

Selection & Applications of Inorganic Finishes: Chromate Coatings

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In general, chromate films are applied by immersing parts in an acidic solution containing dichromate or chromic acid and an activator (usually, nitrate, sulfate, chloride, formate or fluoride). An oxidation-reduction reaction occurs on the metal surface with formation of substrate metal ions and trivalent chromium ions.

An accompanying increase in the pH of the solution immediately adjacent to the metal surface results in the precipitation of a gelatinous film comprised largely of chromic hydroxide (and substrate metal compounds) and in which soluble chromates (hexavalent chromium) are incorporated. This freshly formed coating, after rinsing and drying, is rather soft and vulnerable to damage but soon hardens. If practical, it is sometimes advisable to permit aging up to 24 hr before handling.

The water-soluble chromates are effective corrosion inhibitors for most metals. Corrosion inhibition is a very important factor in the ability for chromate coatings to prevent corrosion of the underlying metal when exposed to many natural environments. However, the coating itself also contributes some protection by presenting a barrier between the metal and the environment.

Chromate coatings exhibit a phenomenon called "self healing" - the ability to protect metal at areas where some of the coating has been removed as the result of a scratch or an abrasion. The inhibitive soluble chromates are leached from the chromate film to protect adjacent bare metal areas when a moisture film is present during environmental exposure.

Zinc and Cadmium

Chromate conversion coatings on zinc- or cadmium-plated steel, zinc die castings or galvanized steel are often used as a final finish to retard the formation of white or gray products from corrosion of the zinc or cadmium during environmental exposure. The chromate coating effectively prevents surface discoloration from fingerprint-perspiration as the result of handling. From this consideration alone, application of a chromate coating is usually advisable.

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Table 1
Salt-spray corrosion resistance of zinc plate

Chromate	Hrs to White Corrosion Product
Single-dip bright	8 to 24
Leach-type clear	24 to 48
Iridescent yellow	96
Bronze	96 to 144
Olive drab	120 to 172

Rarely is it desirable to leave a zinc- or cadmium-plated surface bare, especially considering that the cost of applying a chromate film is a small fraction of that for applying the metal deposit. Chromate coatings are required on zinc and cadmium for most military applications and are applied by immersing racked parts, by slowly rotating the parts in barrels, or by swirling the parts in perforated baskets.

A single-dip clear chromate coating accompanied by chemical polishing can be applied on smooth deposits of zinc and cadmium to provide an attractive, bright finish with a blue-white tint not unlike that of decorative chromium. A clear bright chromate can be formed in a two-step operation that involves the application of a yellow film followed by leaching in mild alkaline (e.g., 20 g/L Na₂CO₃ at 50°C; 122°F) or acid (e.g., 1 mL/L H₃PO₄ at 25°C; 77°F) solution.

The yellow-green iridescent-type chromate coatings are extensively used for improved corrosion resistance. The Cronak process¹ was the first to produce this type of chromate coating and found widespread use for many years. Typical formulations (200 Na₂Cr₂O₇·2H₂O + 6 mL/L H₂SO₄ or 50 g/L CrO₃ + 3 mL/L H₂SO₄) may be employed by a 10-second immersion at 25°C (77°F). However, more effective proprietary solutions are available. Solutions for chromating galvanized steel coil usually contain fluoride activator.

A typical iridescent chromate coating is 0.5 µm (0.02 mil) thick, contains 4 to 12 µg/cm² of leachable hexavalent chromium, and prevents the appearance of white salts from corrosion of the underlying metal for more than 96 hr of salt-spray exposure.

By modifying the solution formulation, chromate coatings of bronze or olive-drab color are readily applied by a single-dip operation. The darker colors, often favored

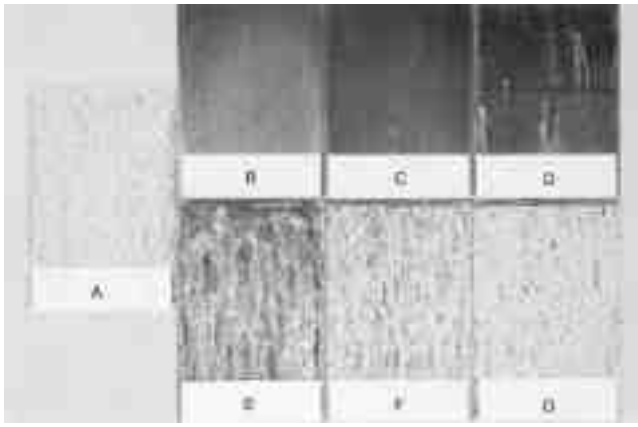


Figure 1—Corrosion of chromated zinc-plated steel after 96 hr of salt-spray exposure: (A) no chromate; (B) chromated, unheated; (C) chromated, heated 2 hr at 500°C (932°F); (D) chromated, heated 2 hr at 750°C (1382°F); (E) heated 2 hr at 1000°C (1832°F); (F) chromated, heated 2 hr at 1500°C (2732°F); (G) chromated, heated 2 hr at 2000°C (3632°F).

by the military for camouflage purposes, are usually indicative of greater concentration of hexavalent chromium and, thus, improved corrosion resistance. Proprietary solutions that form lustrous, black chromate coatings in a single-dip operation are available. Typical salt-spray corrosion resistance of chromated zinc plate is shown in Table I.

A variety of colors may be applied by immersing the freshly formed chromate in organic dye solutions. Pastel colors are attained using the clear or light-colored chromate films. Darker colors can be obtained with the darker chromate coatings. The dyed films have decorative applications but are most often used for identification purposes. For example, fasteners or assembly components may be color-coded to avoid errors in selection where differences in configuration are not readily discernible.

Some studies indicate that chromate films add little to the overall protection of the metal deposit to steel basis metal during outdoor atmospheric exposure while others indicate substantial improvement. Results are apparently dependent on the type of environment involved.

It is usually not advisable to use a chromate coating as a substitute for adequate thickness of a metal deposit. However, it has been shown from salt-spray studies that very thin (1.0 µm; 0.04 mil) metal deposits, which may form at highly recessed areas, are greatly improved in protective value by a chromate film from a solution formulated to keep metal loss to a minimum. In this context, it is best to eliminate or minimize the dilute nitric acid dip that usually precedes chromating, as greater metal loss may result from this treatment than from the chromating process.

The Heat Factor

It is well known that heating of chromated zinc adversely affects corrosion resistance. Heating in dry air at about 75°C (167°F) or above results in a decrease of the available (leachable) inhibitive hexavalent chromium by an irreversible dehydration phenomenon and cracks appear in the surface film.² The adverse effects are worsened as temperature increases and, after heating at above 100°C (212°F), the protective nature of the chromate film may be nullified (Fig. 1). Since zinc- or cadmium-plated high-strength steel (Rockwell C-40 or above) requires heating (191±14°C; 375±25°F) to relieve hydrogen embrittlement, the chromating operation is deferred until after baking.

Chromate coatings on zinc or cadmium are sometimes used as a base for paint, lacquer or varnish and function similarly to phosphate coatings in enhancing the protective properties and

resisting separation of the organic coating from undercut corrosion. However, not all chromate films are a suitable base for paint.

Although chromate coatings are applied predominantly by chemical reaction of metal surfaces and solution, proprietary anodic processes are available that produce coatings claimed superior in wear resistance of the freshly formed films and in corrosion resistance. Steel cartridge cases, rack plated with zinc, are chromated using an anodic process to provide optimum properties for military application.

The effectiveness of chromate coatings is usually determined by either the salt-spray test, the diphenyl carbazide test (for concentration of leachable hexavalent chromium) or the lead acetate spot test. The last simply involves application of a drop of 50 g/L $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ (made with distilled water) at a pH of 6.2±0.6 on the surface after the chromate film has aged 24 to 72 hr. The delay of a black or dark discoloration (> 1 min for zinc substrate; > 6 sec for cadmium substrate) is indicative of a good-quality chromate coating.

Aluminum

Chromate coatings are usually applied to aluminum from a solution containing chromic acid, a fluoride-containing ion and an accelerator (e.g., ferricyanide).³ Parts are usually treated by immersion but many are sprayed or brushed. A number of suppliers have proven that their proprietary formulations can produce coatings to pass military requirements (QPL-81706).

The chromate coatings may be iridescent, yellow, brown or green, with appearance affected by the surface finish of the aluminum. Clear coatings are applied by a brief treatment in special solutions or by the removal of most of the soluble chromate compounds from the yellow chromate coatings by leaching in hot water or immersing in dilute sodium carbonate solution. A wide variety of colors can be produced by immersing the aluminum with freshly formed or leached chromate film into an appropriate dye bath (usually about 2 g/L dye, at pH 4.0 with acetic acid, 600°C; 1400°F) for decorative or color-coding applications. The chromate film is applied with only a negligible change in the dimensions of the metal.

Corrosion Resistance

Chromate coatings provide a high degree of corrosion resistance to aluminum at a low cost. A normal coating of perhaps 0.5 µm (0.02 mil) thickness will protect 2024-T3 alloy for more than 168 hr of salt-spray exposure. The corrosion resistance varies with the alloy and heat treatment, but most wrought materials are less corrodible than 2024-T3. Some castings with a high content of silicon may be more difficult to protect.

Chromate is an excellent corrosion-preventive coating for aluminum, provided a high degree of both wear and abrasion resistance is not also required. Interestingly, chromated aluminum resists corrosion even better in natural environments than is indicated by salt-spray results. For example, iridescent chromate-coated 2024-T3 panels were unaffected in appearance after two years of tropical marine exposure, whereas comparable bare panels were catastrophically deteriorated by exfoliation corrosion (Fig. 2).⁴ It is therefore not surprising that innumerable commercial and military items are chromated as a final finish. Like chromated zinc, the corrosion resistance of chromated aluminum is adversely affected by heat.

Another important application of iridescent to yellow chromate coatings on aluminum is as a base for paint and lacquers to enhance adhesion and prevent the spread of undercoat corrosion from regions where bare metal becomes exposed as the result of impact damage. The combination of an epoxy primer (MIL-P-23377) and

polyurethane topcoats (MIL-C-81773) is representative of a system applied to chromated aluminum for protection of aircraft and other weapon systems. However, the zinc chromate primer (TT-P-1757) and alkyd enamel topcoats (TT-E-529) are used more often.

After painting, chromated aluminum can be subjected to elevated temperature (which would adversely affect the unpainted surface) without apparent effect on the protective value of the painted metal. An alternative to the chromate film as a base for paint is the wash primer.

Other Applications

Colorless chromate coatings are applied to aluminum when the characteristic appearance of the metal is desired. A clear organic coating can be used to provide increased protection. The very thin chromate coatings (clear or light iridescent per MIL-C-5541, Class 3) are also used for electrical or electronics applications where low electrical surface resistivity is required. Though the resistivity of chromated metal is somewhat greater than that of freshly cleaned aluminum, the chromate film prevents formation of oxides and corrosion products that would otherwise greatly increase surface resistivity. Similarly, the thinner chromate films are applied on aluminum parts that require welding since the coating does not appreciably interfere with the process and because it prevents formation of oxides that might interfere.

Mention should be made of the phosphate-fluoride-dichromate treatment⁵ of aluminum that results in formation of an amorphous coating of attractive green or blue-green color but which contains no hexavalent chromium and does not pass the corrosion-resistance requirements of military specifications. However, these coatings have good resistance to weathering and humidity and have found important final-finish applications for such items as screening and cyclone fencing; they also serve as an excellent base for paint or lacquer.

There are efforts to develop conversion films for aluminum (as well as other metals) that will provide the effectiveness of chromate coatings without the use of the toxic chromates in the treatment solutions. One such treatment⁶ is already showing commercial interest and further developments in this area are anticipated.

Magnesium

Magnesium alloys, particularly castings, have found many important applications (*e.g.*, space vehicles, military equipment containers, automotive parts, materials-handling equipment, etc.) primarily because of their high strength-to-weight ratio. It is the lightest and most active (chemically) of the common structure metals and the oceans contain an almost inexhaustible supply.

Magnesium reacts with water or neutral salt solutions to produce hydrogen gas and magnesium hydroxide; a drop of water on a bare magnesium surface will rapidly become distinctly alkaline. Fortunately, the alkalinity produced tends to stifle the initial rapid rate of attack and thus magnesium corrosion occurs at a slower rate than most steels and less catastrophically than some aluminum alloys in natural outdoor environments. However, when magnesium is in contact with most heavy metals, a high potential difference is established and rapid and intense galvanic corrosion of the magnesium will result. It is therefore most important to prevent galvanic corrosion by using protective coatings, tapes, sealants and gaskets to effectively insulate the dissimilar metals, or to coat any dissimilar metals with aluminum, cadmium, tin or zinc for improved compatibility. It is also advisable to avoid sump areas of possible moisture accumulation and to apply organic protective coatings when feasible.



Fig. 2—Corrosion of 2024-T3 aluminum after two years of tropical marine exposure: (A) bare, (B) chromated.

Chromate coating on magnesium provides significant corrosion resistance and is used as a final finish to provide temporary protection during shipment and storage or when relatively mild environmental exposures are expected. Magnesium die castings, used extensively for exterior automotive components (*e.g.*, fuel pumps, engine crankcases, transmission cases, blower fans), have served successfully when protected simply with a chromate coating and film of oil. However, for military applications, the chromate is seldom used as a final finish but serves as an effective base for protective organic coatings. One or more coats of alkali-resistant primers (vinyls or epoxies) containing inhibitive chromate pigment and one or more finish coats are recommended. A minimum of four coats is recommended for severe exposures.

The following types of chromate coatings find most common use:

- Type I—“Chromium Pickle Treatment.”* An iridescent film is applied by immersion (*e.g.*, 1.0 min in 180 g/L $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ + 185 mL/L HNO_3 at 22°C; 72°F) for application to wrought and many cast alloys. A modified solution** is more suitable for certain cast alloys such as AZ91b.
- Type III—“Dichromate Treatment.”*** This is a more involved treatment than Type I entailing an acid-fluoride pickling step (*e.g.*, 5 min in 230 mL/L HF, 49 per cent, at 25°C; 77°F), followed by immersion in dichromate solution (150

*Dow No. 1, The Dow Chemical Co., Midland, MI.

**Dow No. 20, The Dow Chemical Co., Midland, MI.

***Dow No. 7, The Dow Chemical Co., Midland, MI.

g/L $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ + 2.5 g/L CaF_2) at or near the boiling point. The treatment imparts an attractive, uniform brown color to most alloys. The resultant chromate coating is superior in corrosion resistance and as a paint base to the Type I coating.

- Type VI—"Chromic Acid Brush-on Treatment:"^{††} The coating applied by brushing is primarily used as a touch-up treatment and produces coating characteristics similar to that of Type I. The solution is quite dilute (10 g/L CrO_3 + 7.5 g/L $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and the final water rinse may be omitted when rinsing is not feasible or if it is desired to eliminate the need for rinsewater waste treatment. A nonchromate brush-on coating based on phosphate solution, is also available;^{††} studies are currently in progress to develop the treatment for production immersion applications.
- Type VIII—"Chromate Treatment:" This is a proprietary treatment that produces coatings approaching the quality of the Type III finish, but with a much simpler procedure involved.

Beryllium

The remarkable heat-sink capabilities, exceptional dimensional stability, low density and unique nuclear properties of beryllium have led to applications in inertial guidance equipment, high-energy braking systems and nuclear reactors. Beryllium is subject to corrosion in salt environments and the corrosion products can present a safety hazard as they are highly toxic when inhaled. Chromate conversion coatings can be applied from most solutions developed for application to aluminum or by use of the solution: 200 g/L $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ + 1.8 g/L HF (48 per cent) at 25°C (77°F). The coatings are effective for providing corrosion resistance during environmental exposure.

Beryllium is subject to catastrophic oxidation in air at high temperatures, e.g., >700°C (1292°F), particularly when some water vapor is present; the beryllium apparently reacts much more readily with the oxygen of water molecules than it does with gaseous oxygen. Remarkably, a chromate film protects most beryllium alloys against oxidation for considerable time in moist air at up to 900°C (1652°F).

Copper & Brass

Chromate coatings can be applied to brass and copper while providing chemical brightening to produce a lustrous decorative finish with improved resistance to corrosion. Bronze to chocolate-brown-colored chromate coatings of superior protective properties also can be applied and are readily capable of being dyed. Chromate coatings have been applied to brass components of military fuze-timing mechanisms for improved corrosion resistance, but the increase in friction coefficient resulting from the chromate introduced functional difficulties. Chromated copper or brass resists formation of blue-green corrosion products during salt-spray exposure of 48 hr or more, whereas bare copper alloys exhibit corrosion products after several hours of exposure.

Table 2—Applications of Chromate Coatings

Chromate coating type	Substrate	Typical applications
Clear	Zn, Cd, Al	Electronic chassis, fasteners, wire goods, tools
Iridescent	Zn, Cd, Al, Mg	Bicycle parts, auto carburetors, fuel pumps, paint base
Bronze/Olive Drab/Black	Zn, Cd, Al, Mg	Optical equipment, weapons components, springs, hardware
Dyed	Zn, Cd, Al	Simulated brass, color coding, fasteners

Tin

Chromate and chromate-phosphate treatments for tin-plated steel have been developed to enhance the protective properties of the tin while preventing discoloration, particularly from sulfur compounds. The coatings are generally invisible or nearly so; examples are 5-sec immersion in 10 g/L NaOH + 3 g/L Na_2CrO_4 at 90°C (194°F), or 30 sec in 19 g/L NaOH + 9 g/L $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ + 8 g/L $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ at 65°C (149°F). Cathodic dichromate treatment (e.g., 30 g/L $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, pH 5.0, 60°C; 140°F, 6 A/dm²; 60 A/ft²) applied to tin-plated steel provides excellent protection against discoloration during storage and is an effective base for lacquer. An alternative is cathodic treatment in 20 g/L Na_2CO_3 , pH 9.5, 50°C (122°F), 10 A/dm² (100 A/ft²).

Silver

Proprietary solutions produce clear chromate films on polished silver that are quite effective in retarding tarnishing in contact with hydrogen sulfide gas or sodium sulfide solution. The chromate film does not adversely affect, to a significant extent, the low contact resistance and solderability of the surface. However, there is some question of the ability of the chromate film to provide long-term tarnish resistance in mild household environments.

References

1. E. J. Wilhelm, US patent 2,035,380 (1936).
2. A. Gallaccio, F. Pearlstein and R. D. Ambrosio, *Metal Finishing*, **64**, 50 (August 1966).
3. C. W. Ostrander and N. R. Congiundi, US patent 2,796,370 (1955).
4. F. Pearlstein and L. Teitell, *Materials Performance*, **13**, 22, (March 1974).
5. F. P. Spruance Jr., US patent 2,494,910 (1950).
6. N. Das, US patent 3,964,936 (1976).

Editor's note: The preceding article is based on material contributed by Fred Pearlstein for the "AES Update" series that ran in this journal. Since this article was written much has changed. Indeed, the outlook for hexavalent chromate has drastically changed. Nevertheless, these processes remain relevant to a large portion of the finishing community. The reader may benefit both from that information and the historical perspective of the technology. The Update series, was begun and coordinated by the late Dr. Donald Swalheim, and brought practical information to the metal finisher. In some cases here, words were altered for context. *P&SF*

[†]Dow No. 19, The Dow Chemical Co., Midland, MI.

^{††}Dow No. 18, The Dow Chemical Co., Midland, MI.