Decorative & Hard Chromium Plating

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Applications

There are two distinct areas of application for chromium deposits: (1) decorative, because of the reflective and corrosion-resistance properties of the deposit; and (2) engineering, owing to the favorable friction, wear and heat-resistance properties of chromium.

Decorative deposits are found on the surfaces of articles where a bright, highly reflective finish is desired. The characteristic bluish haze of plated chromium offers an attractive, popular surface finish. The most familiar usage is on metal and plastic automotive trim. This finish is also applied on other consumer items, including appliances, marine hardware, furniture plumbing fixtures and bicycles, to name a few.

The production of electroplated engineering chromium is more commonly known as hard chromium plating. This finish provides resistance to wear, abrasion and heat, as well as corrosion. Machine tool cutting surfaces, cylinder bores, MacPherson strut rods, crankshafts, and hydraulic shafts are examples where hard chromium deposits are used. The low friction properties of chromium are ideal for use on the bore surfaces of artillery barrels. Hard chromium is often used to restore the original dimensions of worn or undersized parts, such as heavy-duty shafts for presses, turbines, etc. Here, chromium is over-deposited and machined back to size with no loss in function or properties.

Processes

Chromium coatings are deposited by vacuum evaporation, sputtering, flame and plasma spraying, and electroplating. A clear acrylic lacquer coating over a thin (1000 angstroms) vacuum evaporated or sputtered chromium layer has served as a decorative coating on plastic parts. Engineering coatings of flame or plasma-sprayed chromium have found application where uniform thickness on irregular shapes is required and not easily obtained by hard chromium plating. The primary coating method, for both decorative and engineering applications, however, is electrodeposition.

In general, plated chromium deposits are obtained from a solution of chromic acid (CrO_3) and sulfuric acid (H_2SO_4), using insoluble lead-antimony or lead-tin anodes. While simple in makeup, the solution operates quite differently from other acid- based baths, such as copper, nickel or zinc, where the soluble anode is the metal supply. The chromic acid is the sole source of chromium metal. The chromium is reduced to metal from the hexavalent (Cr^{+6}) state. The sulfuric acid acts as a catalyst in the complex six-electron reduction process. Besides being complex, the reaction is inefficient. About 15 percent of the plating current goes to the production of chromium metal. The bulk of the current evolves hydrogen gas at the part surface. Accordingly, efficient exhaust facilities are mandatory and the possibility of sparking (igniting the hydrogen) must be minimized. Proprietary agents are available to provide a foam blanket to localize the gases just above the solution surface.

In addition to low current efficiency, the chromium plating bath exhibits poor throwing power. As a result, the design and anodes, with supple- mental power supplies, are used in difficult cases where additional power is required to assure coverage. Such devices are critical in the case of hard chromium plating, which involves thick deposits.

Decorative chromium deposits are produced under the plating conditions shown in Table 1. These conditions are selected so as to insure the widest current range under which a bright deposit is obtained. This bright range sensitivity is another result, like throwing power, of the inherent inefficiency of deposition.

In addition to sulfuric acid, proprietary catalysts have been developed to enhance throwing power, current efficiency, bright plating current ranges, and deposit micro-cracking character, to be discussed later. Typical formulations include sulfuric/fluosilicate mixed catalysts and strontium or calcium salts to control the amount of active catalyst.

Decorative chromium deposits range from 0.13 to 1.30 µm (5-50µin) in thickness. These thin deposits are the final layer of a multilayer nickel or copper-nickel-chromium system. The thin chromium deposit replicates the surface appearance of the underlying plated layer. Care must be taken to assure that the finish of the underlying deposit is the desired one. In addition, attention must be paid to the activation of the nickel underlayer prior to chromium plating. If there is a delay

Table 1
Conditions for
Decorative Hard Chromium Deposits

Condition	Range	Optimum
Chromic acid	200 to 400 g/L (27 to 54 oz/gal)	250 g/L (33oz/gal)
Weight ratio*	80 to 125:1	100:1
Current density	7.5 to 17.5 A/dm² (75 to 175 A/ft²)	optimum bright range
Temperature	32 to 50 °C (90 to 122 °F)	43 °C (110 °F)

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*Chromic Acid to sulfuric acid weight ratio.

Table 2
Conditions for Hard Chromium Deposits

Condition	Low Concentration Solution	High Concentration Solution
Chromic acid	250 g/L(33 oz/gal)	400 g/L (53 oz/gal)
Sulfuric acid*	2.5 g/L (0.33 oz /gal)	4.0 g/L (0.53 oz/gal)
Current density	31 to 62 A/dm² (300 to 600 A/ft²)	16 to 54 A/dm² (150 to 450 A/ft²)
Temperature	52 to 63 °C (125 to 145 °F)	43 to 63 °C (110 to 145 °F)

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*Chromic acid to sulfuric acid weight ratio held at 100:1

sufficient to allow drying (and thus passivation) of the activated nickel surface, the result will be a whitish chromium deposit or no deposit at all.

The thin decorative chromium layer is brittle and, with the evolution of hydrogen a major part of the process, stresses result which are sufficient to produce deposit cracks. This characteristic is used in nickel-chromium multilayer deposits to establish a crack pattern, which determines the amount and distribution of nickel area exposed to the environment. During corrosion, the exposed nickel corrodes sacrificially. If the crack pattern is well dispersed, the corrosion current is also dispersed and the ultimate penetration to the basis metal is delayed, enhancing durability. Several methods have been used to establish this pattern, including dual-layer chromium, where a second layer induces cracks in the first, and micro-porous chromium, where a final nickel underlayer contains co-deposited inert particles that induce a network of fine pores in the chromium overlayer.

Hard chromium deposits differ from decorative ones in terms of thickness. Typical thicknesses lie in the 2.5 to 500 µm (0.0001 to 0.020 in.) range. The plating solution conditions are the same as those for decorative plating; the difference is primarily time. Operating conditions for low- and high-concentration solutions are given in Table 2.

The low concentration formulation has the advantages of higher operating currents and lower solution drag-out. The high concentration solution, on the other hand, has better throwing power and is less sensitive to concentration changes. The choice depends on the requirements and geometry of the specific application.

Long residence times require agitation of the workpiece in the bath to avoid solution stratification. The fume exhaust considerations noted earlier also apply to hard chromium plating. The low current efficiency and high engineering chromium thicknesses lead to long plating times. A tool-steel mold for plastics, with a chromium thickness of 5 to 13 µm (0.0002 to 0.0005 in.) will require 30 min. High-strength steel aircraft engine parts, requiring 75 to 180 µm (0.003 to 0.007 in.) will need 10 hr of deposition time. Plating times measured in days are common for the salvage of crankshafts, where 255 to 3800 µm (0.010 to 0.150 in.) of chromium are required. Racking and masking techniques are employed for proper distribution of the chromium. In engineering chromium applications, selected area plating is more common, and masking is important. Shields, conforming anodes and auxiliary anodes are used where complex geometries exist. Industrial chrome plating is a lower-volume operation when compared to decorative chromium plating and involves more complex approaches. Thus, racking and tooling require experience and training on the part of the operator.

Trivalent Chromium

The increasing importance of environmental concerns has required the search for alternatives. The most promising alternative to date is the trivalent chromium plating process. In use for the better part of 20 years, the trivalent processes provide decorative deposits with improved throwing and covering power. With micro-cracked or micro-porous character, the finishes equal the appearance and durability of hexavalent chromium deposits. A variety of commercial processes are available from several suppliers. Solutions are based on both sulfate and chloride chemistry. Current efficiencies are significantly higher than those in conventional hexavalent processes. With reduced gassing, most misting and odor problems are eliminated, enhancing workplace safety. The majority of commercial experience has dealt with decorative applications. At present, the use of trivalent chromium deposits in hard chromium applications has been successful with certain processes. Use in engineering applications is more limited, but the promise of viable trivalent alternatives is in the near-term.

Post-plating

Decorative chromium deposits normally require no additional finishing; the chromium layer is the final finish. Polishing and buffing are seldom used, as the micro-crack or micropore pattern would be destroyed. On occasion, selected areas of the plated surface may be painted. Proper adhesion requires special activation procedures prior to plating.

Hard chromium deposits used for salvage/buildup operations require machining to obtain the desired size. Grinding is often used, but special precautions are required. A soft grinding wheel, sufficient coolant, and light cutting depth are essential to avoid damaging the hard, brittle deposit.

Many steel parts are susceptible to hydrogen embrittlement, owing to pickling and cathodic cleaning prior to plating and to the hydrogen-evolving chromium plating process itself. Further, stresses can be induced in the steel from prior machining, grinding and heat treatment operations. Thermal treatments for hydrogen embrittlement and stress relief are often required prior to and/or after electroplating.

Health Impact

While metallic chromium and trivalent chromium compounds are nontoxic, the hexavalent compounds of the metal are very toxic and hazardous. Preparation of chromic acid-sulfuric acid solutions mandates the use of goggles, rubber apron, boots and respirator. Chromic acid is also a fire hazard if it should contact organic substances, including activated carbon, chemicals, paper and rags. The threshold limit value (TLV) for dusts and mists of hexavalent chromic acid is 0.1 mg/m^3 for an 8-hr exposure.

Environmental Status

Wastewater limits under the EPA Metal Finishing Regulations are 2.77 mg/L for any single day and 1.71 mg/L as a monthly average.

Trends

While current trends in design have led to reduced usage of decorative chromium finishes on automobiles, there remain numerous other applications. Environmental concerns with hexavalent chromium solutions have led to development of trivalent chromium plating baths, which are environmentally compatible and offer reduced pollution control costs. Hard chromium deposits will continue to be used for engineering applications. Despite the environmental problems associated with chromic acid, industrial chromium is often the only finish that fulfills the requirements of a given plating application. On the other hand, heavy electroless nickel (*i.e.*, nickel-phosphorus alloy) deposits possess mechanical properties that are compatible with the needs of many hard chromium applications. In many cases, this process has been used successfully, again with fewer environmental concerns. P&SF