm (1.5 mils) thick coatings, with half of the samples passing ASTM B 117 salt fog testing for 100 hours. The corrosion results were much better than anticipated, but the data were inconsistent. Nevertheless, for wear applications, this new EN deposit shows promise as a chromium replacement[14].

Another proprietary bath that produces thick EN coatings, with occluded boron particles and a small amount of thallium, has been investigated[6]. In the Salt Fog Test, this type of coating withstood 200 hours exposure. Also, these coatings could withstand exposure to an oxidizing atmosphere at 982 °C. However, coatings from this bath were difficult to reproduce, and could not be used on magnesium or carbide-based substrate materials. Another commercially available bath provided thin (1-2 μm) coatings for electronic (circuit board) applications as a replacement for "flash chromium". These coatings can provide > 100 hours of protection in a salt fog environment[6]. Thicker Ni-B coatings from another proprietary bath also provide > 96 hours of protection ("equivalent to chromium") but sulfur in the environment corrodes the nickel matrix, as does nitric acid[6]. Petroleum-based chemicals and most cleaning chemicals have been said not to have an adverse effect on these coatings.

The properties of EN coatings containing 1.43-6.60 % P and 2.11-7.05 % B were studied and the results reported in Reference (15). Electrochemical tests revealed that at low phosphorus contents (< 3 %) the coatings corroded more rapidly than nickel in neutral solutions. When immersed in various low molecular weight alcohols, the corrosion currents increased with decreasing boron content and increasing alcohol chain size. The electroless Ni-P-B coatings were more resistant than conventional electroless Ni-P or Ni-B coatings. In contrast, Ni-P coatings containing 1.5-5 % B exhibited less than 24 hours to red rust in the ASTM B 117 test in another study[6]. This suggests that the addition of a third element to Ni-P coatings lowers the corrosion resistance, at least to salt solutions.

Silicon carbide (SiC) or 7-11 % tungsten (W) additions to Ni-P coatings have less of a detrimental effect, providing 100 hours, or more, to red rust formation, but these additions are added to improve wear resistance not corrosion resistance. Table 4 shows that medium P, and high P, EN coatings alone can provide this level of corrosion protection. Adding a solid lubricant (e.g., particles of polytetrafluoroethylene, PTFE) to a medium P, EN coating to improve its lubricity has an adverse effect on salt fog resistance. Forty eight hours, or less, to red rust have been observed[6] for these coatings. Thick deposits (containing 25 % PTFE) from another type of proprietary bath, on a wide range of substrate materials, have been said[6] to provide 500-1,000 hours of protection in the ASTM B 117 test.

EN coatings and EHC coatings have been used as a barrier layer in multilayer coatings. Reference (16) describes experiments with a

coating system comprised of the barrier layer on a tool steel followed by a hard coating (such as TiN or CrN) deposited by a physical vapor deposition (PVD) technique. The polarization behavior of these multilayer coatings was determined in deaerated, 1 N sulfuric acid solution held at 25 °C. Corrosion attack was evaluated, using a metallographic technique, after the polarization measurements were made. It was found that the EN layer provided better corrosion resistance than the EHC coating used, primarily because the latter contained microcracks. Heat treatments above 350 °C had an adverse effect on the corrosion resistance of the EN deposits, so care must be taken when applying subsequent coatings. Finally, the CrN top layer provided better corrosion resistance than the TiN top layer.

Electrolytically Deposited Coatings

Several proprietary, barrel and tank, nickel alloy plating processes exist for decorative and functional applications. The compositions of the alloys deposited usually are not specified by the vendors but some users have published performance data[5,17].

Corrosion data for a barrel plated, decorative finish to replace chromium are summarized in Table 5. Prior to depositing the nickel alloy, a nickel strike was used on steel and brass components. A proprietary passivation step was used on the electrodeposited nickel alloy to improve its corrosion resistance. The passivated, *proprietary alloy can provide at least 96 hours* protection in the ASTM B 117 test, unlike the EHC and trivalent coatings tested under the same conditions. In fact, this proprietary coating has been reported to resist corrosion for over 500 hours in salt fog testing.

Property data are available in References (4), (18), and (19) for some electrodeposited Ni-Mo and Ni-W alloys. The alloy coatings with tungsten concentrations up to 20-23 % and molybdenum concentrations up to 24-25 % were crystalline. However, amorphous deposits were obtained when pulsed current plating was used for Ni-W alloys, or by increasing the molybdenum content to 27 % in Ni-Mo alloys. These amorphous deposits were a little harder than the crystalline deposits, with the hardness being dependent upon the composition, deposition parameters, and subsequent heat treatments.

It was shown in sulfuric acid immersion, corrosion tests that the resistance of the Ni-Mo coatings increased with increasing molybdenum content up to 27 % molybdenum[18] but then decreased slightly when the content was increased to 33 %. Similarly, the corrosion resistance of the Ni-W coating increased with increasing tungsten content (10 < 20 < 23 %). However, the most corrosion resistant Ni-W alloy, with a tungsten content of 27-28 %, was obtained by using a pulsed current deposition technique. The results of the immersion test are summarized in Table 6 below.

Data for a Ni-35%W alloy coating are contained in Reference (19). While this coating is said to have good corrosion resistance and high hardness, unfortunately it has a yellow tint, making it unsuitable as a replacement for chromium in decorative applications. Open circuit potentials (OCPs, also called corrosion potentials, E_{corr}) were measured for this and other candidate alternatives for chromium. The results have been reported in Reference (19). All the coatings studied were more noble than iron (i.e., -0.560 V *vs.* SCE). The Ni-W alloy coating (-0.510 V) is anodic with respect to chromium, which has an OCP of -0.295 V in the same solution, unlike nickel (-0.300 V).

Table 5. Corrosion Resulting from Salt Fog Testing for a Proprietary Nickel Alloy Coating

Exposure hours	Hexavalent Chromium	Trivalent Chromium	Ni Alloy** No Passivation	Ni Alloy** With Passivation
8	None	10% Red Rust	Blue Tarnish	None
24	None	40% Red Rust	Blue Tarnish	None
48	2% Red Rust	80% Red Rust	- -	None
96	50% Red Rust	- -	- -	None
120	- -	- -	1% Red Rust	None
550	- -	- -	- -	1% Red Rust

*Source: Reference (17). ** Steel substrate with nickel strike and 5 microns (0.2 mil) coating; proprietary alloy.*

Table 6. Corrosion Rates of Ni-Mo and Ni-W Alloys in Sulfuric Acid

Nickel Alloy Coating	Corrosion Rate $mg/cm^2/min$*
95Ni-5Mo	82
83Ni-27Mo	4
67Ni-33Mo	6-11
90Ni-10W	70
80Ni-20W	2
77Ni-23W	4
83Ni-27W (Pulse Plated)	0

* *Source: Reference (18).*

Hardness and wear properties of Ni-W alloy coatings can be modified with minor alloying additions (such as B) or by occluding hard particles (such as SiC). Adding boron produces a proprietary, amorphous type deposit[20]. In the Salt Fog Test, a 10 μm (0.4 mil) coating over brass or steel provided at least 96 hours of corrosion resistance, while a 25 μm (1 mil) coating survived more than 500 hours exposure. Test data also are available for chemical immersion tests using a high-phosphorus (11 %), electroless nickel coating as a control. These data are summarized in Table 7. General attack on the Ni-W-B coatings was about three to four times less in acetic, phosphoric, and hydrochloric acids, but an order of magnitude less in the highly oxidizing nitric and fluoboric acids.

coatings were more corrosion resistant. After 9 hours exposure, the N-W-SiC coating received rating of 10/9, whereas the EHC control had rating of 2/1 after only 24 hours exposure.

Nickel, co-deposited with SiC, Si_3N_4 or CrO_3 submicron particles, also has bee investigated[22] for providing resistance to "ho oxidation and corrosion". Immersion tests i 0.1 M sulfuric acid, with the Ni-Si_3N_4 and Ni-CrO coatings removed from the substrate, gav dissolution rates of 45.4 and 51.3 $mg/m^2/h$ respectively, compared with a rate of 135.4 $mg/m^2/hr$ for the nickel baseline. In hot oxidatio tests conducted at 800 to 1,100 °C, the presence of four to six volume percent of submicron-sized particles of Si_3N_4 or CrO_3 reduced the rate o oxidation of the nickel matrix material by up t 25 times. Coatings containing greater volumes o the particles were unstable or resulted in highe oxidation rates. The authors pointed out tha additives used in the codeposition process coul have a significant effect on the results obtained.

Tin-Based Coatings

A number of tin alloys have been suggested as replacements for cadmium[5] but the only candidate proposed as a possible alternative for chromium in some applications is the alloy containing nickel[5,19]. An alloy coating containing

Table 7. Thickness Loss Data for Ni-W-B Alloy and Electroless Nickel

Chemical (Acid)	Average Thickness Loss (Thinning)*			
	Ni-W-B Alloy		Electroless Ni (High P)	
	μm/yr	mils/yr	μm/yr	mils/yr
1% CH_3COOH	2.5	0.1	20.3	0.8
5% H_3PO_4	7.6	0.3	22.9	0.9
10% HCl	5.1	0.2	22.9	0.9
25% HCl	7.6	0.3	25.4	1.0
25% H_2SO_4	10.2	0.4	20.3	0.8
25% HNO_3	17.8	0.7	>76.0	>3.0
48% HBF_4	2.5	0.1	33.0	1.3

* *Source: Reference (20).*

A Ni-W-SiC composite coating process has been developed and evaluated, as an alternative to EHC, particularly for aircraft applications[21]. In an immersion test using a 15 % hydrochloric acid solution, the composite coating was claimed to exhibit a corrosion resistance "100 times that of a hard chromium film". Salt fog test data reported in Reference (21) also showed that the composite

about 30 % nickel has a more noble open circuit potential than iron, but is anodic to chromium and nickel. Reference (19) states that the "corrosion resistance of Sn-Ni (*alloy coatings*) is not as good as one would expect from its chemical resistance"; however, no data were provided to illustrate this assertion. Nevertheless, Sn-Ni alloy coatings, especially those containing 33 to 35 % nickel

(corresponding to the inter-metallic compound in the system) exhibit good corrosion resistance in strong acids[23]. Service temperature is limited to about 320 °C because above this temperature the intermetallic compound decomposes. It was recommended[19] that a non-porous, nickel strike be used under Sn-Ni alloy coatings, and that they be passivated in a hot, dilute chromic acid solution to improve their corrosion resistance. From an environmental point of view, the latter may not be acceptable.

Inorganic Coatings

A process described earlier uses a laser beam to melt and fuse a Ni-Cr powder with a steel substrate to form a stainless steel type of surface layer[6] having good corrosion resistance. For example, in a 3.5 % NaCl solution the stainless alloy layer had a corrosion rate of about 5 µm/yr after 60 days, while the untreated 1010 steel substrate material exhibited a corrosion rate of about 178 µm/yr. Similarly, a WC coating formed on a 6061 aluminum alloy substrate gave a corrosion rate of about 5.1 µm/yr compared to about 10.2 µm/yr for the untreated substrate in the same environment[6].

Plasma-enhanced, chemical vapor deposition (CVD) has been used to deposit modified quartz films resembling an inorganic polymer in that, although the films are clear and hard, they exhibit some flexibility[24]. These protective SiO_2-based coatings have been applied to brass and aluminum substrates. Their corrosion related performance is summarized in Table 8 below. Excellent resistance to salt fog exposure is one feature of these 4-5 µm thick coatings.

A group of surface enhancements known as "synergistic" coatings can be prepared by a "multi-step process that starts with a series of specialized cleaning treatments which are followed by enhancement of the substrate's surface through conversion, deposition, or by thermal spraying". Several of these coatings, often impregnated with a solid lubricant, have been developed for a wide range of substrate materials, including steels and aluminum alloys[25]. The salt fog resistance of these coatings can exceed 300 hours, and sometimes 1,000 hours, depending of the formulation, thickness, substrate material, and other parameters. Unfortunately, specific coating preparation details could not be found in the technical literature.

A dry deposition technology that produces several coatings as potential replacements for EHC is thermal spraying, which includes the high-velocity oxy(gen)-fuel (HVOF) technique. Driving their development at the present time are the commercial and military aircraft sectors and the defense industrial base. The principal candidates are WC or WC-Co coatings, and coatings containing mixtures of Ni, Cr, Fe, Si, and sometimes other elements. Several of these formulations are proprietary. Although some of the coatings contain chromium, worker exposure is reduced and compliance with environmental regulations is easier to attain. In general, coatings containing small amounts of chromium exhibit better corrosion resistance than the equivalent coatings without chromium.

The following paragraphs describe the performance of some of these HVOF-applied coatings. In reviewing these data it should be noted that corrosion performance can vary considerably as a function of deposition equipment, type of coating powder, deposition parameters, presence of inclusions, porosity, and "unmelts" in the coatings, as well as surface finish. Therefore, the original documents should be consulted for the conditions under which the results were obtained.

Table 8. Corrosion Related Properties of an Inorganic (SiO_2) Polymer Coating

Corrosion Test	Results for Aluminum Substrates*	Results for Brass Substrates*
Salt Fog – ASTM B 117	>2,000 hours	>1,000 hours
CASS – ASTM B 368	120 hours	120 hours
Boiling Water – ASTM D 870	1 hour	1 hour
Chemical Resistance - ASTM D 4652	Pass	Pass
Ultraviolet Exposure – ASTM G 53	>2,000 hours	>3,000 hours
Filiform Attack - Metroline	140 hours	140 hours
Humidity – ANSI/BHMA A 156	>1,000 hours	>1,000 hours

Source: Reference (24).

Tungsten carbide (WC) and WC-Co coatings (typically containing 12 to 17 % cobalt) are most often applied to ferrous substrates, including high strength steels. Table 9 collects together some results of salt fog testing for these and other coatings. Details are discussed below.

A WC-17%Co coating and a Co-28%Mo-8%Cr-2%Si coating applied by HVOF thermal spray to 4340 steel performed much better in the ASTM B 117 test according to Reference (29). After 1,000 hours exposure, these coatings had a rating of 4-5, while the EHC control only had a rating of about 1.5. In a GM 9540 P/B cyclic corrosion test, both coatings also performed better than EHC, as shown in Table 10.

Table 9. Corrosion Resistance of Some Coatings Applied by the HVOF Technique

Composition	Thickness, μm	Substrate	ASTM B 117 Results*
WC	100-150	4130 Steel	Better than EHC (> 200 hours)
WC-Co	100-200	Steels	Comparable to or better than EHC
WC-Co-Cr	100-200	Steels	Excellent (>750 hours)
WC-Co/Ni-Cr-Mo	400	Steel	No evidence of corrosion
Ni-Cr-Mo	400	Steel	No evidence of corrosion
Ni-Cr-Si-B		Steels	Excellent (>750 hours)
Ni-W-Cr-Si-B	- -	Steel	Comparable to EHC
Fe-Cr-Mo	400	Steel	Fair – "corrosion scale" present
Fe-Cr-Ni	- -	Steel	Comparable to EHC
Cr_3C_2/Ni-Cr	- -	Steels	Better than EHC (~390 hours)

*Source: References (26) through (30). * After 72 hours exposure unless otherwise stated.*

A number of WC coatings, applied by several HVOF techniques to AISI 4130 steel panels, have been tested for their corrosion resistance[26]. The surface finish was 125 rms. These coupons were placed in a salt fog chamber (in accordance with ASTM B 117) for 200 hours then inspected. All the coupons passed by not exhibiting any signs of corrosion of the steel substrate.

Performance data on WC-Co, WC-Co-Cr, and WC-Co/Ni-Cr-Mo coatings are provided in References (27) through (30). Reference (27) states that WC-12%Co coatings performed similarly to EHC in the Salt Fog Test, as did the Ni-17%W-15%Cr-4%Si-3%B, Cr_3C_2/25%Ni-Cr, and Fe-17%Cr-12%Ni coatings. Coating thickness and surface finish were not specified. In contrast, in one evaluation[28] a WC-Co coating applied to a high strength steel performed much better than EHC in the ASTM B 117 test, as did the Cr_3C_2/Ni-Cr coating. The WC-10%Co-4%Cr and Ni-Cr-Si B coatings tested exhibited excellent resistance by surviving a 750-hour exposure. Electrochemical polarization curves were obtained (in a 0.05M sulfuric acid solution containing chloride ions) for WC-Co-Cr, Co-Mo-Cr-Si, and Cr_3C_2/Ni-Cr coatings, and an EHC coating as a control[28]. All exhibited similar polarization behavior except for the WC-Co-Cr coating. The latter had better polarization characteristics than the EHC coating.

Table 10. Results for Some HVOF Coatings from a Cyclic Corrosion Test

Approx. Rating After Hrs Listed**	Coating*		
	EHC	WC-17%Co	Co-Mo-Cr-Si
250	8	9	9.5
500	7	8	9
750	7	8	8.5
1,000	7	8	8

*Source: Reference (29). * Substrate was 4340 steel.*
*** GM 9540 P/B Test.*

A number of coatings were tested for 72 hours in a salt fog chamber. The results are cited in Reference (30). WC-Co/Ni-Cr and Ni-Cr-Mo coatings, finished to 12-43 rms and containing less than 1% porosity, did not show signs of corrosion. In contrast, an Fe-Cr-Mo coating, finished to about 25 rms and with less than 1% porosity, was rated as only "fair" because of the presence of some "corrosion scale". The EHC control exhibited evidence of substrate attack where the coating was cracked. The substrate was a steel and all coatings were 100 μm thick.

Non-Metallic Alternatives

Some non-metallic (e.g., organic) coatings provide excellent resistance to salt fog exposure, water, and other chemicals, but usually are not very hard, so performance in wear and erosion tests often is significantly less than for metallic coatings, such as chromium, or surface treatments, such as nitriding. Consequently, most organic coatings are not suitable candidates as alternatives to chromium. However, a nylon powder coating developed for household appliance hardware is said to have excellent impact, abrasion, and scratch resistance[31] as well as superior corrosion resistance (see Table 11 below).

Diamond-like coatings (DLCs) also have been proposed as an alternative to chromium. One type of DLC coating has been reported[32] to be "inert" with respect to chemical resistance, whereas an electroplated hard chromium coating was said to have "moderate" resistance. Reference (32) also states that a DLC on a D2 tool steel was resistant to attack by aqua regia, a hydrochloric/nitric acid mixture.

Summary

Corrosion data exist for a range of EHC alternative coating materials deposited by different techniques. However, as mentioned earlier, not all coating data can be compared directly because of variations in: (a) substrate material and surface preparation; (b) the use sometimes of bond coats and intermediate (under) layers; (c) the deposition parameters; (d) coating thickness; (e) coating porosity and surface finish; (f) the use sometimes of post treatments; (g) the type of corrosion test performed; (h) test conditions (e.g., solution concentration, temperature, pH, agitation); and (i) the interpretation and reporting of the results.

Much of the data presented in this paper has been collected together for convenience and summarized in Table 12 below. Because of the variations mentioned above, to compare different coatings, as part of a selection process for a given application, the text (and original sources, if necessary) should be consulted for details of how the coatings were prepared and the tests performed to obtain the given data. In general, it seems that there are a number of nickel and cobalt containing alloys, as well as a few inorganic (e.g., SiO_2) and organic (e.g., DLC) coatings, that perform very well in terms of corrosion resistance.

In the selection of substitutes for decorative and functional chromium coatings the following should be taken into consideration: (i) besides corrosion resistance, other properties may be important (e.g., hardness, wear resistance, appearance/color); (ii) electrolytic and electroless coating techniques are useful, but usually require a post-deposition heat treatment to remove any occluded hydrogen; (iii) heat treatment often modifies the properties of the coating and can affect substrate properties; (iv) coatings applied by "dry" techniques, such as PVD and HVOF thermal spraying, avoid any problems with hydrogen embrittlement (unless the substrate pretreatment includes an acid cleaning, or activation step); (v) diffusion or cementation coating techniques can provide thick, adherent coatings on parts with simple geometries, but cannot be used for heat sensitive substrate materials (e.g., high strength steels); (vi) constituents of alloy coatings can be susceptible to preferential attack in aggressive environments, but this may be used to advantage for stripping coatings; (vii) the salt fog test, although providing results in a short time period, cannot be related to in service use in most cases; and (viii) a cyclic corrosion test is becoming more popular, and field tests are the most informative, if sufficient exposure time is available for testing.

Finally, there is no single substitute that meets all the desirable performance characteristics of chromium. In addition, some of the coatings being evaluated are applied by methods that have intrinsic limitations. For example, HVOF thermal spray coatings are "line of sight" limited, and internal diameters may be difficult to coat.

Many original equipment manufacturers in the automotive, aerospace, appliance, furniture, plumbing, and architectural hardware industries, for example, have researched alternative coatings and have chosen their preferred solutions, such as electroless Ni-P, electroplated Sn-Ni alloys, and thermal sprayed WC-Co coatings, based on their requirements. However, investigations to find suitable alternatives continue, especially in the defense industrial base, where existing specifications or mission requirements make substitution more difficult, and because alternatives containing nickel, or requiring a chromium-based post-treatment (e.g., chromating) may not be acceptable. As mentioned earlier, nickel as well as chromium are included in the list of 17 high priority chemicals for voluntary reduction published by the U.S. Environmental Protection Agency.

Table 11. Corrosion Resistance of a Nylon Coating Compared to a Decorative Chromium Coating

Performance Requirement	Electroplated Chromium	Proprietary Nylon
Salt Fog (Spray) Resistance	Poor	Excellent
Sea Water Resistance	Poor	Excellent
Water Resistance	Fair	Excellent
Chemical Resistance	Poor	Good
Resistance to Harsh Environments	Poor	Excellent
Exterior Durability	Poor	Excellent

Source: Reference (31).

Table 12. Summary of Corrosion Data for Alternative Coatings

Coating	SALT FOG ASTM B 117	CASS ASTM B 368	CORRODKOTE ASTM B 380	CYCLIC GM 9540P
Cr(VI) - EHC	≥24 hr	8.8/6.7*	7.5/5.7**	7***
Cr(III)	≥24 hr	10/6*	10/7**	- -
Cr_3C_2/Ni-Cr	≥390 hr	- -	- -	- -
Co-Mo-Cr-Si	- -	- -	- -	8***
Fe-Cr-Ni	≥96 hr	- -	- -	- -
Ni-Cr-Mo	>72 hr	- -	- -	- -
Ni-Cr-Si-B	≥750 hr	- -	- -	- -
Ni-W-Cr-Si-B	≥72 hr	- -	- -	- -
WC-Co-Cr	≥750 hr	- -	- -	- -
WC-Co/Ni-Cr-Mo	≥72 hr	- -	- -	- -
Ni Alloy (Proprietary)	≥96 hr	- -	- -	- -
Ni Alloy (Passivated)	≥120 hr	- -	- -	- -
Ni-P	≥50 hr	- -	- -	- -
Ni-P (Passivated)	~1,000 hr	- -	- -	- -
Ni-W-B	≥96 hr	- -	- -	- -
Ni-W-Si	≥96 hr	- -	- -	- -
SiO_2 Polymer	>1,000 hr	- -	- -	Pass+
WC	>200 hr	- -	- -	
WC-Co	≥72 hr	- -	- -	8***

* *Rating after 96 hours;* ** *Rating after 132 hours;* *** *Rating after 1,000 hours;* + *After 120 hours.*

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