Chapter 6. Hexavalent Chromium

Five Chemicals Alternatives Assessment Study

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6.1 Overview

6.1.1 Characteristics of Hexavalent Chromium

Chromium is a metallic element. It is not found in nature in its elemental form, but rather in chromite ore ($FeCr_2O_4$) or, less frequently, the mineral crocoite (PbCr) (Barceloux 1999). Chromium used in industry is derived from chromite ore, the majority of which is imported from South Africa and Kazakhstan. No chromite mines currently exist in the United States (Barnhart 1997).

There are several oxidation (or valence) states of chromium, each with its own chemical characteristics. The most common forms are trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)). Trivalent chromium compounds can be can be either naturally occurring or a by-product of industry, while elemental chromium and the hexavalent compounds nearly always result from industrial activity. The most common hexavalent chromium compounds are chromates and chromic acid (Table 6.1 A) (Page, Loar 1991).

Trivalent chromium is the more stable form, and trivalent chromium compounds generally have low solubility in water and low reactivity (Barnhart 1997). Most hexavalent chromium compounds are soluble in water, and are strong oxidizers. Both trivalent and hexavalent compounds are denser than water. Under low pH conditions and in the presence of organic matter, some hexavalent chromium compounds may reduce to the trivalent form. Conversely, Cr(III) may convert to Cr(VI) in high pH conditions, or in the presence of free chlorine in neutral pH water that has little organic material (Independent Environmental Technical Evaluation Group (IETEG) 2005; Clifford, Dennis 1988).

Table 6.1 A: Hexavalent Chromium Compounds Nomenclature

Name	Synonyms	Chemical Formula	CAS #
Ammonium dichromate	Dichromic acid,,diammonium salt Ammonium bichromate	$(NH_4)Cr_2O_7$	7789-09-5
Barium chromate	Chromic acid, barium salt Barium chromate oxide CI Pigment Yellow 31 Lemon chrome	$BaCrO_4$	10294-40-3
Calcium chromate	Chromic acid, calcium salt Calcium monochromate Calcium chromium oxide Calcium chrome yellow	$CaCrO_4$	13765-19-0
Chromium trioxide	Chromic acid Chromium anhydride Chromium oxide	CrO_3	1333-82-0
Lead chromate	Chromic acid, lead salt Chrome green Chrome yellow	$PbCrO_4$	7758-97-6
Potassium chlorochromate	Peligot's salt Chlorochromic acid, potassium salt	$KCrO_3Cl$	16037-50-6
Potassium chromate	Chromic acid, dipotassium salt Tarapacaite	K_2CrO_4	7789-00-6
Potassium dichromate	Chromic acid, dipotassium salt Bipotassium chromate	K_2CrO_7	7778-50-9
Silver chromate	Chromic acid, disilver salt	Ag_2CrO_4	7784-01-2
Sodium chromate	Chromic acid, disodium salt Chromium disodium oxide Disodium chromate	Na_2CrO_4	7775-11-3
Sodium chromate, dihydrate	Chromic acid disodium salt; dihydrate Sodium bichromate Sodium dichromate, dihydrate	$NaCr_2O_7*2H_2O$	7789-12-0
Strontium chromate	Chromic acid, strontium salt Deep lemon yellow	$SrCrO_4$	7789-06-2
Zinc chromate	Chromic acid, zinc salt Buttercup yellow Chromium zinc oxide	$ZnCrO_4$	13530-65-9
Agency for Toxic Substances and Disease Registry (ATSDR) 2000, International Agency for Research on Cancer (IARC) 1990, Page, Loar 1991			

Table 6.1B presents chemical and physical characteristics of hexavalent chromium compounds.

Table 6.1 B: Hexavalent Chromium Chemical/Physical Characteristics

Name	Melting/boiling point	Solubility in water (g/100 cm$^{3)}$	Density (g/cm^3)	Appearance
Ammonium dichromate	Decomposes at 170° C	30.8 @ 15° C	2.155 @ 25° C	Red-orange crystals
Barium chromate	Decomposes	0.00034 @ 16° C	4.498 @ 25° C	Black-green crystals

Table 6.1 B: Hexavalent Chromium Chemical/Physical Characteristics

Name	Melting/boiling point	Solubility in water (g/100 cm^3)	Density (g/cm^3)	Appearance
Calcium chromate	No data	2.23	2.89 (no temp specified)	Yellow prisms
Chromium trioxide	197° C/decomposes	61.7 @ 0° C	2.7 @ 25° C	Dark red crystals
Lead chromate	844° C/no data	5.8	6.12 @ 15° C	Yellow, orange or red crystals
Potassium chlorochromate	Decomposes	Decomposes in water	2.497 @ 39° C	Orange needles or purplish crystals
Potassium chromate	975° C/no data	62.9 @ 20° C	2.732 @ 18° C	Orange-red crystals
Potassium dichromate	398 °C/decomposes at 500 °C	4.9 @ 0° C	2.676 @ 25° C	Orange-red crystals
Silver chromate	No data	0.014 @ 25° C	5.625 @ 25° C	Maroon crystals
Sodium chromate	792 °C/no data	87.3 @ 30° C	2.723 @ 25° C	Yellow crystals
Sodium chromate, dihydrate	356 °C/decomposes at 400 °C	230 @ 0° C	2.348 @ 25° C	Orange-red crystals
Strontium chromate	No data	0.12 @ 15° C	3.895 @ 15° C	Yellow crystals
Zinc chromate	No data	Insoluble	3.4 (temp not specified)	Lemon yellow prisms
ATSDR 2000, IARC 1990, Page, Loar 1991				

6.1.2 Health and Environmental Impacts

Hexavalent and trivalent chromium compounds differ in their health and environmental effects, with the hexavalent form being far more dangerous. Ingesting small to moderate amounts of trivalent chromium is essential to human metabolism, and there is no current evidence that Cr(III) is carcinogenic. In contrast, exposure to Cr(VI) is known to be a serious human health risk (Cohen, Costa 2000).

Acute (Short-Term) Health Effects

Short-term effects of hexavalent chromium exposure (for example, from chromic acid droplets or chromate dust) include eye irritation and respiratory irritation, sneezing, or sensitization; in high concentrations, acute inhalation can cause ulcers in the nasal septum. In sensitive individuals, inhalation of Cr(VI) can cause an asthma attack. If very small quantities are ingested the body converts it to the trivalent form in the stomach. In larger quantities or concentrations, however, ingestion of hexavalent chromium compounds can result in acute gastroenteritis, vertigo, gastrointestinal hemorrhage, convulsions, ulcers, kidney damage or failure, and liver damage or failure; approximately 1 g of potassium chromate is considered a lethal dose. Significant acute exposure of the skin to Cr(VI) can cause burns, liver damage or failure, kidney damage or failure, and anemia (ATSDR 2000).

Chronic (Long-Term) Health Effects

Long-term inhalation of hexavalent chromium is known to cause lung cancer (IARC 1990). It also can result in damage to the nasal mucous membrane, perforation of the nasal septum, and asthma. If inhaled through the mouth, it can cause periodontitis and gingivitis. Impacts of chronic skin exposure include dermatitis, hypersensitivity reactions, eczema, and kidney or liver damage. The characteristic lesions resulting from hexavalent chromium exposure are referred to as "chrome holes" or "chrome ulcers." Chronic eye exposure can result in conjunctivitis. (Drew et al. 2000).

Exposure Routes

Inhalation (of fumes or mist) and dermal contact with hexavalent chromium compounds used by workers in industrial operations are the primary exposure routes. Ingestion of large amounts most often is accidental or done with suicidal intentions. If soil is contaminated with Cr(VI), it is possible that it will be touched and/or swallowed (for example, by children playing in a contaminated area). In areas where there has been industrial pollution of groundwater, there is the potential for ingesting Cr(VI)-contaminated drinking water from groundwater wells. The family members of chromium workers also may be exposed inadvertently via contaminated work clothes (Pellerin et al. 2000).

Worker Health

Workers, rather than consumers, have the highest risk of adverse health effects from hexavalent chromium exposure. The industries with the greatest risk of occupational exposure to Cr(VI) are chrome electroplating[8], stainless steel welding, metal coating and painting, printing, textiles, leather tanning, wood preservation, and cement or masonry work. Inhalation risk may be from fumes (welding), mists or droplets (electroplating, spray painting.) Dermal exposure can result from contact with fluids, such as those used in electroplating, or materials containing Cr(VI), such as wet cement; smoking can increase the risks from Cr(VI) exposure. (OSHA, 2006)

For many years the OSHA PEL for hexavalent chromium compounds in workplace air was 52 $\mu g/m^3$ (ceiling concentration). That level was challenged by a variety of groups as being too high to adequately protect worker health, and OSHA proposed a rule (under a court-ordered deadline) that would lower the PEL to 1 $\mu g/m^3$ (time-weighted average) (U.S. Department of Labor, Occupational Safety and Health Administration (OSHA) 2006). The final rule, issued on February 28, 2006, set the PEL at 5 $\mu g/m^3$ (time-weighted average). The NIOSH REL is 1 $\mu g/m^3$ (Pellerin et al. 2000). As a general rule, OSHA and NIOSH strongly recommend that all exposures to confirmed human carcinogens, such as hexavalent chromium, be reduced to the lowest possible level.

Public Health

Consumer exposure to hexavalent chromium most often is limited. Situations in which there may be non-worker exposure to Cr(VI) include contact with contaminated soil or ash at a waste disposal site, ingestion of contaminated well water or soil, inhalation of contaminated air near manufacturing operations involving chromium, contact with Cr(VI)-containing products (such as improperly tanned leather), inhalation of wear particles from brake linings or catalytic converters near highways (ATSDR 2000), or exposure from hobbyist uses (for example, gum bichromate photo processing or home electroplating.)

Environmental Hazards

There are both naturally occurring and anthropogenic sources of chromium compounds in the air, soil, and water. Natural sources include volcanic activity and the weathering of chromium-containing rock. Human activities resulting in the release of hexavalent chromium as a waste or by-product include fossil fuel combustion, steel production, chemical manufacturing, metal finishing and paint

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[8] A hexavalent chromium electroplating bath produces severe off gassing, resulting in the creation of a large amount of chromic acid mist at the surface of the plating tank.

manufacturing, ore refining, refractory brick production, cement production, leather tanning, pulp production, and wood preservation (Independent Environmental Technical Evaluation Group (IETEG) 2005).

Chromium in the air is in the form of particles or droplets, which may be transported by wind and/or deposited onto soil or water. The behavior of chromium compounds in soil and water is complex. Factors that determine whether the chromium is in trivalent or hexavalent form in different environmental media (air, soil, surface water, ground water) include pH, oxygen levels, temperature, and the presence of other chemicals and organic matter (Kotas, Stasicka 2000). Cr(VI) can leach out of soil into groundwater and migrate over time (IETEG 2005).

Hexavalent chromium's toxicity to aquatic organisms varies, depending on the species and the chemical characteristics of the water. Algae, saltwater polychaete worms, freshwater and marine crustaceans, rainbow trout, lake trout and some catfish species are relatively sensitive to Cr(VI). Ingestion of CR(VI) compounds by mammals can be lethal or can result in severe developmental effects, and ingestion by birds can cause deformities in embryos or reduced survival rates of chicks. In addition, the presence of Cr(VI) in irrigation water can kill some types of earthworms (Eisler 1986).

6.1.3 Use and Functionality

Chromium compounds have been used since the eighteenth century for a variety of industrial applications. The earliest uses for chromium compounds were as pigments, as mordants in textile dyeing, and in leather tanning. The use of chromium in stainless steel and refractory bricks became common in the early twentieth century. Electroplating, a key use of chromium, was invented in the 1920s (IETEG 2005).

Chromium can provide manufactured products with hardness, shininess, durability, color, corrosion resistance, heat resistance, and decay resistance. For example, decorative chrome plating produces a hard, shiny, durable surface coating on items such as school furniture. Jet turbine engine parts rely on hard chrome plating to resist corrosion, high temperatures, and wear. Chromium-based pigments are valued for their vivid colors and resistance to weathering; they are commonly used in traffic paints for those reasons. Anti-corrosion coatings containing chromium compounds are widely used in marine applications, where their resistance to salt spray and their "self-healing" properties are important. In addition, the biocidal properties of chromium compounds are key to their use in wood preservatives.

Uses in Products

The major application of chromium is in the production of alloys, primarily stainless steel; historically, this has amounted to 50-60% of total chromium use (Independent Environmental Technical Evaluation Group (IETEG 2005). Wood preservation, metal processing, leather tanning, and pigments are the main uses of chromium compounds.

Table 6.1 C: Uses of Hexavalent Chromium Compounds

Compound	Uses
Ammonium dichromate	Magnetic media, photo engraving, textile dyes, leather tanning
Barium chromate	Pigments, anti-corrosion coatings
Calcium chromate	Pigments, anti-corrosion coatings

Table 6.1 C: Uses of Hexavalent Chromium Compounds

Compound	Uses
Chromium trioxide	Chrome plating, stainless steel manufacture, fungicides, wood preservatives
Lead chromate	Pigments for paint, inks and plastics
Potassium chlorochromate	Photographic developing
Potassium chromate	Algaecides, fungicides, textile dyes
Potassium dichromate	Fungicides, wood preservatives, photographic engraving, pigments, textile dyes
Silver chromate	Catalyst, photographic media, conversion coatings
Sodium chromate	Fungicides, insecticides, miticides, wood preservatives, pigments, anti-corrosion coatings, textile dyes
Sodium chromate, dihydrate	Fungicides, insecticides
Strontium chromate	Paint manufacture, anti-corrosion coatings
Zinc chromate	Paint manufacture, anti-corrosion coatings
California Department of Health Services, Hazard Evaluation System and Information Service	

Uses for Chromium and Chromium Compounds in Massachusetts Manufacturing

Based on filings for 2003 under the Massachusetts Toxics Use Reduction Act (TURA), the companies using chromium and chromium compounds in the greatest quantity in Massachusetts are involved in wood preservation; manufacture of metal, metal finishing, and electroplating products; provision of electroplating services; production of paints and pigments; and manufacture of asphalt roofing shingle granules. Chromium also is generated as a by-product of several power plants.

Table 6.1 D: Use of Chromium and Chromium Compounds in Massachusetts
(includes all species of chromium)

Major Use Category	TURA Total Use (2003)	Pounds	Number of Filers
Wood Preservation	32 %	514,846	3
Metals Processing and Plating	24 %	391,598	4
Paints, Pigments, Dyes	21 %	347,199	7
Specialty and Metal Finishing Chemicals	12 %	200,233	3
Power Generation (by-product)	9 %	144,576	3
Photographic Chemicals	2 %	29,840	2
Totals:	**100 %**	**1,628,292**	**22**

6.2 Use Prioritization

Summary of Stakeholder Input

Because of the severity of the hazard that chromium poses to workers in the electroplating industry, stakeholders felt that decorative and hard chrome electroplating should be included as priority uses in this study. In addition, the categories of chromate conversion coatings and paints/pigments were mentioned as ones where there was the potential for worker exposure, and where the chromium still existed in the product in its hexavalent form. While there were concerns about chromium compounds in wood preservatives, it was felt that the use of CCA (chromated copper arsenate) was being phased out because of issues with its arsenic content, and that alternatives to CCA are already being implemented. Some other uses, such as in leather tanning or textile dying, were not listed as priorities because they no longer are important manufacturing uses in Massachusetts.

Priority Uses

Based on a review of stakeholder input, published research on environmental, health and safety issues, and the availability of alternatives, three general categories of use were selected as priorities for this study, with a fourth designated if time allowed (paints and pigments):

- Decorative chrome electroplating;
- Hard chrome electroplating;
- Chromate conversion coatings.

After discussion with industry representatives, the category of chromate conversion coatings was narrowed further to focus on only passivation of zinc and zinc alloy plated parts and zinc galvanized steel.

6.3 Alternatives Prioritization for Hexavalent Chromium

As described in the previous section, three hexavalent chromium use categories were selected for full alternatives analyses:

- Decorative Chrome Electroplating
- Hard/Functional Chrome Electroplating
- Passivation of Zinc Plated Parts and Zinc Galvanized Steel

The alternatives were prioritized using environmental health and safety, performance and the availability of information as the primary criteria. Cost may not be an important factor in evaluating hexavalent chromium alternatives since its severe toxicity is driving many manufacturers to adopt alternatives. For example, it is likely that the new PEL will be very difficult for many manufacturers to meet using traditional engineering controls such as local exhaust ventilation. In addition, EU directives are driving manufacturers to find hexavalent chromium-free alternatives.

6.3.1 Alternatives Associated with Decorative Chromium Electroplating

Available Alternatives

Within the category of decorative chrome electroplating, only two types of alternatives were identified:

- Trivalent chromium plating baths
- Low Temperature Arc Vapor Deposition (LTAVD) of trivalent chromium

Alternatives Screened Out

Both of these alternatives passed the initial environmental, health and safety screening criteria.

Alternatives Prioritization

Sufficient information regarding performance was available on each of the alternatives to proceed with a technical assessment. Therefore, both of the alternatives were selected for full assessments:

- Trivalent chromium plating baths
- Low Temperature Arc Vapor Deposition (LTAVD) of trivalent chromium

6.3.2 Alternatives Associated with Hard/Functional Chromium Electroplating

Available Alternatives

Many alternatives were identified for hard chrome electroplating:

- Electroless nickel and nickel composites
- Thermal sprays: high velocity oxy-fuel and plasma sprays
- Nickel-free electroplates and composites
- Weld facing methods and micro-arc welding
- Heat treatments and plasma nitriding
- Laser modification, alloying and coating
- Electrodeposited nanocrystalline cobalt-phosphorus coating
- Explosive bonding
- Physical vapor deposition/magnetron sputtering
- Chemical vapor deposition
- Nickel/Tungsten/Boron electroplating

Alternatives Screened Out

Based on the environmental, health and safety criteria, those alternatives that involved the use of nickel were screened out. Nickel is listed by IARC as a Group 1 chemical: sufficient evidence of carcinogenicity in humans. Consequently, electroless nickel and nickel composites, and nickel/tungsten/boron electroplating were not carried forward for technical assessments.

Alternatives Prioritization

In order to achieve a manageable list of alternatives for full assessment, two other alternatives were given a lower priority and dropped from further consideration. Nickel-free electroplates and composites had been mentioned only briefly in one reference. The research team was unable to find further information on this alternative, so it also was dropped. In addition, the explosive bonding alternative was determined to be a "niche" application, suitable only for a few very specific types of materials.

Therefore, the final list of alternatives to be assessed was as follows:

- Thermal sprays: high velocity oxy-fuel and plasma sprays
- Weld facing methods and micro-arc welding
- Heat treatments and plasma nitriding
- Nanocrystalline coatings
- Vapor deposition methods
- Functional trivalent chromium coatings

6.3.3 Alternatives Associated with Passivation of Zinc

Available Alternatives

Four alternatives were identified for passivation of zinc plated parts and zinc galvanized steel:

- Molybdates
- Trivalent Chromium Passivates
- Mineral Tie-Coat
- Combination Wet-Dry-Wet-Dry Process

Alternatives Screened Out

All of the alternatives passed the EH&S screening.

Alternatives Prioritization

Because very little published information was available on the combination wet-dry-wet-dry process, and the company that currently holds rights to the process did not respond to inquiries it was removed from the list of alternatives to be considered. Therefore, the following is the final list of alternatives for assessment for zinc passivation:

- Molybdates
- Trivalent Chromium Passivates
- Mineral Tie-Coat

6.4 Alternatives Assessment

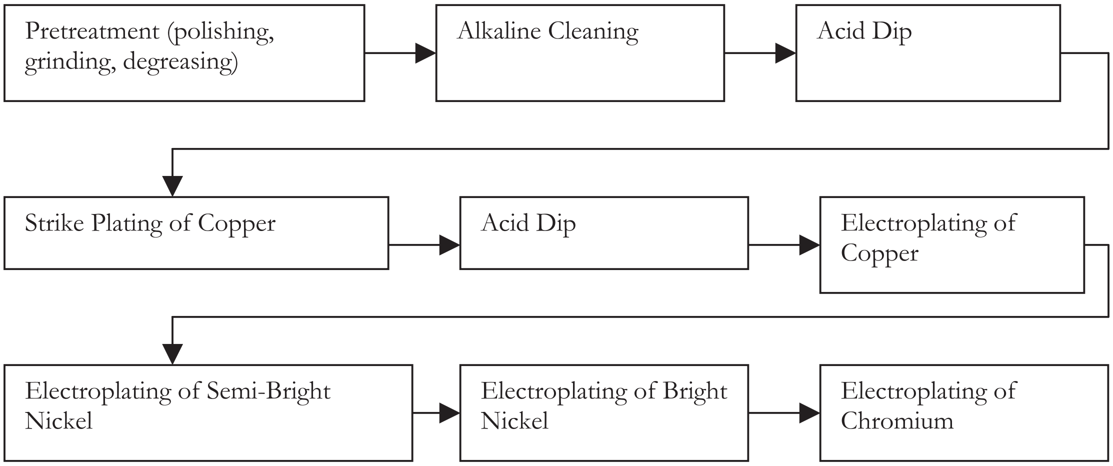
6.4.1 Decorative Chromium Electroplating of Consumer and Automotive Products

Existing Process

Decorative chrome plating (also known as bright chrome) is used for consumer applications such as appliances, metal furniture, plumbing fixtures, knobs and hand tools, and for automotive trim. It creates an attractive, blue-white finish, and helps to reduce tarnishing. Color, shininess and corrosion resistance are the key functional criteria for decorative chrome.

The decorative chrome layer typically is quite thin (0.002 to 0.02 mils) and is deposited onto a metal or plastic substrate over several layers of copper and/or nickel. The plating process has several steps, as shown in Figure 6.4.1 A.

Figure 6.4.1 A: Decorative Chrome Plating Process
(Oklahoma Department of Environmental Quality Air Quality Division 1999)

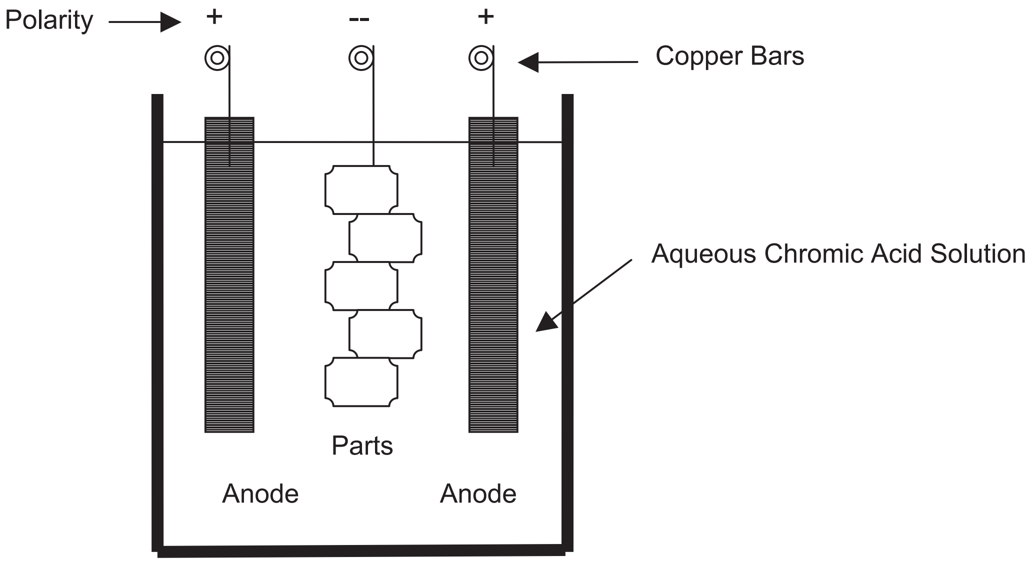


In the actual decorative chrome plating step, parts to be plated are hung from a rack in a tank that contains a hexavalent chromium electrolyte solution and anodes. Direct current is passed through the solution, which causes metal ions to be electrodeposited on the parts (cathodes). (Figure 6.4.1 B) The parts are baked after plating.

The major advantage of decorative hexavalent chromium is its appearance, especially its blue-white color. Functional disadvantages (in addition to health, safety and environmental problems) include poor throwing power/coverage, low resistance to burning during plating, the difficulty in removing impurities from the plating bath, problems in rinsing the plating solution from the plated parts (resulting in a large amount of "drag-out" hexavalent chromium), and intolerance to current interruptions/variations during plating (causing a discoloration known as "white wash") (Jones, Snyder 2005).

Two alternatives to decorative hexavalent chrome plating will be assessed for their feasibility: trivalent chrome plating and Low Temperature Arc Vapor Deposition (LTAVD®).

Figure 6.4.1 B: Hexavalent Chromium Electroplating



Technical Assessments

Trivalent Chromium Plating

The trivalent chromium plating process is basically the same as the hexavalent process, but with some operational variations. There are two types of trivalent chromium plating: single cell and double cell. Both of these processes prevent the formation of hexavalent chromium as a "side reaction" during plating. (California Department of Toxic Substances Control 1993) The single cell process includes an insoluble, inert graphite anode in the trivalent chromium solution with the parts to be plated. The double cell process has a lead anode that is separated from the solution by a membrane. Table 6.4.1A compares the single cell and double cell trivalent processes, and the hexavalent process.

Table 6.4.1 A: Chrome Plating Operating Conditions

(California Department of Toxic Substances Control 1993)

Operating Factor	Single Cell Trivalent	Double Cell Trivalent	Hexavalent Chromium
pH	2.3 – 3.5	3.3 – 3.9	< 1
Temperature, °F	70 – 120	70 – 130	110 - 115
Cathode Current density, A/ft^2	40 – 125	40 – 125	175 - 300
Agitation	Mild Air	Mild Air	Optional
Rectifier Voltage, V	4 – 15	4 – 15	4 - 12
Anode Material	Carbon	Lead – 7% zinc	Lead – 7% tin
Chromium Concentration, g/L	4 – 20	5 – 10	150 - 300
Max. Thickness at Room Temperature, mil	0.01 – 0.03	N/A	5 or more
Max. Thickness at High Temperature, mil	1 or more	About 0.01	N/A
Plating Rate at Room	0.005 – 0.007	N/A	0.005 – 0.007

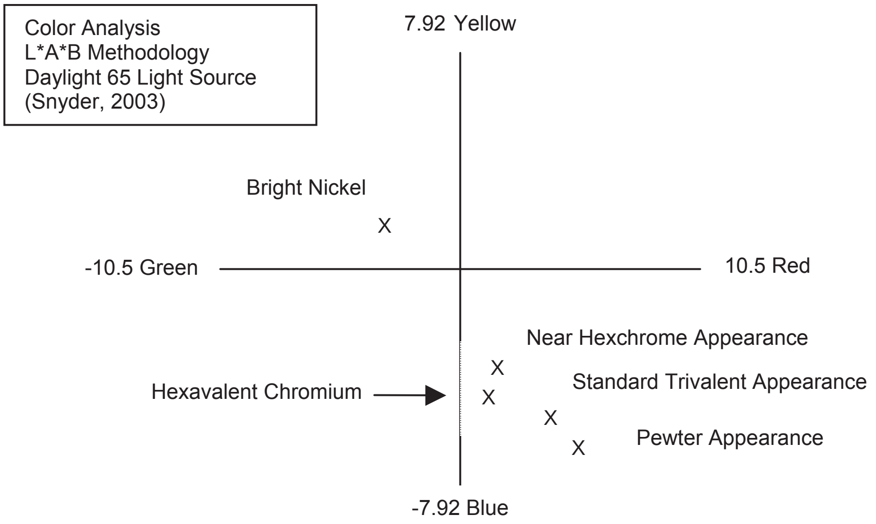
Table 6.4.1 A: Chrome Plating Operating Conditions
(California Department of Toxic Substances Control 1993)

Operating Factor	Single Cell Trivalent	Double Cell Trivalent	Hexavalent Chromium
Temperature, mil/min			
Plating Rate at High Temperature, mil/min	0.007 – 0.010	0.004 or less	N/A

Although double-cell trivalent chromium electroplating was developed before the hexavalent process (both in the mid-19th century), the Cr(VI) process was simpler to use and therefore became the standard for decorative chrome plating. Commercially viable trivalent plating, using single-cell technology, became available in the 1970s. That technology generation had problems with color and plating rate that have since been overcome as the methodology has been refined and improved (Snyder 1988).

The darker, pewter-like appearance of parts plated with the earlier technology is attractive, but noticeably different from the blue-white hexavalent chromium finish. Use of a sulfate-based, double-cell process can produce trivalent plating that is very similar in appearance to hexavalent plating, if that parameter is important for the product consumer (Zaki 2002, 492-501). Varying the operating conditions during plating will produce deposits with different color traits, ranging from gray-black to "near hexavalent" (Snyder 2003). Figure 6.4.1 C compares the color of nickel, hexavalent and trivalent chromium plating; the intersection of the two axes represents "white standard appearance."

Figure 6.4.1 C: Color Analysis of Plating Types
(Snyder 2003)



While corrosion resistance for decorative chrome is less important than it is for hard chrome, it is appreciated by end users. A long-term atmospheric corrosion resistance test was begun in the 1970s at the LaQue Corrosion Center in North Carolina that compared a number of plating systems. ASTM Standard B456 for severe (SC3) and very severe (SC4) service conditions were used to compare test panels exposed to the elements over several years. Both hexavalent coatings made micro-porous and trivalent coatings (which are naturally micro-porous) performed well, exceeding the 10 years of corrosion resistance desired by automotive parts manufacturers. Trivalent plating outperformed untreated (not micro-porous) hexavalent plating (Snyder 2005).

Decorative trivalent chromium plating has many functional advantages over hexavalent chromium plating, as shown in Table 6.4.1 B:

Table 6.4.1 B: Advantages of Trivalent Chromium Over Hexavalent Chromium for Decorative Plating (Jones and Snyder 2005)

Factor	Trivalent Chromium	Hexavalent Chromium
Throwing Power	Good	Poor
Covering Power	Good	Poor
Tolerance to Current interruptions	Tolerant	Intolerant
Tolerance to Rectifier Ripple	Tolerant	Intolerant
Micro-discontinuous Structure	Micro-porous or micro-cracked	Special Process Required
Susceptibility to burning	Little	Great
Ease of Rinsing	Easy	Moderate
Color Buffing Required	Never	Occasional
Removal of Impurities	Easy	Hard
SO4, Cl, H3BO3 Contamination	No effect	Very Detrimental

Although the effect of impurities on the trivalent process is greater than for hexavalent chromium, the removal of impurities is much easier. Three methods of removing bath impurities are by dummy plating, chemical precipitation using a purifier, or continuous ion exchange (Zaki 2002).

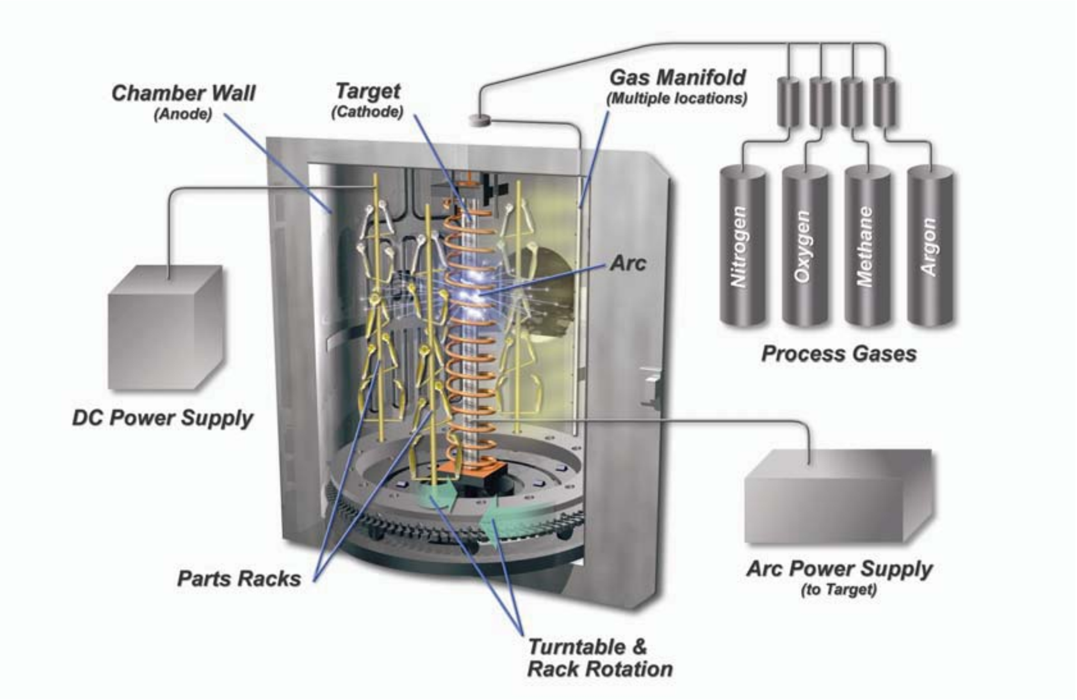
Low Temperature Arc Vapor Deposition (LTAVD®)

Low Temperature Arc Vapor Deposition (LTAVD®) is a proprietary form of physical vapor deposition (PVD See also Section 6.4.2.). It involves several steps:

- parts to be coated are placed on a turntable in a processing chamber under vacuum
- an inert gas (such as argon) is fed into the chamber
- a strong current is applied to create an arc across a solid metal target (cathode), evaporating the metal and sending off charged atoms
- the metal atoms and energized argon form a gas or plasma, which provides a conductive path that sustains the arc in the vacuum
- the parts are rotated around the target
- the gas containing the vaporized metal condenses on the parts, depositing a thin, solid film

By using different combinations of gases and metals, a variety of coatings with different characteristics can be formed. The specific combination of metals and gases chosen will dictate the color, hardness, and durability of the final coating (Sullivan, Larson 2005).

Figure 6.4.1 D: Low Temperature Arc Vapor Deposition (LTAVD®) Process
(Diagram reproduced courtesy of Vapor Technologies, Longmont, CO)



Most of the technical assessments of this proprietary process have been conducted by the company that holds the patent rights, Vapor Technologies of Longmont, Colorado. That company is a division of Masco Corporation, which is using the LTAVD technology for products produced by several of its companies, including Delta Faucet, Brass Craft, Weiser Lock, and Baldwin Hardware.

A major advantage of LTAVD is that it operates at room temperature, and the process does not heat the substrate. This means that a coating with a high melting point can be used on a substrate with a low melting point, such as plastic. Metals with dissimilar characteristics, such as titanium and aluminum, can be alloyed using the process, creating unique coating materials.

Parts are coated all over at one time (360 degree field), resulting in a very uniform coating. The rate of coating varies, with higher density and melting point metals having a slower rate. Adhesion to the substrate is good (Graves 1996).

In a 2005 article (Brondum, Larson 2005), Vapor Technologies reported on testing conducted on carbon steel coated with nickel base coats, and then with either a hexavalent chromium bath, or LTAVD-applied chrome or chromium nitride. CASS (copper accelerated salt spray) corrosion testing, spectrophotometer color testing, Vickers hardness testing and Taber abrasion testing were performed.

In 24-hour CASS testing, nearly all of the samples performed well. The main variable affecting performance was the type of nickel coating, rather than the chrome top layer. The LTAVD sample exhibited corrosion resistance that was similar or better than the hexavalent chrome samples.

With color being a key performance criterion for decorative chrome, the samples were compared using a spectrophotometer. The color difference (ΔE) between hexavalent and LTAVD chromium coated panels was measured at 1.4; differences less than 2.0 are generally not noticeable to the human eye.

In Vickers hardness testing, the LTAVD samples performed better than the hexavalent chromium samples. Cr(VI) coatings measured between 600 and 700 VHN; LTAVD chromium measured 800-1400 VHN, and PVD chromium nitride measured up to 2200 VNH.

Taber abrasion tests were done using a CS 10 wheel and a 1 kg load. The hexavalent and LTAVD chromium samples performed about the same on this test. LTAVD chromium nitride samples, however, were about 30% more wear resistant.

Financial Assessment

Trivalent Chromium Plating

Snyder (1988) prepared a comparison of the cost of waste treatment, which is a major considerations in plating, for typical trivalent and hexavalent plating processes. He estimated that the hexavalent treatment costs were nearly 10 times that of the trivalent process (Table 6.4.1 C).

Table 6.4.1 C: Estimated Annual Waste Treatment/Disposal Costs for Hexavalent and Trivalent Plating (Snyder 1988)

Operating Cost Factor	Hexavalent Chromium	Trivalent Chromium
Hexavalent Chromium Reduction	$1,480	---
Chromium Hydroxide Precipitation	$ 255	$ 38
Sludge Disposal	$3,805 (14,200 lb.)	$ 538 (2,000 lb.)
Total Annual Cost	$5,540	$ 576

Trivalent plating chemicals are more expensive than hexavalent plating chemicals, although that is likely to change as trivalent systems increase in popularity. The cost of chemicals, however, is offset by the greater efficiency of the trivalent process. In a case study conducted by the City of Los Angeles Department of Public Works in the 1990s, "net profit per shift" for a shop that converted to a trivalent process was about 15% higher than for the hexavalent process. Major reasons for the higher profit rate were the greater number of parts that could be put on each plating rack, and the higher rate of rejected parts with the hexavalent process. The Cr(III) plating also had lower waste treatment costs, required less auxiliary equipment such as tank ventilators, and less maintenance (Los Angeles Board of Public Works 1996) (Table 6.4.1 D).

Table 6.4.1 D: Comparison of Hexavalent and Trivalent System Costs

(Los Angeles Board of Public Works 1996)

Factor	Hexavalent			Trivalent		
	Unit Cost	Qty Used Per Shift^	Cost Per Shift	Unit Cost	Qty Used Per Shift^	Cost Per Shift
Plating Chemicals						
Chromic acid	$1.08/lb	28.8 lb	$31.10			
Chrome catalyst	15.00/lb	0.3 lb	4.32			
Trivalent additive #1				$28.75/gal	1.9 gal	$54.63
Trivalent additive #2				28.25/gal	1.5 gal	43.38
Trivalent base salts				1.97/lb	18.0 lbs	35.68
Boric acid				0.36/lb	10.0 lbs	3.60
Trivalent wetter				12.75/gal	0.6 gal	7.65
Hydrogen peroxide				8.00/gal	0.5 gal	4.00
Treatment Chemicals						
Sodium metabisulfite	0.33/lb	86.4 lbs	28.51			
Lime	0.09/lb	28.8 lbs	2.71			
Energy Usage						
Electrical	$0.085/kwh	196.0 kwh	16.66	$0.085/kwh	114.0 kwh	9.69
Natural Gas	$0.65/therm	6.9 thms	4.47	$0.675/therm	9.6 thms	6.24
Operating Variables						
Rejects		1.5%	81.00*		0.5%	27.00*
Operating Costs						
			168.77			190.87
Gross Profit Per Shift (Calculated at $0.20 per sq ft of parts plated)						
	0.20	7200 ft2**	1440.00	0.20	8220 ft2**	1644.00
Net Profit Per Shift (= Gross Profit - Oper. Costs)						
			$1271.23			$1453.13
Difference in Profits Per Shift (= Trivalent - Hexavalent)						
						$181.90

^ Shifts are eight hours in length.

* Cost for rerunning rejected parts.

** Trivalent Process is able to plate 15% more parts per shift, due to higher parts densities on racks.

Low Temperature Arc Vapor Deposition (LTAVD)

Cost information for this process has not been published; the process is being used by several major manufacturers of consumer hardware, indicating that it is commercially viable. Since a wide variety of gases and metals are used, material costs also would vary accordingly. A major operating cost would be energy. Waste treatment costs are likely to be minimal.

Environmental Assessment

Trivalent Chromium Plating

In hexavalent chromium plating, rinse water effluent must be treated with sulfur dioxide or sodium bisulfate to reduce the Cr(VI) to Cr(III). Zaki (2002) estimates that the volume of sludge generated by the hexavalent process is about 30 times that of the trivalent process.

Hexavalent plating typically involves the use of a lead-tin anode. While the double-cell trivalent process also uses this type of anode, the single cell process uses a less environmentally problematic graphite anode.

Trivalent plating involves the use of several chemical mixtures, which vary according to manufacturer. Using Enthone's Tricrolyte® (a single cell process) as an example, ingredients may include chromic sulfate, sodium sulfate, a proprietary ammonium compound, ammonium chloride, potassium chloride, ammonium formate, ammonium bromide, boric acid, butanedioic acid, sulfo-1,4-bis(1,3-dimethylbutyl) ester sodium salt, and ethanol. The manufacturer has not conducted "specific studies on the ecotoxicity or environmental fate" on the Tricrolyte® product.

Low Temperature Arc Vapor Deposition (LTAVD)

Vapor Technologies reports that the only effluent from this process is a small amount of vaporized oil from the vacuum pumps.

Human Exposure Assessment

Trivalent Chromium Plating

Trivalent plating involves the use of several chemical mixtures, which vary according to manufacturer. Using Enthone's Tricrolyte® as an example, ingredients may include chromic sulfate, sodium sulfate, a proprietary ammonium compound, a proprietary additive, ammonium chloride, potassium chloride, ammonium formate, ammonium bromide, boric acid, butanedioic acid, sulfo-1,4-bis(1,3-dimethylbutyl) ester sodium salt, and ethanol.

None of these chemicals is classified as carcinogenic, or is included on California's Proposition 65 list (chemicals known to cause cancer, birth defects or other reproductive harm). The MSDS notes that boric acid is a potential developmental toxin and ethanol is a proven developmental toxin. Many of the chemicals can be hazardous to human health if measures are not taken to avoid overexposure. Chemical specific effects from overexposure of the trivalent process chemicals are listed in Table 6.4.1 E.

Table 6.4.1 E: Potential Effects of Overexposure to Chemicals in Trivalent Plating Process Solutions (Source: Cookson Electronics MSDSs)

Chemical	Symptoms of Over-Exposure
Boric Acid	Skin, inhalation and ingestion: nausea/vomiting, diarrhea, drowsiness/fatigue, headache, low blood pressure. Lower body temperature, coma and possible death. Absorbed through the skin. Chronic weight loss, convulsive seizures, and skin rash or hives. Prolonged overexposure may cause damage to the teeth, liver and kidneys.
Ethanol	Eyes: blinking, redness or swelling. Skin: Defatting to the skin. Ingestion: dizziness/vertigo, euphoria, uncoordination, motor and sensory paralysis, developmental abnormalities. Inhalation: high concentrations of vapor may affect the central nervous system.
Chromic Sulfate	Eyes: may cause irritation or burns. Prolonged contact may cause eye damage. Skin: causes skin irritation. May cause sensitization by skin contact. Eczematoid dermatitis caused by trivalent chromium compounds has been reported. Inhalation: material is irritating to the mucous membranes and upper respiratory tract. Symptoms include coughing, shortness of breath/breathing difficulty, headache, fever, pulmonary edema. May cause sensitization by inhalation. Ingestion: can cause gastrointestinal disturbances. Symptoms include dizziness/vertigo, abdominal cramps/pain, nausea/vomiting, loss of consciousness/coma. Chromic effects: prolonged skin contact may cause dermatitis. Repeated of prolonged exposure to the substance can cause kidney damage. Inhalation may cause ulceration and perforation of the nasal septum.
Sodium Sulfate	Ingestion: fluid loss, blood in stool or urine, low blood pressure and high sodium levels.
Ammonium Chloride	Eyes and skin: irritating to the eyes, mucosa and skin and may cause burns. Causes dermatitis. Inhalation: material is irritating to mucous membranes and upper respiratory tract. Exposure can cause coughing, chest pains, difficulty in breathing. Ingestion: can cause gastrointestinal disturbances.
Potassium Chloride	Ingestion: drowsiness/fatigue, heart and circulatory problems. Large amounts can cause gastric upset and nausea/vomiting. Eyes: blinking, redness, or swelling. Skin: skin rash or hives.
Butanedioic acid, sulfo-,1,4-bis(1,3-dimethylbutyl) ester sodium salt	May be irritating to eyes, skin and respiratory system. Large amounts may cause gastrointestinal irritation, nausea, vomiting and diarrhea.
Ammonium Formate	Eyes: blinking, redness or swelling, pain. Skin: itching and pain. Inhalation: coughing, sore throat, breathing difficulty, shortness of breath and chest tightness/wheezing. Ingestion: gastrointestinal irritation.
Proprietary Ammonium Compound	Eyes: blinking, redness, swelling or pain. Skin: itching and pain. Inhalation: coughing, sore throat, breathing difficulty, shortness of breath and chest tightness/wheezing. Ingestion: gastrointestinal irritation.
Proprietary Additive	Eyes: tearing, blinking, redness or swelling. Skin: Defatting to the skin. May cause irritation. Inhalation: material is irritating to mucous membranes and upper respiratory tract. Ingestion: can cause gastrointestinal disturbances.

Recommended worker controls to prevent overexposure to the trivalent plating process chemicals include ventilation and eye, skin and respiratory protection.

Low Temperature Arc Vapor Deposition (LTAVD)

Information on possible human exposure factors for this process has not been published. The process is conducted in a sealed vacuum chamber, minimizing worker exposure to emissions. A variety of gases and metals can be used in the process; any hazards associated with those materials would be present. For example, a chromium nitride is deposited by feeding ionized chromium metal into a plasma of ionized argon and nitrogen. The chromium in CrN is trivalent. In addition, parts often are coated with one or more layers of nickel under the surface coating in order to improve corrosion resistance; this is true of hexavalent and trivalent chrome coated parts as well.

Table 6.4.1 F: Summary of Decorative Chromium Electroplating Alternatives

Assessment Criteria		**Cr(VI) (Reference)**	**Comparison Relative to Cr(VI)**	
			Trivalent Chromium	**LTAVD**
Technical/Performance Criteria	Corrosion Resistance	Good	=	=/+
	Appearance	Blue-white	-/=	=
	Throwing Power/Coverage	Poor	+	+
	Uniformity of Coating	Variable	+	+
	Tolerance to Current Interruptions	Poor	+	?
	Micro-discontinuous Structure	Need Special Process	+	?
	Susceptibility to Burning	High	+	**N/A**
	Ease of Rinsing	Moderate	+	**N/A**
	Color Buffing Required	Occasional	+	?
Financial Criteria	Effect of Impurities	Low	-	?
	Removal of Impurities	Difficult	+	**N/A**
	Waste Treatment & Disposal	Expensive	+	+
	Chemical Cost	Inexpensive	-	?
	Energy	196 kwh/8 hrs.	+	?
	Efficiency (number of parts per rack)	Moderate	+	**Varies**
	% Rejects	1.5%	+	?
Environ-mental Criteria	Amount of Waste Generated	High	+	+
	Use of Lead Anode	Yes	=/+	+

Table 6.4.1 F: Summary of Decorative Chromium Electroplating Alternatives

Assessment Criteria		Cr(VI) (Reference)	Comparison Relative to Cr(VI)	
			Trivalent Chromium	LTAVD
Human Health Criteria	Carcinogenicity	EPA Group A IARC Group 1	+	+
	Occupational Exposure: PEL (8-hour TWA)	~ mg/m^3	+	+
	Skin Irritant/Sensitizer	Yes	+/=	+

Comparison Key + Better = Similar - Worse ? Unknown

6.4.2 Hard Chromium Electroplating of Industrial Components

Hard chrome plating, also known as functional or industrial chrome, typically is thicker than decorative chrome. It is used on industrial components that must perform under demanding conditions such as high temperatures, and repetitive grinding and impact forces. Unlike decorative chrome, appearance usually is not an important issue.

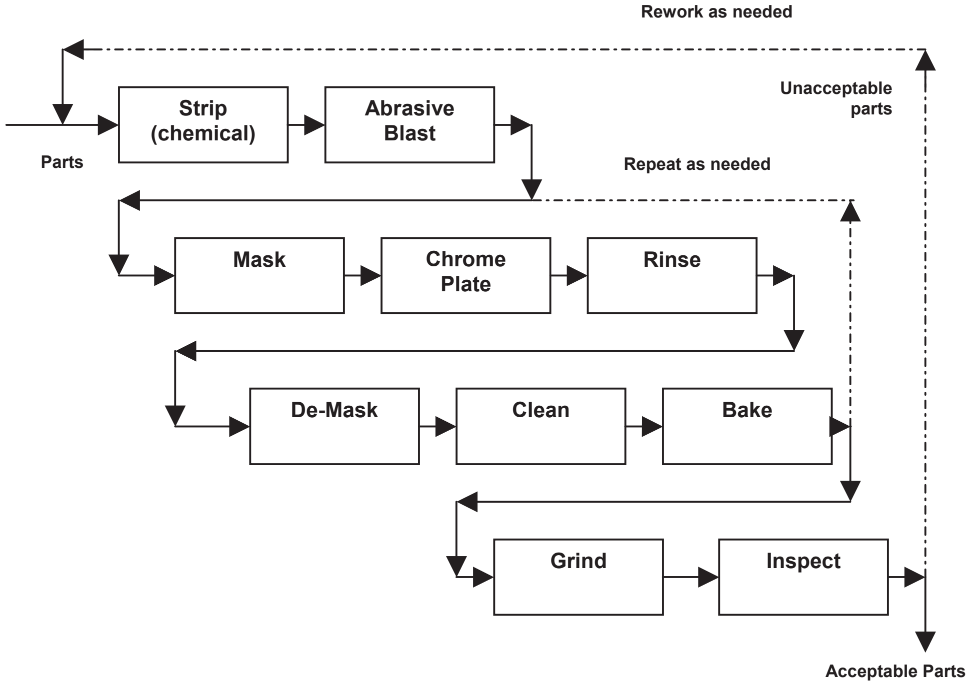
The two main reasons that hard chrome is used are to provide wear and corrosion resistance, and to rebuild worn components to precise dimensions. It has a low coefficient of friction, is hard and heat-resistant, adheres well to substrates of various geometries, and provides corrosion resistance. Industrial parts that often are hard chrome plated include aircraft engines and landing gear, oil well equipment, crank shafts, hydraulic cylinders, paper making equipment, molds, stamps, dies, drill bits, and power industry equipment.

The key performance characteristics for replacements of the hard chromium include:

- Hardness
- Wear Resistance
- Embrittlement
- Fatigue Properties
- Corrosion Resistance
- Surface smoothness/machinability
- Application-specific performance such as hydraulic seal wear

The hard chrome plating process is a multi-step process that is essentially the same as that used for decorative chrome plating (Fig. 6.4.2A)(see Section 6.4.1). The coating thickness is greater, and parts may be plated more than once. Chromium is deposited from a highly concentrated solution of chromium oxide, typically 33 oz/gallon. In solution, the chromium exists in the hexavalent state and electrons for the electrodeposition reaction are provided by electrical current: $Cr^{+6} + 6e^{-} \Rightarrow Cr^{0}$. In addition to the chromium compound, hard chromium plating baths also contain catalysts for the deposition reaction. These typically are sulfate or fluoride/sulfate catalysts at low concentrations (~1% of the chromic acid concentration).

Figure 6.4.2.A: Hard Chrome Plating Process
(Sartwell et al. 2003)



Hard chrome plating has a number of limitations in addition to its health and environmental impacts. There are numerous steps in the plating process, and some steps may need to be repeated in order to get an adequate coating. The coating can be brittle, leading to failure or reduced corrosion resistance. In electroplating operations, plating thickness is generally greater on edges, corners and other high current density areas. This situation is greatly exacerbated in hard chromium electroplating. Intricately constructed anoding is required for even plating thickness.

Plating efficiency refers to the percentage of electrical current that is used directly for the deposition reaction. The major side reaction is splitting of water into oxygen (at the anode), and hydrogen (at the cathode). The efficiency of hard chromium plating baths ranges from 10 – 25%. Most other plating solutions range from 80 – 99% efficient. As a result of the low efficiency, a large quantity of gas is generated, which forms bubbles that rise to the top of the solution and break with enough force to generate significant chromic acid mist. The quantity of mist generated is also proportional to the viscosity of the solution, which is relatively high due to the high chemical concentration.

Maintenance of chromium plating tanks is essential to prevent solution contamination that adversely affects the quality of the plating. Solution contamination consists of:

- Excessive sulfate contamination. This is removed by the addition of Barium salts to create the insoluble barium sulfate.
- Trivalent chromium. Trivalent chromium is continuously formed during the oxidation-reduction plating reaction; it is also continuously reoxidized at the anode surface during plating. If the trivalent chromium concentration exceeds 1 – 2%, it is likely the anodes are scaled and require cleaning, or excess metallic contamination may be present. If the anodes are scaled, they may be descaled by plating with a high surface area "dummy" to reoxidize the trivalent chromium to the hexavalent state; chemically cleaning the anodes; or physically scrubbing the anodes.

Table 6.4.2 A: Functional Advantages and Disadvantages of Hard Chrome Electroplating

Advantages/Strengths	Disadvantages/Limitations
Deposit is extremely hard and wear resistant	Slow rate of deposition; multiple coats often needed
Thick deposits can be machined for repair/tolerance applications	Machining needed to get uniform thickness
Simple, well-understood technology	Susceptible to hydrogen embrittlement
Wide range of applications	Exhibits brittleness, leading to micro-cracking and reduced corrosion resistance
Surface offers good lubricity characteristics	Decontamination of plating solutions is difficult
In combination with nickel underplating, it can offer good corrosion resistance	

- Metallic contamination. This can cause plating quality problems such as rough deposits, hazy or milky deposits, or a decreased bright range. Membrane electrolysis or the use of "Porous Pot" technologies can remove excess metallic contamination, as well as re-oxidize trivalent chromium to the hexavalent state. Extensive contamination of the solution may require replacement of some or all of the solution.

During the plating process, the base material may absorb hydrogen generated during the plating operation, resulting in hydrogen embrittlement. Hydrogen embrittlement is the phenomenon by which absorbed hydrogen migrates to grain boundaries in the base material, seriously weakening the part. If not post-treated by a bake cycle (typically 375° F for 24 hours, but varies depending on base material), cracking of the base material may occur, causing failure of the part.

Hard chromium plating may need to be stripped from the part for repair purposes or due to quality defects. In either case, stripping is accomplished using a strong sodium hydroxide solution and electrical current. This creates a corrosive, toxic hazardous waste that must be disposed of.

Description of Alternatives

Six categories of alternatives to hard chrome plating were selected for study:

- Thermal sprays
- Weld facing methods
- Heat treatment methods
- Vapor deposition methods
- Nanocrystalline coatings
- Functional trivalent plating

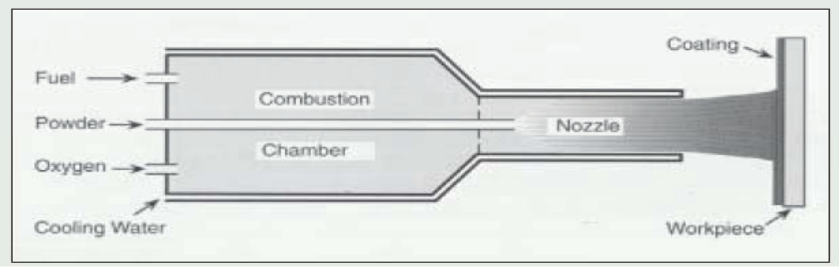
It should be noted that some of these categories include several related processes that differ in their functional details, and a variety of metals can be deposited with most of the processes. In addition, the categories often overlap to a certain extent, with a particular process sometimes being classified differently by various scientists.

Thermal Sprays

Thermal spray is a coating process in which wire or metallic powder is melted by a high temperature flame and sprayed as particles or droplets onto a substrate. During the application the spray torch used makes several passes as it accelerates the soft powder into the surface.

Figure 6.4.2 B: HVOF Process

(Devereaux, Stricklin 2004)



A type of thermal spray that is being used as a hard chrome replacement is high velocity oxy-fuel (HVOF). HVOF involves metal powders (e.g. cobalt, tungsten) being heated in a combustion chamber by an oxygen/fuel gas mixture and expelled at high velocity and temperature (up to 1,800 m/s and 2,700° C) onto the material to be coated (Hermanek 2001).

Weld Facing Methods

Weld facing (also know as hard facing) is a dry method of joining a hard coating, edge, or point to a metal or alloy substrate to improve its resistance to abrasion, corrosion, heat or impact. It also is used to restore worn surfaces.

The weld facing process involves applying metal or ceramic to a part with welding equipment. That equipment can be the traditional oxyacetylene welding torch, one of the many types of arc welders, or a type of specialized micro-arc welder. Micro-arc welding uses very small energy levels and is good for use on conductive surfaces; this category includes Electro Spark Deposition (ESD), which is used in the open air with a hand held electrode for repairs over small areas, and Electro Spark Alloying (ESA), a technique used over a much smaller area. Also included in this category is laser cladding -- the melting of metallic powder on to the surface of a substrate using the finely controlled energy of a laser beam.

Laser alloying is a surface modification technique where a ceramic/metal (cermet) coating mixture is heated using a laser to fuse the coating to the substrate. It forms a thin, permanent alloy layer. A variant on laser alloying is laser induced surface improvement (LISI^{TM}), which was developed at the University of Tennessee Space Institute. These processes are intended to make a surface more resistant to corrosion and wear, and to increase hardness.

Laser alloying is similar to laser cladding. One way to differentiate one technique from the other is by comparing the relative amounts of the consumable material added and the substrate melted. The two categories are arbitrarily separated by their relative amount of dilution, with laser alloying having a greater percentage of dilution than laser cladding. (www.lvitech.com/technology_cladding_2.htm)

Heat Treatment Methods

These methods, sometimes called thermal diffusion methods, use heat to diffuse elements into the top surface of a substrate metal to form an alloy or layer with desired properties, such as hardness or lubricity. The names of some of the processes in this category are derived from the type of element used: nitriding (nitrogen), boronizing (boron), and carburizing (carbon.)

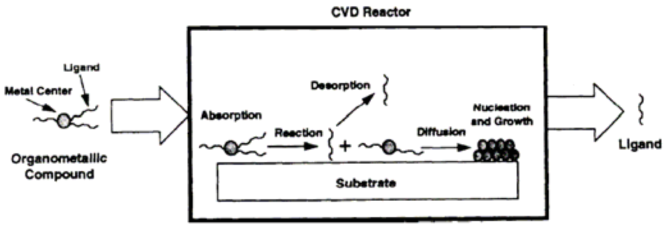
Plasma diffusion is the process whereby elements are introduced into the surface of the substrate by the use of a gas activated with the desired element at elevated temperatures. Variations on this process include plasma nitriding, nitrocarburizing, and low pressure nitiriding. (plasmaindia.com)

Vapor Deposition Methods

Physical vapor deposition (PVD) employs a coating material created from a solid that is vaporized by an electric arc or an electron beam. The material is then transported through a vacuum, low-pressure gas or plasma (which accelerates the ions), condensing on the component surface and forming a thin and very hard layer. Types of PVD processes are ion plating, vacuum evaporation, thermal evaporation, electron beam evaporation, and sputter deposition (Mattox 2001; Singh, et al. n.d.)

Chemical vapor deposition (CVD) is similar to PVD; however, the coating material comes from the gases that combine on the hot surface to form the hard coating. Variations on the CVD process include atmospheric CVD (conducted at atmospheric pressure and high temperature); low pressure CVD (sub-atmospheric pressure and high temperature); and plasma enhanced CVD (lower temperature with heat generated by an electrical plasma.) (National Defense Center for Environmental Excellence (NDCEE) 1995)

Figure 6.4.2 C: Chemical Vapor Deposition (NDCEE 1995)



Nanocrystalline Coatings

This process involves deposition of very small grains (5-15 nm) of crystalline alloys (for example, cobalt-iron-phosphorus) on a metal substrate (McCrea, Marcoccia & Limoges 2003). Nanocrystalline materials exhibit unique properties resulting from the large proportion of grain boundary atoms (Tjong, Chen 2004). Hardness, fracture toughness and yield strength increase as the size of article grains get smaller; this is known as the Hall-Petch effect (Klingenberg, Broonam & Naguy 2005). The coating can be applied through electrodeposition, vapor deposition, or spray conversion processing.

Trivalent Chromium Plating

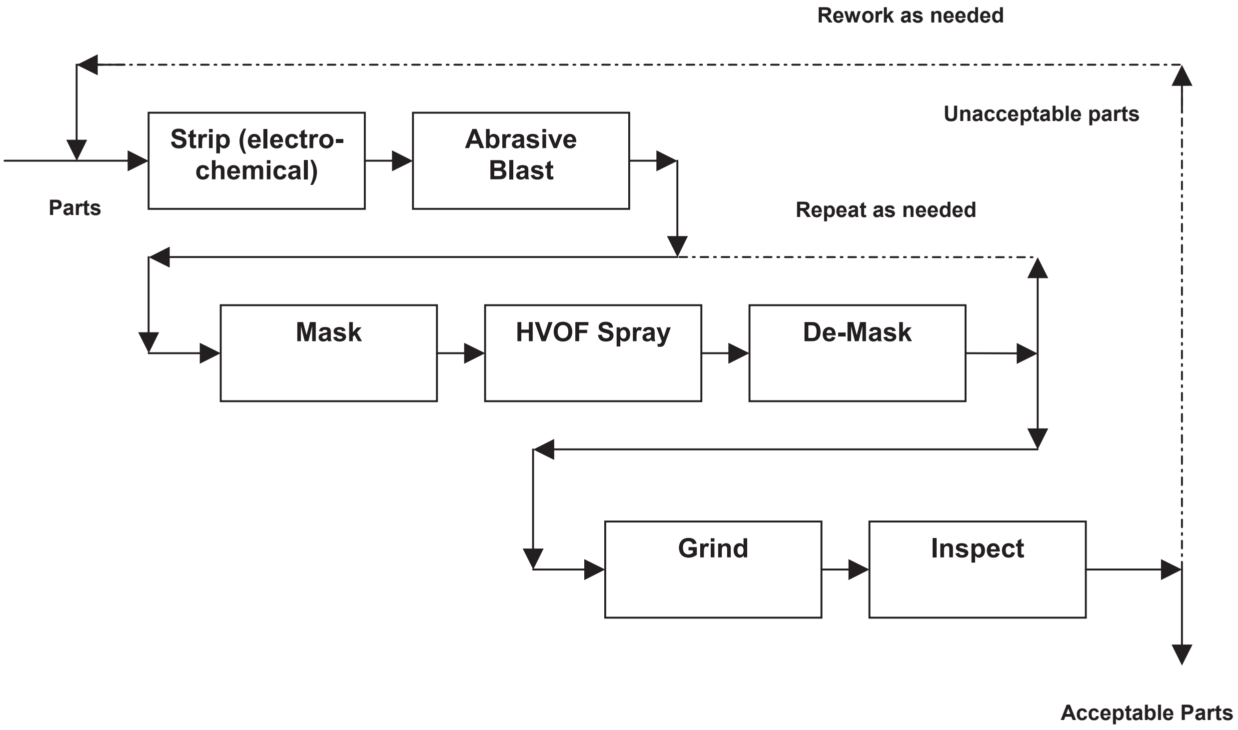
Conventional trivalent chromium plating is not suitable for replacing functional (hard) chrome because its low plating efficiency and low plating rate limit the thickness of trivalent deposits to no more than 0.1 mil/2.5 µm. (Renz et al. 2003) The United States Environmental Protection Agency's Small Business Innovation Research Program funded development of a trivalent chromium alternative to hard chrome plating that attempts to overcome that limitation. Faraday Technologies' Faradaic™ process is similar to the wet hexavalent plating process, with the capability to plate a thick, functional chromium coating using a trivalent chromium plating bath. Described as a charge modulated electrochemical deposition (CM-ECD) process, it is intended as a "drop-in" alternative to hexavalent baths.

Technical Assessment

Thermal Sprays

High velocity oxy-fuel (HVOF) is a type of thermal spray/dry spraying process that is capable of depositing a wide array of single-metal, alloy, cermet and ceramic coatings that can provide similar or better functional characteristics than hard chromium plating. Figure 6.4.2 D shows the steps in the HVOF process.

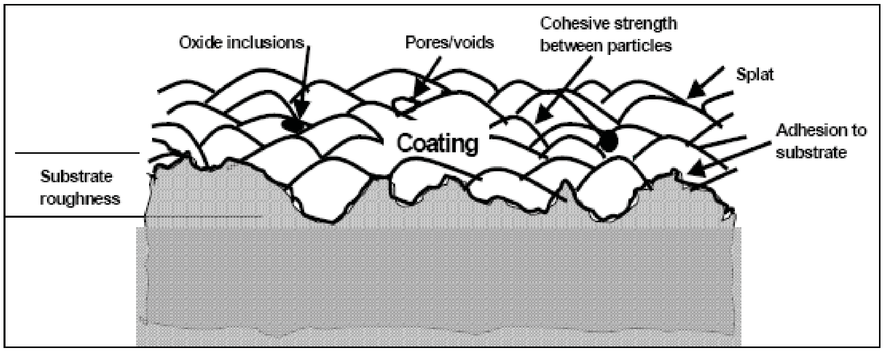
Figure 6.4.2 D: HVOF Process
(Sartwell et al. 2003)



The HVOF spray process uses pure oxygen mixed with one of a variety of fuels such as propane, acetylene, hydrogen, etc. to generate supersonic gas velocities on the order of 1,800 m/s. The material to be deposited is in the powder form, generally 20 – 100 µm in size (Sartwell, et al. 1999). The powder is fed into the spray gun combustion chamber, along with the oxygen and fuel, and the combustion heated stream, at approximately 2,700° C is directed at the part to be coated. Typical distances from the spray gun to the part are 15 – 30 cm (Sartwell, et al. 1999).

As the materials are heated, the particles change to a more plastic (or molten) form. The coating is formed as the particles impinge on the surface, flatten and form platelets (splats) that build a laminar, non-homogeneous coating (United States Army Corps of Engineers 1999). The degree of porosity in the coating is dependent on the materials and processing conditions. The deposition rate is approximately 0.002 in. per minute (Sartwell, et al. 1999). The total time to coat a part will depend on part configuration and size as well as the speed of the spray gun and/or part relative to each other. Thicknesses in excess of 0.1 in. may be deposited (Fedrizzi, et al. 2004).

Figure 6.4.2 E: Cross Section of a Typical Thermal Spray Coating
(United States Army Corps of Engineers 1999)



One drawback to HVOF is that it cannot be used to deposit materials on internal diameters – it is a "line of sight" deposition process. There are other thermal spray technologies such as plasma spray that are being developed to allow internal diameter coating (Legg, Sauer 2005). Additionally, due to the high temperatures involved, heat sensitive components may be damaged.

Examples of coating materials[9] that can be applied by HVOF include (Stokes 2003):

- Tungsten carbide/cobalt (WC/Co) – various percentages of WC and Co
- Aluminum bronze alloy
- Copper
- Cobalt base superalloy
- Aluminum alloy/polyester

Some applications for the HVOF coatings include (Stokes 2003):

General Manufacturing Industry:	Extrusion Dies, Thread Guides, Forging Tools, Wire Drawing Capstans, Cam Followers, Roller Bearings, Hot Forming Dies
Gas Turbine Industry:	Turbine Nozzles, Jet Engine Ducts, Jet Engine Manifold Rings, Gas Turbine Fan Seals, Aircraft Flap Tracks, Expansion Joints, Mid Span Supports (Fan Blades)
Petroleum Industry:	Pump Plungers, Liners, Sleeves, Compressor Rods
Chemical Process Industry:	Gate Valves, Pump Components
Paper/Pulp Industry:	Printing Rolls, Digesters, Liquor Tanks
Automotive Industry:	Piston Rings, Cylinder Liners

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[9] There are also several nickel-based coatings that are used: Nickel/Chromium/Molybdenum, Nickel/Chromium/Iron, Fusible Nickel Based Alloy, Nickel Based Alloy/Tungsten Carbide, and Chromium Carbide/Nickel Chromium.

HVOF coating materials are chosen on the basis of function, such as improvements in fretting wear, abrasive wear, corrosion control, high or low temperature application, etc.

The Hard Chrome Alternatives Team (HCAT) is a bi-national team comprising a U.S. team concentrating on replacing chrome plating in Department of Defense (DoD) repair depots, and a Canadian team working primarily to replace chrome on commercial and military aircraft landing gear. They have performed extensive testing and data collection/analysis on HVOF. Their work can be accessed at: http://www.hcat.org/) Much of the literature on HVOF has been produced by HCAT.

There are many materials/material combinations that can be deposited by HVOF. For the replacement of hard chromium plating on aerospace components, the primary material that has been extensively tested is WC-Co (Tungsten carbide/cobalt), a cermet (ceramic/metallic) material.

The choice of materials must be carefully considered. In some cases, coatings optimized for wear resistance have exhibited poor base-material fatigue properties (Legg, Sauer 2000). Optimization of the coating materials must consider both the base material and coating properties and interactions.

Hardness

Typical requirements for hard chrome hardness are 850 – 1000 Vickers (VHN). In one study conducted on gas turbine engine components, HVOF deposited WC-Co was found to have hardness values >1,100 VHN. In research conducted by the Naval Research Laboratory, WC-Co coatings were found to have average Vickers hardness of 1,220 versus an average hard chrome hardness of 873 VHN (Sartwell, et al. 2003).

Wear Resistance

"ASTM G65 Standard Test Method for Measuring Abrasion Using the Dry Sand/Rubber Wheel Apparatus" is the method that covers laboratory procedures for determining the resistance of metallic materials to scratching abrasion by means of the dry sand/rubber wheel test. In tests performed by Sulzer Metco, hard chromium had a mass loss of 60.6 mg, while various WC-Co alloys applied by HVOF had no greater than 40.6 mg (Kirsten, et al. 2005). Another ASTM G65 test performed by Hart et al. showed a volume loss of ~28 mm^3 for an HVOF applied WC-metal alloy versus ~52 mm^3 for hard chrome (Hart et al.)

Fatigue Properties

Substrate fatigue occurs during hard chromium plating as the stress in the deposit increases, increasing the residual stress at the substrate surface. This can lead to reductions in the fatigue strength of the substrate, resulting in fracture of the part (Nascimento, et al. 2001). HVOF offers significantly improved fatigue properties.

Embrittlement

Because hydrogen is not generated during HVOF processing, as it is in hard chrome plating, embrittlement of the substrate material is not a concern.

Environmental embrittlement stress corrosion cracking occurs as a result of exposure to materials in the environment (such as salt). Susceptibility to this phenomenon is tested via Test Method F-519 notch test (Sartwell et al. 2003), and has been performed by the Hard Chrome Alternatives Team. Their data show that HVOF performs much better than hard chrome, that is, the parts are less susceptible to this type of embrittlement.

Corrosion Resistance

Hard chromium plating is a barrier coating in regards to corrosion resistance. If the barrier is breached, corrosion of the substrate material will occur. HVOF coatings also act as a barrier coating, but in this case, the coating itself will corrode, typically due to dissolution of the cobalt in the coating (Legg, Sartwell). This may result in some flaking of the coating, but not the catastrophic failure that can occur with hard chrome when the underlying surface corrodes, delaminating the coating from the substrate.

The primary effect of HVOF corrosion is roughening of the surface, which can reduce the life of seals associated with hydraulic units. However, testing so far has shown that under service-life conditions, corrosion is not evident (Legg 2000).

Surface smoothness/machinability

Hard chrome plating is often used for repair of equipment. The worn area is plated to a thickness greater than required, then ground and/or polished to the specified dimension. For hydraulic seal applications, as well as other critical sliding applications, a smooth finish is critical to prevent seal wear and subsequent hydraulic fluid leakage. The HVOF finish is similarly capable of being ground and polished to fine or superfine finishes (Nuse, Falkowski 2000).

Application-specific developments

HVOF-applied coatings have been approved for landing gear components on the military A-10, C-130, C-141, and other aircraft, as well as certain F-22 engine components. Boeing and Airbus also have specified HVOF coating on various commercial aircraft equipment parts (Sartwell et al. 2003).

Table 6.4.2 B: Advantages and Limitations of HVOF as a Hard Chromium Electroplating Alternative (Sartwell et al. 2003)

Advantages/Strengths	Disadvantages/Limitations
Higher hardness, better wear resistance, longer overhaul cycle, less frequent replacement	Brittle, low strain-to-failure; can spall at high load (issue primarily for carrier-based aircraft)
Better fatigue, corrosion, embrittlement	Line of sight only. Cannot coat internal diameters
Material can be adjusted to match service requirements	More complex than electroplating. Requires careful quality control.
Can coat large areas quickly. Can be chemically stripped. Many commercial vendors.	WC/Co requires diamond grinding wheel. Only HVOF can be plunge ground.
No air emissions, no high volume rinse water.	Co toxicity

Weld Facing Methods

Weld facing methods generally are used for the rebuilding of worn parts, one of the primary uses of hard chrome. The forms of weld facing most likely to be used in replacing hard chrome are electrospark deposition (ESD) and laser alloying.

The team that is investigating alternatives to hard chrome for military applications (Hard Chrome Alternatives Team – HCAT) categorizes ESD as being appropriate for “niche” applications, such as on-site repair of small areas of localized damage to metal parts, where the material to be deposited is the same as the parent material. It has been used for repair of gas turbine engine (GTE) parts, and for shafts of ships, submarines and vehicles. Table 6.4.2 C lists some of the advantages and disadvantages of ESD for repair of worn parts:

Table 6.4.2 C: Advantages and Disadvantages of ESD for Repair of Worn Parts

Advantages	Disadvantages
Inexpensive, portable, can repair-in-place	Very slow
Can get into very small spaces and re-entrant geometries	Some materials (carbides) self-limiting in thickness
Wide variety of coating materials	Coating has high tensile stress; cracks common, fatigue debit
Hand-held or robotic	Rough surface; sometimes have to file between layers
Very thin heat-affected zone (HAZ)	

The National Defense Center for Environmental Excellence (NDCEE 2003) has evaluated the feasibility of using ESD to replace hard chrome in applications where some of the other hard chrome alternative, such as HVOF, are not suitable. It found that ESD rebuilt surfaces with a hardness and smoothness that were comparable to hard chrome, and that wear performance was similar or better.

Another weld facing method is Laser Induced Surface Improvement (LISI). Developed by the University of Tennessee Space Institute (UTSI), it has been tested at the United States Air Force's Arnold Engineering Development Center (AEDC). The results of the testing have not been published, but UTSI indicates that it can be effective in improving corrosion resistance, wear resistance, and hardness. Although there have been some trials using the technique for applications such as tractor-trailer fifth-wheel hitches, no company has adopted it on a commercial level, and the project team has disbanded (Dahotre, pers. comm. 2006).

Heat Treatments and Plasma Diffusion

Unlike weld facing methods, heat treatments are not suitable for rebuilding parts. Rather, they are used to make surfaces more resistant to wear, corrosion or oxidation (Rowan Technologies, n.d.) They have the advantage of being commercially available, well-defined processes, and can be used for large parts (such as hydraulic rods and pistons) (Legg 1999). A key disadvantage is that the part is subjected to high temperatures (500-1000° C), which can distort or melt some alloys.

Plasma nitriding (sometimes called ion nitriding) does not involve the very high temperature of traditional heat treatments. The plasma typically is 400-590°C, making it an option for a greater range of metals. As a replacement for hard chrome, it may be used in combination with another process. For example, a substrate is hardened with plasma nitriding, and then coated with a Physical Vapor Deposition (PVD) process.

Northeast Coating Technologies, a company that performs plasma nitriding, lists the following advantages of the process over hard chrome:

- It imparts a hard, wear resistant diffused layer, without problems with flaking, spalling, edge build-up, and chipping
- Cutting edges remain sharp during plasma nitriding, and the process achieves a consistent hardness and case depth
- There is no build-up that causes the rounding of edges and webbing at the base of cavities
- Ion nitriding provides good resistance to indentation
- It improves the fatigue strength of the material

A German company (Metaplas Ionon) tested their patented IONIT OX process, which is suitable for ferrous materials, in comparison to hard chrome. The results are shown in Table 6.4.2 D.

Table 6.4.2 D: Characteristics of Corrosion-Protection Processes for Steel, IONIT OX Compared to Hard Chromium Electroplaing (auf dem Brinke and Krug, 2001)

Factor	Chromium Electroplating	IONIT OX
Treating Temperature, °C	<100	500-580
Environmental Concern	Cr(VI)	CO_2/NOx
Coating	Chrome with Cr(VI)	Oxide
Structure	Porous, brittle	Dense
Depth, mm	20	0.2-0.3
Vickers Hardness, VHN	900	800-1400
Hardness Gradient	Steep	Very good
Salt Spray Test Duration, h	300	500
Production Costs	High	Low

Nanocrystalline Coatings

Much of the research on this method has been conducted by a team that originally worked in the Canadian power industry (Integran Technologies). The United States Department of Defense Strategic Environmental Research and Development Program (SERDP) sponsored development and refinement of the method, with a goal of replacing hard chrome at Department of Defense rework, maintenance and manufacturing facilities (SERDP, n.d.). Additional work on using nanocrystalline coatings for non-line-of-sight applications has been done under the auspices of the Air Force Research Laboratory, and the Department of Defense's Hard Chrome Alternatives team (HCAT). A Massachusetts company, Xtalic, Inc., also has developed nanotechnology that can be used to replace hard chrome.

The interagency Strategic Environmental Research and Development Program (SERDP), a joint venture of the United States Department of Defense, Department of Energy, and Environmental Protection Agency, sponsored a three year, three-phase study of nanocrystalline coatings as a replacement for hard chrome on non-line-of-sight applications. In the first phase evaluation was done on three alloy coatings – cobalt-phosphorus (Co-P), cobalt-molybdenum (Co-Mo) and cobalt-iron-phosphorus (Co-Fe-P). The second phase looked at performance characteristics of a electrodeposition process using the Co-P alloy. The third phase involved applying the Co-P coating on test internal-diameter (ID) pieces, and to an actual landing gear shock strut. Tables 6.4.2 E and 6.4.2 F summarize some of the test results from that project (McCrea, Marcoccia & Limoges 2003).

Table 6.4.2 E: Nanocrystalline Co-P Process Data Summary Compared to Hard Chromium Electroplating (McCrea et al. 2003)

Factor	Nano Co-P Alloy	Hard Chrome
Bath Chemistry	Co 2-twt%P ($CoCl_2/H_3PO_4/H_3PO_3$)	Cr (CrO_3/So_4^{-2})
Efficiency	85-95%	15-35%
Deposition Rate	Up to 8 mil/hr	Up to 1.6 mil/hr
Thickness	Demonstrated up to 0.020"	Typically <0.005"
As-deposited Appearance	Pit/Pore Free	Microcracked
Microstructure	Nanocrystalline	----
Relative Process Cost	1.3	1.0
Emission Analysis	Below OSHA limits	Cr^{+6}

Table 6.4.2 F: Nanocrystalline Co-P Property Data Summary Compared to Hard Chromium Electroplating (McCrea et al. 2003)

Factor	Nanocrystalline Co-P	Hard Chrome
Hardness (as deposited)	600-700 VHN	800-1200 VHN
Hardness (heat treated @ 250° C)	700-800 VHN	----
Hardness (heat treated @ 400°C	1000-1200 VHN	----
Ductility	2-7% elongation	<0.1%
Thermal Stability	400° C	----
Wear (Abrasive – Taber)	27 mg/1000 cycles (CS-17)	3.2 mg/1000 cycles (CS-17)
Wear (Adhesive – Pin on disk)	11 mg/1000 cycles (CS-10)	1.0 mg/1000 cycles (CS-10)
Corrosion (Salt Spray)	Protection Rating 8 @ 1000 hours	Protection Rating 2 @ 1000 hours
Corrosion (Potentiodynamic)	0.1-1 mpy	0.01 mpy
Internal Stress	10-15 ksi (tensile)	Cracked – exceeds cohesive strength
Hydrogen embrittlement	None	Yes – min. bake 24 hrs.
Fatigue	Retesting required	Fatigue debit

The nanocrystalline Co-P coating compared favorably with the hard chromium electroplating in most respects:

- Efficiency of the coating process was greater
- Deposition rate was greater
- Air emissions were below OSHA limits
- Ductility was greater
- Sliding wear resistance was greater
- Corrosion resistance was greater (with the exception of Co-Fe-P alloys)
- Tensile strength was greater
- Hydrogen embrittlement did not occur

The functional areas where only some of the nanocrystalline coatings equaled hard chrome were abrasive wear and hardness (which usually are correlated.)

The hardness of the nanocrystalline deposits varied according to the amount of phosphorus used and whether a heat treatment was added at the end of the process. Samples were subjected to a Vickers hardness test, which measures the hardness of metals. A pure nanocrystalline cobalt exhibited a Vickers Hardness Number (VHN) of 550; this increased to a VHN of over 800 with a Co-P alloy with 5 percent (weight) phosphorus. The addition of a short (ten minutes) annealing time at 400 degrees C further increased the hardness to 1000 VHN or more. This is close to the maximum VHN for hard chrome.

Abrasive (Taber) Wear testing of the nanocrystalline coatings generally showed them to be less resistant to wear than hard chrome. The Taber Wear Index (TWI) is measured in mg per 1000 cycles; a lower index number means that the material is more wear resistant. Hard chrome has a TWI of 3.4. The pure cobalt samples had TWIs of more than 38. The Co-P coatings had TWIs between 12 and 30 (depending on the amount of phosphorus, and annealing time/temperature.) A Co-High Fe-P alloy showed a TWI of 11.0, and a Fe-Low Co-P sample had a TWI of 6.8. The only sample that was comparable or better than hard chrome in wear resistance was a Co-P alloy with added boron carbide (B_4C): its TWI was 2.3. Some of the test results indicated that the texture of the crystals had an effect on their wear resistance.

The Air Force/HCAT team compared hard chrome plated steel panels with several nanocrystalline coated panels. A variety of electroplated and electroless coating formulas were tested, some of which featured occluded diamond particles.[10] Federal specification QQ-C-320B for electrodeposited chromium engineering plating (Class II) was used as a guide for evaluation (Klingenberg, et al. 2005).

A minimum coating thickness of 2 mils (0.002 in.) – the thickness that the specification dictates for hard chrome -- was required in order for samples to be considered adequate. Only the electrodeposited Nano-Co with 2000 nm WC met this standard, but several others came close to it. The project team felt that fine-tuning the plating process was likely to improve the performance of the electroless nano-coatings in respect to this parameter.

All samples except the electroless Co-B passed the adhesion test (ASTM B571). There were some questions as to whether the re-use of the test panels (they had been coated, stripped and re-coated) affected the adhesion of the Co-B coating.

In the test for hardness, most of the nano coating did not achieve a hardness level comparable to hard chrome. The exceptions were the Co-P and Co-P/diamond coatings, which met or exceeded the hard chrome standard. This result is similar to that of the SERDP study; the inclusion of phosphorus in the coating makes it harder.

The nano-coatings that did not have occluded diamond particles failed the Taber wear resistance tests. Those that did have the diamond particles, however, performed better than the hard chrome sample.

Vapor Deposition Methods

Physical Vapor Deposition (PVD) is a method of building a thin film, atom by atom, on the surface of a substrate. The solid or liquid coating material is placed in a vacuum or low pressure plasma environment where it vaporizes and condenses back into the solid phase on the surface of the substrate. There are many variations of this process, some in a vacuum environment, with or without ion beam assist, and some in a low pressure plasma environment. Each is unique in the way that the coating material is generated and deposited, but all share the common vapor deposition process. A few of the PVD variations are described below.

Vacuum evaporation is the most basic of these processes. The source (coating) material is thermally vaporized in a vacuum, and follows a "line of sight" trajectory to the substrate where it condenses out as a solid film. Vacuum evaporation is widely used in diverse industries, for applications such as mirror coatings, barrier films on flexible packaging, as well as corrosion and wear resistant coatings.

The more advanced methods of vacuum evaporation use "ion assisted deposition" or ion plating to enhance the quality of the deposited film. Ion plating bombards the depositing film with energetic particles. The energetic particles may be the same material as the depositing film, or it may be a different inert (argon) or reactive (nitrogen) gas. In a vacuum environment where the ions originate from an ion gun, the process is termed "ion beam assisted deposition" (IBAD) (Mattox 1999). The US Department of Defense has done a considerable amount of development of these types of coatings for aerospace and defense applications.

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[10] Several nickel-alloy coatings also were tested; some of these performed better than the non-nickel alloys.

Sputtering is a non-thermal vaporization process where the surface atoms on the source material are physically ejected from the solid surface by the transfer of momentum from bombarding particles. Typically the particle is a gaseous ion accelerated from a low pressure plasma or an ion gun (Mattox 2001). Sputtering is widely used in the semiconductor and other industries for thin film metallization.

These processes can be used to apply many elements, alloys or compounds to the surface of a substrate. PVD coatings that are potential substitutes for hard chrome plating include:

- titanium nitride (TiN)
- titanium-aluminum nitride (TiAlN)
- zirconium nitride (ZrN)
- chromium nitride (CrN)
- chromium carbide (CrC)
- diamond-like carbon (DLC)
- silicon carbide (SiC)

In addition, multi-layer deposits (e.g., TiN / Ti / TiN) can provide improved corrosion resistance with a thinner overall coating (Navinsek, et al. 1999).

The quality of the substrate surface also directly effects the quality of the deposit and its corrosion resistance. An irregular surface, or one with many defects or contaminants will not produce a good, corrosion resistant finish. Similarly, the surface preparation and resulting cleanliness of the substrate surface also heavily influence the final finish quality.

Legg (1999) notes that PVD coatings are being tested by the Department of Defense for the inside of gun barrels. Table 6.4.2 G lists some of the advantages and disadvantages of the PVD process for replacing hard chrome on internal diameters.

Table 6.4.2 G: Advantages and Disadvantages of PVD for Internal Diameters

Advantages	Disadvantages
Very hard, wear resistant	Vacuum complexities
Smooth coating	Expensive
Good adhesion	Not suitable for rebuilds
	Through holes only
	Slow deposition rate
	Ion cleaning essential but difficult

Two European research teams (Hurkmans, et al. 1999; Hurkmans, et al. 2003) have investigated the use of PVD coatings as an alternative to electroplated hard chromium. Some of the coating materials include chromium nitride (CrN), diamond like carbon (DLC), carbide forming metals (Me-C:H), molybdenum disulfide (MoS_2) and titanium nitride (TiN). CrN has the advantage that it can be deposited in a layer up to 50 µm thick (for example, as a coating for piston rings), unlike some the other coatings which typically are quite thin.

Their assessment indicates that PVD coatings – including those that use a combination of materials with different characteristics (such as CrN and MoS_2) -- have potential for specific applications where a hard, corrosion resistant surface with low friction is required. Uses that they mention are automotive parts (e.g. high pressure fuel injection systems, turbo compressor shafts), punching and forming tools, and molds and dies.

CVD – Chemical Vapor Deposition

In chemical vapor deposition (CVD) reactant gases (typically diluted with inert gases) at room temperature enter a chamber and are heated or passed over a heated substrate. Gases contain the desired coating materials in vapor phase. As the reactants are adsorbed onto the surface of the substrate, decomposition and chemical reactions with the substrate forms the coating. Byproduct gases are then removed from the chamber.

Unlike PVD, CVD is not a line of sight process, so it is appropriate for complex geometries, such as blind holes. Similar to PVD, there are many process variations that enhance or modify the performance of CVD. Plasma enhanced CVD (PECVD) adds a plasma to the process which allows for a lower substrate surface temperature than CVD. Because the substrate doesn't need to be heated as much, it is applicable to a broader range of materials. Additional advantages include higher deposition rates and improved control of film properties.

An advantage of CVD is that it can deposit a uniform coating on complex shapes, can be used for a variety of coating materials, and a high deposition rate. Disadvantages include the high temperatures involved, which limits its use where substrates may deform under heat, the difficulty in accommodating large parts, and the many variables to be controlled in the process (Mattox 1999). Legg notes that the major application for CVD is thermal and barrier coatings (Legg 1999).

Trivalent Chromium Plating

Technical assessment of the CM-ECD Faradaic™ process was conducted with EPA funding by Faraday Technologies, the developer of the method. The results were sufficiently favorable for EPA to fund a second phase of the project involving implementation trials with businesses at different points in the supply chain: chemical vendors, equipment suppliers, fabricators, repair facilities, and original equipment manufacturers (NTTC, n.d.) The full report for that phase, which included tests by the United States Navy, has not been made public because it contains confidential business information.

The process developers note several additional technical advantages of trivalent chromium plating baths:

- They are not sensitive to current interruptions;
- Drag-in of chloride and sulfate from previous plating operations do not upset the catalyst balance;
- Cr(III) has better throwing power than Cr(VI).

They also assert that the charge modulation used in their process reduces the evolution of hydrogen during plating. This increases current efficiency, lowers the amount of energy required for plating, and reduces the risk of hydrogen embrittlement or hydrogen bubble inclusion in the plating. (Renz et al. 2003)In pilot stage testing, a variety of materials plated with the trivalent CM-ECD process were compared to traditional hexavalent chromium plating. Parameters that were measured included chromium thickness, plating efficiency, plating rate, hardness, and cost.

Using the Vickers hardness test (which is used to compare the hardness of metals, on a scale of 0 to 6000 kg/mm), trivalent and hexavalent chromium plated rods exhibited approximately equivalent results. In the first test, two Cr(III) treated rods had hardness values of 772 and 777, versus 772 for the Cr(VI) plated rod. In a second test where the plating variables were changed slightly, the two Cr(III) plated rods had values of 873 and 805, with the Cr(VI) rod at 825.

The trivalent process showed better results than the hexavalent chromium process in terms of plating rate and efficiency. The average plating rate for the CM-ECD process was 80 μm/h, as opposed to a rate of 135 μm/h for a hexavalent bath. Similarly, CM-ECD had a plating (current) efficiency of 24%, in comparison to a 30 % rate for the Cr(VI) process. (USEPA NCER, n.d.)

Financial Assessment

Thermal Sprays

Factors that must be considered when evaluating the switch from hard chrome plating to HVOF include the usual items in a direct comparison:

Processing Costs -- Power Costs, Fuel Costs

Consumable Costs -- Powders, fuel, equipment part repair/replacement

Labor Costs -- Processing/turn-around Time

Capital Costs -- Capital Equipment/depreciation; capital improvements such as soundproofing, equipment housing, etc.

Additional factors may be more difficult to quantify, but also are important:

Environmental compliance

One analysis shows that many cost/benefit analyses do not consider key environmental costs such as building/operating wastewater treatment plants, environmental compliance office costs or equipment depreciation (Legg 2005).

Health and Safety Compliance

The Surface Finishing Industry Council estimates that the costs for compliance with the OSHA PEL for hexavalent chromium of 5 μg/m^3 TWA will be extensive. The capital and annualized operating costs for existing hard chrome plating installations to comply with the PEL are estimated at several hundred thousand dollars. These costs include capital costs to install ventilation systems and operating costs for power, consumables, monitoring, testing, training, personal protective equipment, etc. (Richter, Hannapel 2005).

Improvements in product quality

HVOF coatings have shown improved product quality in many cases, which may reduce the amount of rework/replacement costs associated with these parts in the future. In one case, Luftansa Airlines has been able to increase the service life of hydraulic seals from ~1,000 flight cycles to >4,700 (Nuse, Falkowski 2000).

A detailed cost/benefit analysis (CBA) was conducted using the Environmental Cost Accounting Methodology (ECAM) at a landing gear overhaul facility that processes more than 1000 components per year. The results showed an annual cost avoidance of approximately $200,000 and a 15-year net present value (NPV) of approximately $1,800,000. The payback period on the $700K initial capital investment was 3-5 years (Anonymous 2004).

The table below shows cost comparison for a facility that processes 1,500 parts 4 in. in diameter and 36 in. long. This analysis was prepared by the Joint Service Pollution Prevention Team (Anonymous 2003).

Table 6.4.2 H: Cost Comparison of HVOF and Hard Chrome Plating

Factor	HVOF	Hard Chromium Electroplating
Capital and Installation	$250,000	$0
Operational Costs		
Powder/Plating	$60,000	$375,000
Gas	$21,600	$0
Labor	$45,000	$76,500
Rinsewater Treatment	$0	$500
Waste Disposal	$0	$1,000
Annual Total (without capital expense)	**$126,000**	**$453,000**

Weld Facing Methods

Legg (2004) estimates the cost of an electrospark alloying machine to be approximately $25,000. Because the process is most often used for small, localized repairs of parts, the cost of material is unlikely to be a major factor in selected this method. The machine is portable, so one unit can be used for on-site repairs throughout a facility.

It should be noted that in some cases the alternative to using this process would be to replace the part. Legg gives an example of a damaged compressor shaft with a value of $47,000 where ESA repair would be an alternative to replating or replacing the part.

Heat Treatments and Plasma Nitriding

Auf dem Brinke and Krug (Auf dem Brinke, T., Krug 2001) assert that their company's plasma nitriding plus oxidation process (IONITR OX) can result in production cost savings of 30-60% over hard chrome when used for automotive parts. They also state that the part-life of nitrided parts can be up to three times that of hard chrome plated parts.

Nanocrystalline Coatings

The SERDP study (McCrea, Marcoccia & Limoges 2003) compared the costs for hexavalent plating, conventional nickel plating, nanocrystalline cobalt, and nanocrystalline cobalt-3%phosphorus (Table 6.4.2 I). Only the plating cost and energy cost were included; environmental and production costs were not quantified.

Table 6.4.2 I: Cost Comparison of Hard Chromium Electroplating and Nanocrystalline Coating Processes (McCrea et al. 2003)

Plating Process	Nominal Plating Efficiency	Consumables	Relative Plating Cost (by weight)	Relative Power Cost (by weight)	Total Relative Process Cost
Chrome(VI)	25	Cr_2O_3	1.00	1.00	1.00
Nano Co	>90	Co	1.83	0.08	1.09
Nano Co-3%P	>90	Co, H_3PO_3	2.21	0.08	1.31

The cost of consumable materials for the hard chrome process was less than for the nanocrystalline processes. The amount of power needed for the chromium plating was much greater, however, partially balancing out the material costs. It should be noted that this study used a price for cobalt of $7/lb., and an energy price of $0.10 per kilowatt hour.

Vapor Deposition Methods

Physical vapor deposition (PVD) equipment has a high capital cost. One source (JSPPOH 2003) estimates the cost of installing a new PVD set-up at several hundred thousand dollars. The cost of operating PVD equipment is similar to electroplating, although waste-related costs are likely to be less.

Trivalent Chromium Plating

The CM-ECD Faradaic™ trivalent process has not yet been implemented at a commercial scale. Based on the pilot testing, costs associated with it should be equivalent or less than for hexavalent chromium plating. In 1999-2000, the cost for Cr(III) plating chemicals were about $5.33 per pound of chromium; Cr(VI) chemicals were around $4.61 per pound of chromium. Waste treatment, ventilation, and energy costs (as reported by one of Faraday Technologies' commercial partners) were less than those associated with hexavalent chromium plating.

Environmental Assessment

As noted earlier, a number of different materials may be used in most of these processes, depending on the nature of the end use. Consequently, an in-depth environmental and human exposure assessment for all the possible combinations of chemicals and processes is beyond the scope of this study. The following sections provide an overview of some the key issues for which there is published information.

Thermal Sprays

The pre-processing of parts for the application of HVOF coatings is fundamentally similar to that for hard chromium plating – the parts must be free of grease, oil, dirt and other contamination. Materials (such as solvents) used to clean the parts may have adverse environmental impacts.

Hard chrome plating results in two forms of hexavalent chromium waste: liquid wastes from rinsing and solution contamination, and air-borne hexavalent chromium emissions. Wastewater treatment and air emission scrubbing are generally used to mitigate these environmental exposures, but in both cases low amounts are allowed to be emitted to sewers and the atmosphere.

Inefficiencies in HVOF occur as overspray or bounce-back. Overspray occurs when the spray gun is not oriented directly at the part. Bounce-back occurs when the coating particles hit the surface of the part but do not adhere. It is estimated that ~35% of the material put into process does not become part of the coating. Overspray and bounce-back may be collected in ventilation/filter units and recycled for coating powders that have cost-effective metal contents. In some cases, the material may need to be disposed of as hazardous waste or solid waste, depending on the specific constituents.

The fuel and electrical power usage comparisons would need include several elements:

- Heating of chrome plating tanks
- Power used for solution agitation
- Electrical Current for the plating operation
- Energy usage for hydrogen embrittlement relief baking
- Power used for ventilation/scrubbing units (both coating methods)
- Air tempering of make-up lost to ventilation (both coating methods)

- Fuel use of HVOF equipment

The elimination of hard chrome plating solutions eliminates the risk of catastrophic tank failure with potential releases to the environment, or failure of wastewater treatment or air scrubbers, resulting in higher emissions of hexavalent chromium to the atmosphere.

Weld Facing Methods

There are unlikely to be significant environmental impacts from electrospark surface deposition (ESD). The technique is used for small areas, with small amounts of alloying filler metals being bonded to the part under repair. Waste products are minimal to none.

Heat Treatments and Plasma Nitriding

These processes may require cooling water. Some facilities (Anonymous 1996) extract the heat from the cooling water and use it in the facility heating system.

Nanocrystalline Coatings

The SERDP study (McCrea, et al. 2003) makes some general statements about environmental impact from the Co-P nanocrystalline process. It says that the waste stream volumes from the method are likely to be similar to those from hexavalent chromium plating. However, the materials used are not currently on EPA lists of hazardous chemicals, so the impacts from waste disposal should be less. The nanocrystalline process also is more efficient, and therefore uses less energy.

Vapor Deposition Methods

Chemical vapor deposition (CVD) can involve the use of precursor materials that are hazardous (*e.g.*, silane), and it also generates waste gases that must be collected. The chamber also needs periodic cleaning; fluorinated gases (greenhouse gases) may be used for this.

Trivalent Chromium Plating

Trivalent chromium baths produce much less hydroxide sludge than hexavalent chromium baths. This is due to the lesser concentration of chromium in the Cr(III) bath. The Cr(III) bath also does not need additives, so rinse water can be recycled without treatment (Renz et al. 2003).

Human Health Assessment

Thermal Sprays

For the most popular coating materials, tungsten carbide/cobalt, cobalt powder is the primary hazard. International Agency for Research on Cancer (IARC) classifies cobalt as a Group 2B material, possibly carcinogenic to humans. Hexavalent chromium is an IARC Group 1 material known to be carcinogenic to humans. Other HVOF coatings may contain metallic chromium, copper and other metals.

The OSHA PEL for Cobalt is 0.1 mg/m^3, versus 5 $\mu g/m^3$ for hexavalant chromium. The HVOF operation is typically carried out in an enclosure with particulate filtration; there should be no exposure of the operators to the coating material during spraying.

Exposure to powders may occur during handling of the powders to prepare them for spraying, during clean out of equipment, or spraying outside of an enclosure. Grinding of the coating will also create airborne particulates. Proper PPE should be worn to prevent exposure. One MSDS recommends supplied air respirators for these activities.

There is some question as the particle size distribution of the airborne coating. Particles less than 2.5 µm in diameter (PM 2.5) may be created. If this is the case, finer filtration may be required to prevent exposure to the coating materials (Legg, et al. 2001).

The American Welding Society has produced a safety and health fact sheet for thermal sprays (American Welding Society 1998). It notes that chlorinated hydrocarbon solvent vapor should not be present in areas where thermal spraying is being done, as dangerous phosgene gas can be produced if they are exposed to ultra-violet radiation. The ultra-violet and infra-red radiation that is involved with thermal spraying also has the potential to cause eye damage and skin burns.

Thermal spraying processes are very noisy, and generally are conducted in sound-proof booths. HVOF spraying can generate noise levels as high as 150 dBA (American Welding Society 1998).

Weld Facing Methods

Weld facing methods involve the use of welding equipment. Worker safety measures typically associated with welding (such as appropriate eye and respiratory protection) would be necessary. In addition, if the part being repaired contains stainless steel or a chromium coating, Cr(VI) fumes can be produced. Electrospark Deposition generally is used on a small scale, so risks are likely to be less than for traditional welding. Safety measures associated with the use of a laser are appropriate.

Heat Treatments and Plasma Nitriding

Very little has been published on human exposure concerns relative to these technologies. Plasma nitriding is considered safer than traditional nitriding because it does not use ammonia in the process.

Nanocrystalline Coatings

During the SERDP study (McCrea, et al. 2003) air emissions were sampled above the plating tanks for each of three electrolyte solutions: Co, Co-P, and Co-Fe-P. The samples were tested for cobalt, iron, chloride, sulphate and additives. The samples were taken about one inch above the plating solution surface, at a rate of 100mL/min, over a 5 hour period during plating. Table 6.4.2 J shows the results of the testing.

Table 6.4.2 J: Emissions Measurements for Co, Co-P and Co-Fe-P Baths

(McCrea et al. 2003)

Element/Compound	Toxicity Level[1] (mg/m³)	Bath #1 Cobalt (mg/m³)	Bath #2 Co-P (mg/m³)	Bath #3 Co-Fe-P (mg/m³)
Cobalt	0.05	0.0039	<0.0005	<0.0005
Iron	1.0	<0.0005	<0.0005	<0.0005
Chloride	N/A	0.216	0.043	0.053
Sulphate	N/A	0.258	0.014	0.29
Additive #1	N/A	N.A.B.	N.A.B.	N.A.B.
Additive #2	N/A	N.A.B.	N.A.B.	N.A.B.

[1] OSHA Time Weighted 8 Hr. Average N.A.B. = Not Above Background

Vapor Deposition Methods

Objects being coated using physical vapor deposition must be thoroughly clean and grease-free in order for the coating to adhere properly. Solvents used in the pre-cleaning of parts have the potential to be hazardous. Cleaning of the chamber to remove accumulated deposits sometimes is done by sand blasting, which can generate dust and particles. Chemical vapor deposition involves the use of several hazardous materials: carbon monoxide gas, hydrogen gas, hydrochloric acid and liquid chlorides (e.g. titanium chloride, vanadium chloride) (Midtgard, Jelnes 1991).

Trivalent Chromium Plating

Trivalent chromium plating has significantly fewer potential human health effects than hexavalent chromium plating. Cr(III) is not know to be carcinogenic, while the carcinogenic properties of hexavalent chromium are well-established. The TLV-TWA for trivalent compounds is 0.5 mg/m^3; for water soluble hexavalent compounds, it is 0.05 mg/m^3, and for insoluble compounds it is 0.01 mg/m^3 (American Conference of Governmental Industrial Hygienists (ACGIH) 2006).

Table 6.4.2 K: Summary Assessment of Alternatives to Hard Chromium Electroplating of Industrial Components

Factor		Cr(VI) Plating (Ref.)	Thermal Sprays	Weld Facing Methods	Heat Treatments & Plasma Nitriding	Nano-crystal-line Deposits	Vapor Deposition Methods	Functional Cr(III)
Technical and Performance Criteria	Wear Resistance	Very good	+	+	+	-/=	+ (CrN)	=/+
	Hardness	800VHN	+	+	=/+	-/=/+	+	=/+
	Impact Resistance	Poor	=	?	+	?	+	?
	Non-Line-of-Sight Plating	Yes	**No**	?	**Yes**	**Yes**	**Yes (CVD)** **No (PVD)**	**Yes**
	Hydrogen Embrittle-ment	Poor	+	?	+	+	+	?
	Corrosion Resistance	Moderate	+	**N/A**	+	+	**Varies**	=
	Smoothness	Requires grinding	=	=	?	+	+	=
	Fatigue Strength	Poor	+	=	?	?	?	?
	Deposition rate	Slow	+	?	?	+	+	?
Human Health Criteria	Carcinogenic	Yes	+	+	+	+	+	+
Environmental Criteria	Volume of waste generated	Significant	+	+	+	+	+	+

Comparison Key + Better = Similar - Worse ? Unknown

6.4.3 Passivation of Zinc Plated Parts and Zinc Galvanized Steel

Existing Process Overview

Passivation refers to a surface treatment that provides resistance to corrosion in which the protection is afforded by a film or thin coating that interacts with the underlying metal. Hexavalent chromium is a standard passivating chemical for zinc and zinc-alloy plated parts, and zinc galvanized steel. It slows the formation of white corrosion/white rust (zinc oxide) and subsequent oxidation of the underlying metal (typically steel).

In the process that uses hexavalent chromium, zinc plated parts are dipped into a tank containing a chromate salt such as sodium dichromate, along with other chemicals such as nitric acid, chromic acid and fluorides. The acidic solution reacts with the zinc plating to form a complex film that consists of zinc chromate and other chromate compounds in both the trivalent and hexavalent state. This is referred to as a "conversion coating" because the hexavalent chromium solution converts the surface to zinc chromate. The hexavalent chromium reacts with the metal, forming an inert trivalent chromium layer with "releasable" hexavalent chromium ions that inhibit corrosion (The Ohio State University 2005). The residual hexavalent chromium in the film will repassivate any areas on the surface that become compromised due to chemical or mechanical damage to the area – this property is referred to as "self-healing" (Wynn, Bishop 2002).

The conversion coating provides corrosion protection to the zinc plated parts. The color of chromated zinc varies according to the chemistry of the coating solution and the thickness of the coating. The thinner films are usually blue in color, with thicker coatings being yellow, and the thickest coatings being brown, olive or black (Eppensteiner, Jenkins 1999).

Table 6.4.3 A: Desirable Performance and Cost Characteristics of Hexavalent Chromium Passivates

(Wynn and Bishop 2005)

• Prevents Oxide Formation • Provides Color • Slows corrosion in prototypic tests (e.g. salt, spray) • Provides adhesion for organics (e.g. paint) • Helps prevent corrosion of painted surfaces (e.g. creep) • Conductive • Thin	• Flexible • Lubricious • Easily applied • Durable • Resilient (repairs itself) • Coats in recesses • Easy to strip • Inexpensive equipment • Single tank • Inexpensive chemistry

Description of Alternatives

Three alternatives were selected for study: molybdates, trivalent chromium compounds, and mineral tie-coat. A fourth alternative, the combination wet-dry-wet-dry process, was dropped from consideration because insufficient information on it was available.

Molybdates

Molybdate-based coatings inhibit corrosion by forming a protective oxide layer on metal. Solvent-based molybdate coatings most often contain zinc molybdate or zinc phosphomolybdate, while water-based molybdate coatings generally use calcium molybdate or calcium zinc molybdate (Simpson 1997). Sodium molybdate also may be used. A common brand name for molybdate corrosion inhibitors is Moly-White®. The molybdate-based chemistry can be added to various coating systems such as such as acrylic latex or alkyd paint, depending on the needs of the end user.

Trivalent Chromium Compounds

There are a number of types of trivalent chromium-based passivates, including trivalent blue, trivalent iridescent/green, low-temperature iridescent, and trivalent black. They vary in appearance, performance characteristics, thickness of the coating, the additional metal or metals that are used in the bath, and the temperature at which they are applied. Typically, the blue color is characteristic of a thinner film, and the iridescent and/or green color is a thicker layer.

The way in which the zinc plated or galvanized metal is treated here is similar to the process using hexavalent chromium Zaki (2002) describes the steps in a typical process, using "conventional plating lines": zinc or zinc alloy plate; rinse; activate with dilute acid; trivalent chrome passivate; optional drag out rinse; counter-current flow rinse; dry; seal and/or topcoat; and dry.

Sealers and topcoats are used to affect the color of the coated part, increase corrosion resistance, and improve lubricity and torque-tension properties. Sealers have a film thickness of 1-2 μm; topcoats are thicker, typically 4 μm or more (Bishop et al. 2003).

Mineral Tie-Coat

The mineral tie-coat process is a patented method of applying a thin mineral film on the surface of metal parts to inhibit corrosion and improve temperature resistance, flexibility, coating adhesion, and chemical resistance. It involves pretreating the material to be coated in order to clean and condition the surface, immersing it in a bath that contains a sodium silicate solution (which may contain various additives), and then electrodepositing the mineral coating with low voltage and current. The reaction between the coating and the metal surface forms a new protective surface. The process also is called cathodic mineralization, and is trade marked by Elisha Technologies as Elisha Mineral Coat (Elisha®EMC™). A topcoat or sealer may be used in conjunction with this process (Heimann 2001).

Technical Assessment

Key performance criteria for passivation of zinc include corrosion resistance, heat resistance, and appearance.

The test most often used for evaluating the corrosion resistance of passivation films is the neutral salt spray (or fog) testing, specified as ASTM B117. It involves subjecting the test material to a 5% neutral pH (6.5 to 7.2) sodium chloride solution for a specified length of time (depending on the performance requirements for the coating) at a controlled temperature. The test has some known limitations (for example, materials tend to corrode more quickly in actual marine conditions than under test conditions) (Baldwin and Smith 1999), but it is generally accepted as a way to compare different coatings (Wynn and Bishop 2005). Alternative methods for testing corrosion resistance include Electrochemical Impedance Spectroscopy (EIS), the Prohesion/QUV[11] test, humidity test, immersion test and the GM9540P Accelerated Corrosion Test developed by General Motors. In all cases, the coating is visually inspected for white rust formation, which indicates oxidation of the zinc surface, and red rust, which indicated oxidation of the steel substrate.

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[11] The test incorporates UV/condensation cycles with wet/dry salt-spray cycles.

Torque tension testing, which is used to evaluate repeatable clamp force, is done using a method employed by the automotive industry called USCAR-11. Torque tension is a key criterion for fasteners, such as bolts and screws (Donohue and Simpson 2003).

Much of the available information on testing of alternatives to hexavalent chromium for passivations has been conducted by scientists associated with the manufacturers of various chemical products. To the extent that this research has been published or presented at public conferences, it has been available for public review; however, much of it has not appeared in peer-reviewed journals. In the following sections it will be noted when the source of information is affiliated with a manufacturer or vendor.

Molybdates

There have been several studies by scientists in Europe, Asia and South America of the effectiveness of molybdate mixtures in preventing the corrosion of zinc and zinc galvanized steel. The consensus of these studies is that molybdates do protect against corrosion, but do not perform as well as hexavalent chromium passivations.

Magalhães et al. (2004) compared chromate treatment of electrogalvanized steel with a variety of sodium molybdate treatments. Variables included bath temperature, length of treatment, pH, type of acid used to adjust the bath pH, and additives. Using a long-term immersion test (in a Na_2SO_4 solution) the best of the molybdates (0.3 M molybdate acidified with H_3PO_4 to pH 3.0, at room temperature, 10 min treatment time) had a time to white rust of 21-22 d, compared to 27-28 d for the chromate control. Untreated samples corroded within 3-4 d (Magalhaes, et al. 2004).

A group of scientists in Portugal (Almeida et al. 1998) looked at the structure and performance of several alternatives to chromates: molybdates, tungstates, permanganates, and vanadates. Sodium molybdate outperformed the other chromate alternatives in a salt spray cabinet test, with its time to white rust (7 h), first red rust (75 h), and 10% red rust (85 h) being two to three times that of the other substances. However, the chromated comparison sample was superior in this test, with first red rust appearing at 340 h, and 10% red rust at 350 h. The molybdate did provide a better surface for paint adhesion than the chromate.

In a second phase of that study, the structure of the chromate and molybdate coatings was examined using scanning electron microscopy with energy X-ray dispersive spectrometry (SEM/EDS), X-ray diffraction (XRD) and X-ray photon spectroscopy (XPS) in order to investigate the possible reasons for the performance differences of the molybdate and the chromate coatings. The chromate conversion layer showed "…a fine and relatively regular structure, microrugous, with some pinholes and rich in chromium and zinc. Such a structure is … a result of a dehydration mechanism, which occurs during drying time, by volume retraction." In contrast, the molybdate layers "…revealed little zinc in the surface… showed a black-brown homogeneous color…and an amorphous and compact structure, more or less cracked, revealing a significant retraction after formation" (Almeida, et al. 1998).

The authors suggest that the cracks in the molybdate layer allow salt spray to penetrate to the substrate. In addition, the chromium ions in the chromate layer provide significant corrosion protection. The smoother surface of the molybdate layer is the likely reason for its better paint adhesion (Almeida, et al. 1998).

In a European study, two commercial products (Actirox 106 and Shieldex CP-7394, zinc phosphate modified by molybdate and calcium ion exchange silica, respectively) were compared to strontium chromate paint. When the two products were combined, they showed better corrosion protection performance than either individually, and “approached” the performance of strontium chromate (Zin, et al. 2003).

Tang (1994) examined the performance of a molybdate/phosphate process in passivating zinc-plated parts. They concluded that the process was superior to a hexavalent chromium-based process at low pH, similar in an outdoor exposure and prohesion (accelerated weathering) test, and not as good in a neutral salt-spray test (Tang, et al. 1994).

The manufacturers of Moly-White® make a variety of claims in their literature about the characteristics of their products, but provide only visual results of testing, not quantitative information. The products are white in color, and generally “heat stable at temperatures incurred for baking finishes.”

Trivalent Chromium Passivates

Trivalent chromium coatings differ in appearance from hexavalent chromium films. Thin trivalent coatings typically are blue, with thicker coatings being iridescent or greenish; traditional chromate coatings most often are yellow. For most applications, the issue of appearance (specifically, color) is a matter of user preference rather than of the performance of the passivate. In cases where a specific color is required, topcoats or sealers often can be used to get the desired effect.

The difference in performance between trivalent and hexavalent passivates is due to the lack of soluble hexavalent chromium compounds at the metal surface. In the presence of atmospheric humidity, the soluble hexavalent chromium will migrate to areas where the coating has been compromised, providing corrosion protection (Wyrostek and Wynn 2006; Zaki 2002, 492-501). Trivalent films are not self-healing, and require a sealer or topcoat to perform adequately.

In tests conducted by SurTec International, a purveyor of passivation systems, thin coats of (blue) trivalent chromium passivates on zinc did not perform as well as yellow hexavalent passivates in salt spray testing. In barrel plating, thick layer trivalent coatings (also called chromiting) were slightly worse or equal to hexavalent coatings; in rack plating the trivalent was slightly better or equal to hexavalent. Time to corrosion for zinc and zinc/cobalt was 300 h; for zinc/iron and zinc/nickel, time to corrosion ranged from 350 h to 450 h (Zaki 2002, 492-501). SurTec’s tests of heat resistance indicated that trivalent chromium passivations were superior to hexavalent coatings. The hexavalent coatings started to fail quickly at temperatures above 55° C, while the trivalent films remained crack-free and retained much of their corrosion resistance up to 200° C.

Upton (2001), affiliated with Macdermid, Inc., describes the results of salt fog testing on zinc and zinc-iron electroplated substrates. Test panels showed the trivalent passiavate to perform as well or better than the hexavalent. In barrel plating, however, the trivalent films were inferior to the hexavalent. Upton suggests that this is due to the lack of self-healing properties of the trivalent material; barrel plating is likely to result in some damage to the materials being treated (Upton 2001, 68-71).

In examining the effect of various sealers and topcoats (silicate-type, organic clear lacquer, and silane-based) on the corrosion resistance of trivalent passivates, Upton found that any of the sealers/topcoats improved resistance to salt fog. The improved performance was most noticeable in the barrel plated test material, where the sealer increased the corrosion resistance of the trivalent-treated items to a level similar or better than the hexavalent-treated materials. Similar findings about the efficacy of trivalent chromium passivates with a sealant were made by Bellezze, et al (2002): trivalent chromium films followed with a sealer are more corrosion resistant than unsealed hexavalent chromium films (Bellezze, Roventi, and Fratesi 2002/6/17, 221-230).

Thiery and Pommier (2004) of Coventya SAS, a French chemical manufacturer, reported on tests of trivalent blue, trivalent thick layer, and trivalent thick layer with added silica nanoparticles. They noted that the blue and thick layer passivates were not self-healing, and that the effectiveness of the electrolyte bath deteriorated over time. The addition of silica improved heat resistance (Thiery, Pommier 2004).

Mineral Tie-Coat

The manufacturer of the mineral tie-coat process, Elisha Technologies, has worked with the U.S. Department of Defense (DoD) and the automotive industry in refining and testing the EMC™ process. The process is most applicable to barrel coating applications of small to medium-sized parts, such as fasteners (Donohue, Simpson 2003).

While individuals associated with Elisha Technologies have published a number of articles comparing the performance of its process with chromate conversion coatings, they contain very little quantitative information on testing – they generally feature photographs of sample materials after testing rather than numerical comparisons. According to the manufacturer, Elisha EMC™ with a topcoat improved the corrosion resistance of zinc by three to six times over a chromate conversion coating with a topcoat. The tie coat also is more heat resistant than the hexavalent chromium, retaining its corrosion resistant properties up to 400° C. In addition, Elisha claims that treated parts can be topcoated several months after treatment (unlike chromate coatings), and that the mineral tie-coat is more flexible than chromate and less likely to delaminate in secondary operations.

In torque tension testing done under the USCAR-11 protocol, Elisha Technologies found that the samples treated with the mineral tie coat had lower values with less variability than samples with a yellow chromate coating (2.56 n/15.4 vs. 5.57 n/33.4). This means that the Elisha EMC™ treated fasteners had less surface friction and were more consistent than the hexavalent chromium samples (Donohue and Simpson 2003).

One of the EMC™ systems, Elisha® 7201B, is approved by General Motors as a sealer for zinc nickel plating. The General Motors specification that the process meets is the revised GM 4205.

In an independent study (Aramaki 2001) that examined the use of a sodium silicate solution in preventing corrosion (sodium silicate is one of the components of the mineral tie-coat process), SiO_5^{2-} was found to be highly effective. It exhibited inhibition efficiency of up to 90%. That study did not compare it to chromate passivations.

Financial Assessment

As noted by Dr. John Sinko, technical director at Wayne Pigment Corporation, "The contemporary selection/qualification paradigm for corrosion inhibitor pigments concerns toxicity, efficiency, and price" (Challener 2005). The cost of an alternative is measured not just in the price of treatment, but also in how well it performs over time. In addition, the monetary and societal costs of using toxic products and in complying with environmental and health standards are significant factors.

Hexavalent chromium-based products traditionally have been the least expensive and most effective corrosion inhibitor products. However, increased awareness and concern about the environmental and health effects of chromates has resulted in industry trying to phase out such products. European Union (EU) Directives restrict the use of hexavalent chromium in vehicles and electronic products sold in EU countries. Consequently, the difference in cost between hexavalent chromium and the alternatives is not a major factor considered by manufacturers that wish to compete in the EU.

In addition, the specifications for particular uses are likely to be more important in selecting an alternative rather than the cost differential between the alternatives. For example, in marine applications resistance to corrosion from salt spray is a critical factor that affects ship safety. In some cases only certain alternatives can be applied to parts of particular types, limiting the feasible choices. Because of the number of factors that come into play when selecting a passivation process for a particular use, it is difficult to make a direct cost comparison of the alternatives.

Tang (1994) noted that factors such as labor and capital investment account for about 65% of the cost of a passivation process, with the remainder being the actual materials, energy, and waste disposal/processing. Their analysis indicated that a molybdate-based process would be similar to a hexavalent chromium process in terms of labor and capital, more expensive for chemicals and energy, and less expensive for waste processing (Tang, et al. 1994, 20-22).

A manufacturer of a molybdate, Moly-White®, has provided some cost information for that product (Simpson pers. com. 2006). The list price of the material, which is added to paint or other coatings, ranges from about $1.50 -$4.00/lb. At a use level of around 0.5 lb/gal, the Moly-White additive increases the cost of the paint by $0.75 -$2.00/gal. With a typical coverage of about 250 ft^2/gal, the molybdate cost would be around $0.003 -$0.008/ft^2.

Environmental Assessment

Molybdates

As mentioned earlier, molybdates are added to a variety of coating formulations for application. Many of the environmental impacts from use of this alternative will be due to the characteristics of the coating, rather than the molybdate additive. If a solvent-based paint is used as a vehicle for the molybdate, any adverse impacts of that formulation also would need to be taken into consideration.

Molybdates that are used most often in corrosion inhibitors include sodium molybdate, zinc molybdate, and calcium molybdate. Some molybdate-based products may also include zinc oxide, calcium carbonate, and/or zinc phosphate. Zinc oxide and zinc phosphate are classified under ESIS as R50/53: very toxic to aquatic organisms and may cause long term adverse effects in aquatic environment.

Molybdenum sewer discharge is regulated in some sewer districts, as it is a regulated contaminant in wastewater treatment sludge. If the molybdenum level is too high in the sludge, it cannot be used for composting, as it becomes harmful to plants and animals (New England Biosolids Case Study #3, 2001)

Trivalent Chromium Passivates

Like the process for trivalent electroplating, the trivalent chromium passivation process requires a set of several chemicals. For example, the SurTec 680 chromiting process uses three complementary formulations:

- Chromium nitrate, disodium oxalate, and cobalt-(II)-nitrate;
- Phosphoric acid ester, isododecan, mixture of C-12 isoparafine
- Oxalic acid and salts of oxalic acid.

All of these mixtures have the potential to contaminate ground water or surface water if spilled or discharged. The MSDSs warn that even small quantities pose a danger to drinking water, and that the product must not be discharged to a sewer system.

Mineral Tie-Coat

Sodium silicate solution, the main component of the mineral tie-coat process, is harmful to aquatic life (when undiluted) due to its high pH (11.3 +/-). It is not persistent and does not bioaccululate. If it is diluted it depolymerizes into dissolved silica. It is not classified as a hazardous waste (MSDS for N® sodium silicate solution).

Human Health Assessment for All Alternatives

Molybdates

Molybdates are added to a variety of coating formulations for application. Many of the human exposure concerns from use of this alternative will be due to the characteristics of the coating, rather than the molybdate additive. If a solvent-based paint is used as a vehicle for the molybdate, any adverse impacts of that formulation also would need to be taken into consideration.

Molybdenum compounds have not been identified as having significant human health concerns. However, zinc oxide, which may be a component in molybdate-based formulations, produces toxic fumes when heated to decomposition. It is associated with metal fume fever – a "flu-like illness" that results from inhaling zinc oxide fumes, generally during welding. (American Welding Society 2002) The PEL for zinc oxide is 5 mg/m^3 for fume and respirable dust, and 15 mg/m^3 for total dust. The IDLH level is 500 mg/m^3 (NIOSH Pocket Guide). Another component of some of the products, calcium carbonate, can result in eye and respiratory system irritation.

Table 6.4.3 B: Summary of MSDS Recommendations for Moly-White® Products

Products	Components	Worker Safety Recommendations
Moly-White 101	Zinc Molybdate Zinc Oxide	Safety glasses should be used. Use sufficient general area ventilation. NIOSH-MSHA approved dust/mist/fume respirator is required when dust levels of 10 mg/M^3 are exceeded or fume is produced. If material is heated above 700 degrees C, full protective equipment, including self contained breathing apparatus, should be used.
Moly-White ZNP	Zinc Molybdate Zinc Oxide Zinc Phosphate	
Moly-White MZAP	Calcium Molybdate Calcium Carbonate	
Moly-White 212	Zinc Oxide Zinc Phosphate Calcium Molybdate Calcium Carbonate Zinc Oxide	

Trivalent Chromium Passivates

Several of the chemicals used in trivalent chromium passivates are hazardous to human health. Chromium nitrate is a skin, eye and respiratory system irritant, and over the long-term can damage the kidneys and cause a skin allergy. (New Jersey Department of Health and Senior Services 2001) The PEL for chromium nitrate and all other chromium(III) compounds is 0.5 mg/m^3 , compared to the hexavalent chromium PEL of 5 μg/m^3 (NIOSH Pocket Guide). There is no evidence that chromium(III) chemicals are carcinogenic. Disodium oxalate and oxalic acid are corrosive and can damage the kidneys, mucous membranes, and central nervous system. The REL for oxalic acid is 1mg/m^3 (NIOSH Pocket Guide). Isododecan is flammable, irritates the skin and respiratory system, can cause pulmonary edema if aspirated, and depresses the central nervous system if the fumes are inhaled.

Mineral Tie-Coat

Sodium silicate solution, which is a component of the mineral tie-coat process, is alkaline and corrosive. It irritates the respiratory tract if the mist is inhaled and the eyes and skin if there is contact, and can burn the intestinal tract if ingested. When it dries it forms a glass film that can cut the skin. The MSDS for sodium silicate solution recommends that workers use a NIOSH-approved dust and spray mist respirator where spray mist occurs, and body-protecting protective clothing, gloves, and chemical goggles. It has not been shown to be mutagenic or carcinogenic. Sodium silicate is component of many steel cleaning solutions currently used in metal processing shops, so the incremental increase in silica exposure is likely to be very low.

Table 6.4.3 C: Summary of Alternatives for Passivation of Zinc and Zinc Galvanized Steel

Assessment Criteria		Cr(VI) (Reference)	Comparison Relative to Cr(VI)		
			Molybdates[12]	Trivalent Chromium	Mineral Tie-Coat
Technical/ Performance Criteria	Corrosion Resistance (time to white rust)	Very Good	-	-/=/+[13]	+ (with topcoat)[14]
	Heat Resistance	Poor	+	+	+
	Torque/Tension	Good	?	?	+
Environmental Criteria	Toxic to Aquatic Species	Varies – toxic to some species	Varies – chemicals used in some formulations are toxic to aquatic life	+	+
	Drinking water MCL	~1 ppm	**Varies**	=	+
	Carcinogenicity	EPA Group A IARC Group 1	+	+	+
Human Health Criteria	Occupational Exposure: PEL (8-hour TWA)	~mg/m^3	+	+	+
	Skin Irritant/Sensitizer	Yes	+/=	-/=	=

Comparison Key + Better = Similar - Worse ? Unknown

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[12] This assessment is for the molybdate only, not the coating that it is applied in.

[13] Performance of trivalent chromium depended on thickness of coating, plating method, addtives and whether a topcoat was used.

[14] Not suitable for barrel plating

6.5 Summary and Conclusions

There are several oxidation (or valence) states of chromium, each with its own chemical characteristics. The most common forms are trivalent chromium -- Cr(III) -- and hexavalent chromium -- Cr(VI). Trivalent chromium compounds can be either naturally occurring or a by-product of industry, while elemental chromium and the hexavalent compounds nearly always result from industrial activity. Trivalent chromium is the more stable form, and trivalent chromium compounds generally have low solubility in water and low reactivity. Most hexavalent chromium compounds are soluble in water, and are strong oxidizers.

Chromium can provide manufactured products with hardness, shininess, durability, color, corrosion resistance, heat resistance, wear resistance, and decay resistance. For example, decorative chrome plating produces a hard, shiny, durable surface coating on items such as school furniture. Jet turbine engine parts rely on hard chrome plating to resist corrosion, high temperatures, and wear. Chromium-based pigments are valued for their vivid colors and resistance to weathering; they are commonly used in traffic paints for those reasons. Anti-corrosion coatings containing chromium compounds are widely used in marine applications, where their resistance to salt spray and their "self-healing" properties are important. In addition, the biocidal properties of chromium compounds are key to their use in wood preservatives.

Hexavalent and trivalent chromium compounds differ in their health and environmental effects, with the hexavalent form being far more dangerous. Short-term effects of hexavalent chromium exposure (for example, from chromic acid droplets or chromate dust) include eye irritation and respiratory irritation, sneezing, or sensitization; in high concentrations, acute inhalation can cause ulcers in the nasal septum. In sensitive individuals, inhalation of hexavalent chromium can cause an asthma attack. Long-term inhalation of hexavalent chromium is known to cause lung cancer. It also can result in damage to the nasal mucous membrane, perforation of the nasal septum, and asthma.

Inhalation (of fumes or mist) and dermal contact with hexavalent chromium compounds used by workers in industrial operations are the primary exposure routes. If soil is contaminated with hexavalent chromium, it is possible that it will be touched and/or swallowed (for example, by children playing in a contaminated area). In areas where there has been industrial pollution of groundwater, there is the potential for ingesting hexavalent chromium-contaminated drinking water from groundwater wells.

Workers, rather than consumers, have the highest risk of adverse health effects from hexavalent chromium exposure. The industries with the greatest risk of occupational exposure to hexavalent chromium are chrome electroplating, stainless steel welding, metal coating and painting, printing, textiles, leather tanning, wood preservation, and cement or masonry work. Inhalation risk may be from fumes (welding), mists or droplets (electroplating, spray painting.) A hexavalent chromium electroplating bath produces severe off gassing, resulting in the creation of a large amount of chromic acid mist at the surface of the plating tank. Dermal exposure can result from contact with fluids, such as those used in electroplating, or materials containing hexavalent chromium, such as wet cement (OSHA, 2006).

For many years the OSHA PEL for hexavalent chromium compounds in workplace air was 52 $\mu g/m^3$ (ceiling concentration). That level was challenged by a variety of groups as being too high to adequately protect worker health, and OSHA proposed a rule (under a court-ordered deadline) that would lower the PEL to 1 $\mu g/m^3$ (time-weighted average). The final rule, issued on February 28, 2006, set the PEL at 5 $\mu g/m^3$ (time-weighted average). The NIOSH REL is 1 $\mu g/m^3$. As a general rule, OSHA and NIOSH strongly recommend that all exposures to confirmed human carcinogens, such as hexavalent chromium, be reduced to the lowest possible level.

Cost may not be an important factor in evaluating hexavalent chromium alternatives since its severe toxicity is driving many manufacturers to adopt alternatives. For example, it is likely that the new PEL will be very difficult for many manufacturers to meet using traditional engineering controls such as local exhaust ventilation. In addition, EU directives are driving manufacturers to find hexavalent chromium-free alternatives.

Based on a review of stakeholder input, published research on environmental, health and safety issues, and the availability of alternatives, three general categories of use were selected as priorities for this study: decorative chrome electroplating, hard/functional chrome electroplating, and passivation of zinc. Decorative and hard chrome plating were selected because of the severity of the hazard that chromium poses to workers in the electroplating industry. Passivation of zinc was selected as being representative of chromate conversion coatings, which was of concern to stakeholders both because of the potential for worker exposure and because chrome remains in the hexavalent state in the finished product.

Decorative Chromium Electroplating

Only two alternatives to decorative plating with hexavalent chromium were identified: trivalent chromium electroplating and low temperature arc vapor deposition (LTAVD®) of trivalent chromium. The trivalent electroplating technique has many technical and process advantages over the hexavalent method ("hexchrome"), but traditionally has produced a plate with a pewter-like color rather than the shiny blue-white plate from hexavalent plating. Recent developments in the trivalent plating process, however, now make it possible to produce a trivalent plate with a "near hexchrome" appearance. LTAVD® is a proprietary vapor deposition process that can produce a plated surface that is similar or better than hexchrome in hardness and corrosion and wear resistance and is very similar in color. It requires completely new equipment and so is not a "drop-in" replacement for hexchrome.

The environmental and human health impacts of the two alternatives are much improved compared to hexavalent chromium electroplating.

Trivalent plating chemicals are more expensive than hexavalent plating chemicals, although that is likely to change as trivalent systems increase in popularity. The cost of chemicals, however, is offset by the greater efficiency of the trivalent process and greatly reduced disposal costs. Cost information for this process has not been published, although the process is being used by several major manufacturers of consumer hardware, indicating that it is commercially viable. A major operating cost would be energy, but waste treatment costs are likely to be minimal.

Hard Chromium Electroplating

Six categories of process alternatives to "hard chrome" plating were selected for study: thermal sprays, weld facing, heat treatment, nanocrystalline coatings, vapor deposition, and trivalent chromium plating. Surface coatings of various materials, typically other metals, alloys, and metal carbides or nitrides, can be applied using these processes. Coatings that may be used to replace hard chrome include those based on titanium, tungsten, cobalt, aluminum and silicon. All of the alternatives have the potential to offer equivalent or better performance compared to hard chrome plating, although several have some limitations in their application. For example, thermal sprays are a line-of-sight technique, so cannot be used on complex geometries, and weld facing is limited to the rebuilding of worn parts. There should be at least one alternative that can meet the technical requirements of each different hard chrome plating application.

Many of the alternatives require a significant capital investment, ranging as high as several hundred thousand dollars in the case of a vapor deposition system. On the other hand, the manufacturers of these systems claim reduced operating costs. For example, a detailed cost-benefit analysis performed for the application of the high velocity oxy-fuel (HVOF) system at a landing gear overhaul facility showed an annual cost avoidance of approximately $200,000 and a 15-year net present value (NPV) of approximately $1,800,000. The payback period on the $700K initial capital investment was 3-5 years.

As is the case with decorative chrome plating, all of the hard chrome plating alternatives offer significant environmental and human health improvements over hexavalent chromium electroplating.

Passivation of Zinc

Three alternatives to the passivation of zinc plated parts and zinc galvanized steel were assessed: molybdate-based coatings, trivalent chromium-based passivates, and the mineral tie-coat process. Several technical evaluations have concluded that molybdates do protect against corrosion, but do not perform as well as hexavalent chromium passivations. On the other hand, the molybdates offer better heat resistance than hexavalent chromium. Trivalent chromium coatings differ in appearance from hexavalent chromium films. Thin trivalent coatings typically are blue, with thicker coatings being iridescent or greenish; traditional chromate coatings most often are yellow. For most applications, the issue of appearance (specifically, color) is a matter of user preference rather than of the performance of the passivate, and topcoats or sealers often can be used to get the desired effect. Trivalent chromium compounds are not “self-healing” like hexavalent chromium, and require a sealer/topcoat in order to offer the same level of corrosion resistance. The manufacturer of the mineral tie coat process claims that it is equal to or better than hex chrome in corrosion resistance (with topcoat), heat resistance, and torque/tension performance.

Little cost information is available for these alternatives. One analysis indicated that a molybdate-based process would be similar to a hexavalent chromium process in terms of labor and capital, more expensive for chemicals and energy, and less expensive for waste processing.

All of the alternatives should offer significant improvements over hexavalent chromium in terms of their environmental and human health impact, although chemicals used in some molybdate formulations are toxic to aquatic life.

References

1. Agency for Toxic Substances and Disease Registry (ATSDR) 2000, *Toxicological Profile for Chromium*, U.S. Dept. of Health and Human Services, Atlanta, Georgia.

2. Almeida, E., Fedrizzi, L. & Diamantinio, T.C. 1998, “Oxidising alternative species to chromium VI in zinc-galvanised steel surface treatment. part 2--an electrochemical study” *Surface and Coatings Technology* vol. 105, nos. 1-2, pp. 97-101.

3. Almeida, E., Diamantino, T.C., Figueiredo, M.O. & Sa, C. 1998, "Oxidising alternative species to chromium VI in zinc galvanised steel surface treatment. part 1--A morphological and chemical study" *Surface and Coatings Technology* vol.106 no. 1 pp. 8-17.

4. American Conference of Governmental Industrial Hygienists (ACGIH) 2006, *TLVs and BEIs Based on the Documentation of the Threshold Limit Values for Chemical Substances and Physical Agents & Biological Exposure Indices*.

5. American Welding Society 1998, *Thermal Spraying Safety*. Safety and Health Fact Sheet no. 20.

6. American Welding Society 2002, *Metal Fume Fever*. Safety and Health Fact Sheet no. 25.

7. Aramaki, K. 2001, "The inhibition effects of chromate-free, anion inhibitors on corrosion of zinc in aerated 0.5 M NaCl" *Corrosion Science* vol. 43 no. 3, pp. 591-604.

8. Arburg GmbH+Co 1996*,* "Plasma Nitriding: Material Upgrading and Environmental Protection" *Arburg Today*, Issue 2, March 1996.

9. Auf dem Brinke, T. & Krug, T.G. 2001, "Plasma-Assisted Nitriding Offers Production Flexibility", *Industrial Heating*. May 2001.

10. Baldwin, K. R. & Smith, C. J. E. 1999, "Accelerated corrosion tests for aerospace materials: Current limitations and future trends" *Aircraft Engineering and Aerospace Technology* vol. 71 no. 3, pp. 239-244.

11. Barceloux, G.D. 1999, "Chromium", *Journal of Toxicology: Clinical Toxicology; Journal of Toxicology: Clinical Toxicology,* vol. 37, no. 2, pp. 173.

12. Barnhart, J. 1997, "Occurrences, uses, and properties of chromium", *Regulatory toxicology and pharmacology: RTP,* vol. 26, no. 1 Pt 2, pp. S3-7.

13. Bellezze, T., Roventi, G. & Fratesi, R. 2002, "Electrochemical study on the corrosion resistance of Cr III-based conversion layers on zinc coatings" *Surface and Coatings Technology* vol. 155 nos. 2-3, pp. 221-230.

14. Bishop, C.V., Vogel, R., Kochilla, J.R. & Wennefors, C. 2003, "Corrosion resistant films from trivalent chrome based solutions applied to electrodeposited zinc and zinc alloys" Paper presented at *Heat Treating: Manuscripts from the 22nd Heat Treating Society Conference, 2003*.

15. California Department of Health Services, Hazard Evaluation System and Information Service*, Hexavalent Chromium*. Available: www.dhs.ca.gov/ohb/HESIS/cr6.htm [2005, 9/26].

16. Challener, C. 2005, "Corrosion prevention in paints and coatings (market update)" *JCT CoatingsTech*. October 2005.

17. Clifford, D. & Chau, J.M. 1988, *The Fate of Chromium (III) in Chlorinated Water*, United States Environmental Protection Agency (USEPA).

18. Cohen, M.D. & Costa, M. 2000, "Chromium" in *Environmental toxicants: human exposures and their health effects*, ed. M. Lippmann, Second edn, Wiley-Interscience, New York, pp. 173-191.

19. Devereaux, J. & Stricklin, D. 2004, *HVOF on Navy Landing Gear Forges Ahead*.

20. Donohue, D. P. & Simpson, G.T. 2003, "Surface mineralization as an alternative to cadmium and chromate treatment" Paper presented at *U.S. Navy RUST 2003 Corrosion Technology Exchange*.

21. Drew, D., Izuchukwu, S. & Tucker, P. 2000, *Case Studies in Environmental Medicine: Chromium Toxicity*, Agency for Toxic Substances and Disease Registry (ATSDR).

22. Eisler, R. 1986, *Chromium hazards to fish, wildlife, and invertebrates: a synoptic review*, United States Fish and Wildlife Service, Laurel, MD.

23. Environmental Security Technology Certification Program (ESTCP) 2004, *Cost and Performance Report-Replacement of Chromium Electroplating on Landing Gear Components Using HVOF Thermal Spray Coatings.* United States Department of Defense. Report PP-9608.

24. Eppensteiner, F. W. & Jenkins, M. R. 1999. "Chromate conversion coatings" *Metal Finishing* vol. 97 no. 1, pp. 494-496, 498, 506.

25. Fedrizzi, L., Rossi, S., Cristel, R. & Bonora, P.L. 2004, *Corrosion and wear behaviour of HVOF cermet coatings used to replace hard chromium.*

26. Hart, K.W.D., Harper, D.H., Gill, M.J. & Heath, G.R. *Case Studies in Wear Resistance Using HVOF, PTAW and Spray Fusion Surfacing*

27. Heimann, Nancy. 2001, *A cathodically-deposited mineral coating for replacement of Cr (VI) and Cr (III) treatments of zinc.*

28. Hermanek, F.J. 2001, *Thermal Spray Terminology and Company Origins*, ASM International, Materials Park, OH.

29. Hurkmans, A., Lewis, D.B. & Munz, W.D. 2003, "Magnetron Sputtered CrNx Coatings as an Alternative to Electroplated Hard Chromium", *Surface Engineering,* vol. 19, no. 3.

30. Hurkmans, T., Kubinski, J., Trinh, T., Fleischer, W. & Van der Kolk, G.J. 1999, "Perspective for Replacement of Hard Chrome by PVD", .

31. Independent Environmental Technical Evaluation Group (IETEG) 2005, *Chromium (VI) Handbook,* CRC Press, Boca Raton, Florida.

32. International Agency for Research on Cancer (IARC) 1990, *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans: Chromium, Nickel and Welding*, World Health Organization, Lyon, France.

33. Joint Services Pollution Prevention Team 2003*, Joint Service Pollution Prevention Handbook*.

34. Kirsten, A., Oechsle, M. & Moll, R. 2005, *An In Perspective View of HVOF Sprayed, Carbide-Containing Materials as an Alternative to Hard Chromium Plating.*, Sulzer Metco.

35. Klingenberg, M.L., Broonam, E.W. & Naguy, T.A. 2005, *Nano-particle Composite Plating as an Alternative to Hard Chromium and Nickel Coatings*, Concurrent Technologies Corporation, Johnstown, PA.

36. Kotas, J. & Stasicka, Z. 2000, "Chromium occurrence in the environment and methods of its speciation", *Environmental Pollution,* vol. 107, pp. 263-283.

37. Legg, K. 2000, *HVOF in Repair and Overhaul: Higher Reliability at Lower Cost?*.

38. Legg, K. 1999, *Replacing Chrome on Internal Diameters.*

39. Legg, K. 2005, "Evaluating the Capabilities, Costs, Risks and Benefits of Green Products,", *15th Workshop on Alternati9ves to Toxic Materials in Industrial Processes.*

40. Legg, K. & Sartwell, B. *Hard Chromium Alternatives Team Update: Improving Performance While Reducing Cost.*

41. Legg, K., Sartwell, B. & Legoux, J. 2001, *Safety, Health and Hazardous Waste Issues of Overspray in Thermal Spray*, Strategic Environmental Research and Development Program & Hard Chrome Alternatives Team.

42. Legg, K. & Sauer, J. 2005, *Clean Dry-Coating Technology for ID Chrome Replacement.*

43. Legg, K. & Sauer, J. 2000, *Use of Thermal Spray as an Aerospace Chrome Plating Alternative.*

44. Magalhaes, A. A. O., Margarit, I. C. P. & Mattos, O. R. 2004, "Molybdate conversion coatings on zinc surfaces" *Journal of Electroanalytical Chemistry* vol. 572 no. 2, pp. 433-440.

45. Mattox, D.M. 2001, "Physical Vapor Deposition Processes" *Products Finishing*. September 2001.

46. Mattox, D.M. 1999, "Vacuum Deposition Processes" *Products Finishing*. June 1999.

47. McCrea, J.L., Marcoccia, M. & Limoges, D. 2003, *Electroformed Nanocrystalline Coatings: An Advanced Alternative to Hard Chromium Electroplating.*

48. Midtgard, U. & Jelnes, J.E. 1991, "Toxicology and Occupational Hazards of New Materials and Processes in Metal Surface Treatment, Power Metallurgy, Technical Ceramics and Fiber-Reinforced Plastics", *Scandinavian Journal of Work and Environmental Health,* vol. 17, pp. 369-79.

49. Nascimento, M.P., Souza, R.C., Miguel, I.M., Pigatin, W.L. & Voorwald, H.J.C. 2001, *Effects of tungsten carbide thermal spray coating by HP/HVOF and hard chromium electroplating on AISI 4340 high strength steel.*, Elsevier.

50. National Defense Center for Environmental Excellence (NDCEE) 1995, *Regulatory Analysis of the Chromium Electroplating Industry and Technical Alternatives to Hexavalent Chromium Electroplating.*

51. Navinsek, B., Panjan, P. & Milosev, I. 1999, "PVD coatings as an environmentally clean alternative to electroplating and electroless processes", *Surface and Coatings Technology,* vol. 116-119, pp. 476-487.

52. New Jersey Department of Health and Senior Services 2001, *Hazardous substance fact sheet: Chromium nitrate.*

53. Nuse, J.D. & Falkowski, J.A. 2000, *Surface Finishing of Tungsten Carbide Cobalt Coatings Applied by HVOF for Chrome Replacement Applications.*

54. Ohio State University 2005, *Critical factors for the transition from chromate to chromate-free corrosion protection.* The Strategic Environmental Research and Development Program, U.S. Department of Defense, PP-1119.

55. Page, B.J. & Loar, G.W. 1991, "Chromium Compounds" in *Kirk-Othmer Encyclopedia of Chemical Technology*, eds. J.I. Kroschwitz & M. Howe-Grant, Fourth edn, John Wiley & Sons, New York, pp. 263-311.

56. Pellerin, C. & Booker, M.S. 2000, "Reflections on hexavalent chromium", *Environmental Health Perspectives,* vol. 108, no. 9, pp. A402.

57. Renz, R.P., Fortman, J.J., Taylor, E.J. & Inman, M.E. 2003, *Electrically Mediated Process for Functional Trivalent Chromium*, June,2003 edn, Faraday Technology Inc, Ohio.

58. Richter, C.M. & Hannapel, J.S. 2005, *Post-Hearing Comments of the Surface Finishing Industry Council.*

59. Sartwell, B.D., Legg, K. & Bodger, B. 1999, *HVOF Thermal Spray Coatings as an Alternative to Hard Chrome Plating on Military and Commercial Aircraft*, Naval Research Laboratory.

60. Sartwell, B., Kestler, R., Keith, L., Assink, W., Nardi, A. & Schell, J. 2003, *Validation of HVOF WC/Co, WC/CoCr and Tribaloy 800 Thermal Spray Coatings as a Replacement for Hard Chrome Plating on C-2/E-2/P-3 and C-130 Propeller Hub System Components*, Naval Research Laboratory.

61. Simpson, C. 1997, "Improved corrosion- inhibiting pigments" *Chemtech.*

62. Singh, J., Schriempf, J.T. & Wolfe, D.E. n.d., *Electron Beam Physical Vapor Deposition Technology: Present and Future Applications*, Pennsylvania State University.

63. Stokes, J. 2003, *The Theory and Application of the HVOF (High Velocity Oxy-Fuel) Thermal Spray Process.*

64. Tang, P.T., Bech-Nielsen, G. & Moller, P. 1994. "Molybdate-based alternatives to chromating as a passivation treatment for zinc" *Plating and Surface Finishing.* November 1994.

65. Thiery, L. & Pommier, N. 2004, *Hexavalent chromium-free passivation treatments in the automotive industry.*

66. Tjong, S.C. & Chen, H. 2004, "Nanocrystalline Materials and Coatings", *Materials Science and Engineering R,* vol. 45, pp. 1-88.

67. United States Army Corps of Engineers 1999, *Thermal Spray Fundamentals.*

68. United States Department of Labor, Occupational Safety and Health Administration (OSHA) 2006, *Safety and Health Topics: Hexavalent Chromium* [2006, 03/02].

69. Upton, P. 2001, "The effect of sealers on increase of corrosion resistance of chromate-free passivates on zinc & zinc alloys" *Plating & Surface Finishing.* February 2001.

70. Wynn, P.C. & Bishop, C.V. 2005, "Replacing hexavalent chromium in passivations on zinc plated parts" *PF Online.*, http://www.pfonline.com/articles/020102.html.

71. Wyrostek, M. & Wynn, P. 2006, Driving away from hex chrome coatings. *Metal Finishing.* 03 April 2006.

72. Zaki, N. 2002, "Trivalent chrome conversion coating for zinc and zinc alloys" *Metal Finishing.* 1 January 2002.

73. Zin, I. M., Lyon, S. B. & Pokhmurskii, V. I. 2003, "Corrosion control of galvanized steel using a phosphate/calcium ion inhibitor mixture" *Corrosion Science* vol. 45 no. 4, pp. 777-788.