7

ELECTRODEPOSITION OF CHROMIUM

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Electroplated chromium deposits rank among the most important plated metals and are used almost exclusively as the final deposit on parts. Without the physical properties offered by electroplated chromium deposits, the service life of most parts would be much shorter due to wear, corrosion, and the like. Parts would have to be replaced or repaired more frequently, or they would have to be made from more expensive materials, thus wasting valuable resources.

The thickness of electroplated chromium deposits falls into two classifications: decorative and functional. Decorative deposits are usually under $0.80\,\mu m$ in thickness. They offer a pleasing, reflective appearance while also providing corrosion resistance, lubricity, and durability. Decorative chromium deposits are typically plated over nickel but are occasionally plated directly over the substrate of the part.

Functional "hard chrome" deposits have a thickness customarily greater than $0.80\,\mu m$ and are used for industrial, not decorative, applications. In contrast to decorative deposits, functional chromium is usually plated directly on the substrate and only occasionally over other electrodeposits, such as nickel. Industrial coatings take advantage of the special properties of chromium, including resistance to heat, hardness, wear, corrosion, and erosion, and a low coefficient of friction. Even though it has nothing to do with performance, many users want their functional chromium deposits also to be decorative in appearance. Functional deposits are also used on parts such as cutting tools and strip steel and are even thinner than decorative deposits.

The most common and oldest commercial type of chromium process utilizes hexavalent chromium (Cr^{6+}) in an aqueous solution containing one or more catalysts. The commercial process of hexavalent chromium plating resulted principally from the work in 1923 and 1924 of Dubpernell [1] and Fink [2]. Liebreich [3] made similar discoveries more or less simultaneously, but his work was masked by an overemphasis of the importance of the trivalent chromium ion.

Early in the 1970s aqueous decorative trivalent chromium (Cr^{3+}) processes started to attain commercial success. It took to the early 2000s for functional (thick deposits) trivalent processes to become available. Most functional trivalent chromium deposits are not crystalline like those produced from hexavalent chromium processes resulting in reduced physical properties.

Noteworthy improvements in hexavalent chromium plating came with the introduction of double- and organic-catalyzed systems. Double-catalyzed (mixed-catalyst) systems introduced in 1949 generally contain sulfate and silicofluoride in forms that are either self-regulating [4] or operator regulated. In comparison to the initial commercial processes that were only sulfate catalyzed, double-catalyzed processes offer higher plating speeds and help activate the part prior to plating by mildly etching the substrate. Fluoride compounds with limited solubility supply the free-fluoride catalyst in self-regulating processes. Undissolved fluoride compounds stayed in the bath until they dissolved to increase the concentration of free fluoride. Operator-regulated baths depend upon the proper additions of free fluoride from outside the tank.

Organic-catalyzed processes have increased plating speeds and improved deposit physical properties, and they do not etch iron substrates. Proprietary organic additives are added from outside the tank to maintain the proper

concentration. This process is well suited for functional applications.

For more details on the history of chromium plating, see [1, 5–7]. Blum and Hogaboom [7] emphasize the effect of the introduction of chromium plating on other electroplating processes.

7.1 PRINCIPLES

Unlike most other platable metals, chromium cannot be deposited from an aqueous solution containing the metal ions only. Chromium processes must contain one or more acid radicals that act as catalysts (for hexchromium) or complexers (for trichromium) to bring about or aid in the cathodic deposition of chromium metal. The catalysts most commonly used for double- (mixed-) catalyzed, hexchromium processes are sulfate and fluoride. The fluoride is generally in the form of a complex such as silicofluoride (SiF_6^{2-}) [8], since simple fluorides are effective in such small quantities that process control becomes difficult. For successful continuous operation, the ratio (by weight) of chromic acid to total catalyst acid radicals must be maintained within definite limits: preferably about $100:1$ in the case of sulfate [2, 3].

Proprietary organic additives introduced in the mid-1980s are used in conjunction with sulfate for organic-catalyzed, high-speed hexavalent chromium processes. Since fluoride is not used, these processes do not etch steel, which could contribute to a buildup of iron contaminate. Concentrations of hexavalent chrome, sulfate, and organic acids must be controlled within range to operate. These processes can also operate at higher temperatures than other hexavalent chromium processes, permitting the use of higher current densities to obtain faster plating speeds.

The conductivity and density of pure chromic acid solutions are shown in Figure 7.1. They are based on measurements made at the National Institute for Standards and Technology (NIST) [9] (originally named the National Bureau of Standards, NBS). Small amounts of Cr(III) (Cr^{3+}, trivalent chromium) and other cations decrease the conductivity. The maximum conductivity is not achieved until a concentration of $400–500 \, g \, L^{-1}$ chromic acid is reached. Commercial chromium plating processes generally use baths containing $200–400 \, g \, L^{-1}$ chromic acid in order to obtain the best conductivity possible, along with acceptable current efficiency, satisfactory deposits, and stable, easy-to-maintain solution composition. In practice, chromic acid concentrations are increased to overcome the effect of contaminates that decrease bath conductivity. Higher chromic acid concentrations increase solution losses due to higher drag-out, resulting in an increased requirement for solution recovery or

waste treatment. The specific gravity of the baths provides a rough measure of the concentration of chromic acid, especially if due allowance is made for other salts known to be present.

Sulfate is ordinarily present in all hexavalent chromium plating baths, because even the best commercial grades of chromium trioxide (CrO_3) contain sulfate as an impurity. Chromium trioxide, also called chromium anhydride, is the most common source of hexavalent chromium ions. Even though chemically incorrect, chromium trioxide is usually referred to as chromic acid. The acid is actually formed in aqueous solution.

Sulfuric acid and sodium sulfate are the most common sources of additional sulfate; fluorosilicic acid and silicofluorides [8] are the most common sources of fluoride. References to the amount of catalytic agent or acid radical in a bath usually mean the total quantity of sulfate and fluoride ions, although the method of determining those may vary among the processes and needs to be well understood when using a particular process.

Although the current efficiency in hexavalent chromium plating baths is low (generally between 10 and 25%, depending on the process), a fairly high rate of bright plate is obtained when relatively high current densities are used. Figure 7.2 shows deposits offering the best physical properties. In this figure the semidashed lines A and B circumscribe bright plate areas of low and high concentrations of chromium trioxide, respectively. The complete bright plating area is circumscribed by line X.

The voltages required are higher than in most other electroplating processes, generally 4–12 V depending on operating conditions. Also the high current and voltage must be applied with very low ripple [the percentage of alternating current (ac) superimposed on the direct current (dc)]. Consequently rectifiers used must have a lower ripple and higher capacity for chromium plating than is required for most other metal plating, but this disadvantage has not seriously hindered the widespread and increasing use of this process.

The throwing power (coating distribution over the part's current density range) of hexavalent chromium plating is relatively poor compared to most other platable metals such as nickel. Trivalent chromium processes have much greater throwing power and closely approximate that of Watts-based nickel processes. However, usable coverage is obtainable with hexavalent chromium processes even in the plating of irregular shaped articles if the optimum bath conditions are carefully maintained. Special auxiliary anodes, masks, and shields are sometimes used in order to cover deep hollows or recessed portions and especially used to obtain more uniform thickness. These techniques are similar to those used with other plating processes but must be designed in
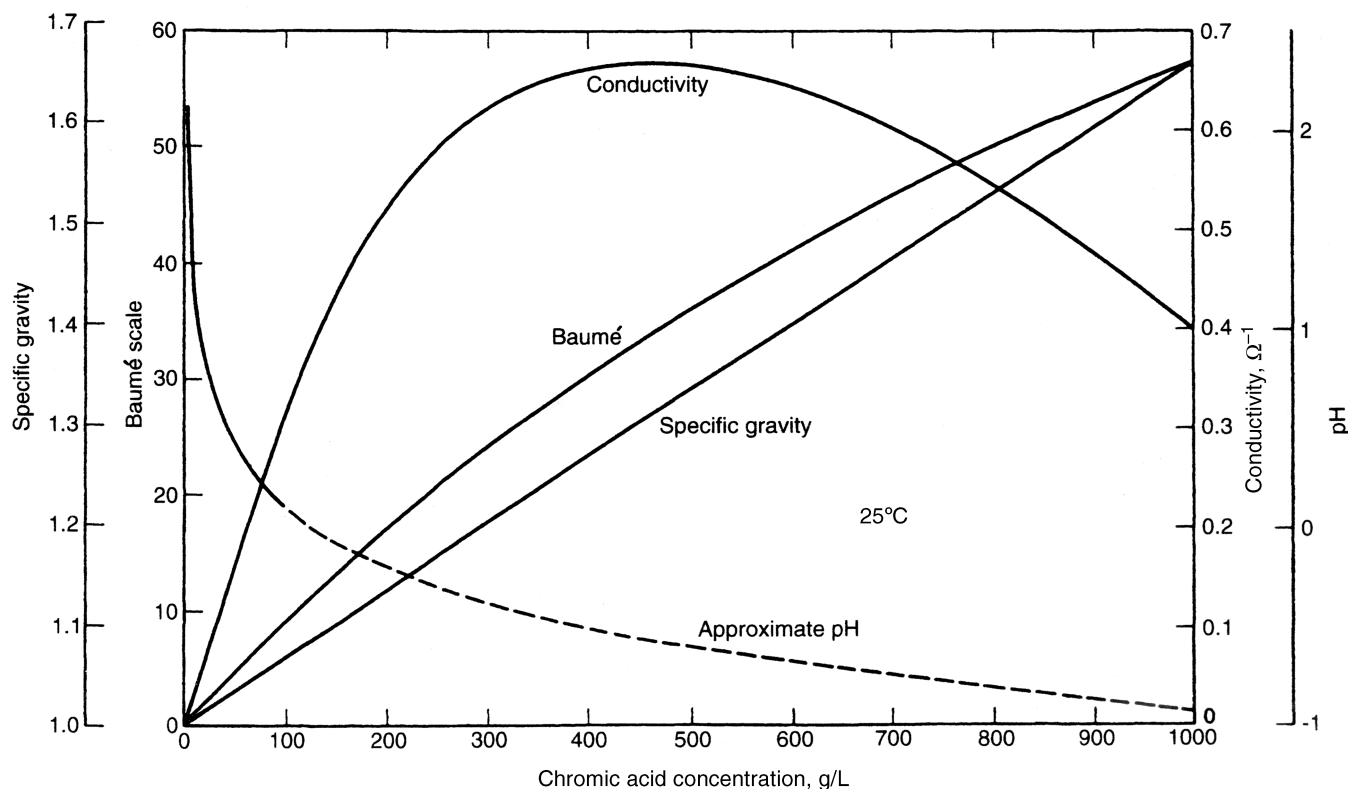
FIGURE 7.1   Some physical properties of chromium plate.

accord with established principles of ample size for current-carrying requirements and proper spacing for uniform current distribution.

Proprietary complexers in the form of organic acid radicals stabilize the trivalent chromium ions in an aqueous, pH 2–4, solution [10, 11]. Sulfates and chlorides, in varying amounts, are used to increase bath conductivity. Commercial trivalent chromium formulations are much more complex than hexavalent chromium formulations and, at present, are all proprietary. Trivalent processes plate between two and three times faster than hexavalent chromium processes at much lower current densities.

The current altering techniques used in hexavalent chromium processes are not typically necessary with trivalent chromium processes, since both the throwing and covering (ability to plate in low current density) powers are better than those of hexavalent chromium processes. Since they are already present, sulfate and chloride ion concentrations do not have to be tightly controlled in trivalent chromium processes as is required in hexavalent chromium processes. Hexavalent chromium processes, on the other hand, are less sensitive to metallic contamination than trivalent processes, but metallic contaminates are easily removed from trivalent processes by continuous bath circulation through ion exchange resins. Organic contamination can usually be removed by carbon filtration. Bath operation and maintenance for trivalent chromium processes are much closer to what is required for nickel processes than for hexavalent chromium processes. Very little process information has been published for trivalent chromium processes because it is still kept proprietary, much new, and several different chemistries are commercially available.

7.2   THEORY OF CHROMIUM ELECTRODEPOSITION

A typical transition element, chromium forms many compounds that are colored and paramagnetic. Chromium has oxidation states as follows: -2, -1, 0, $+1$, $+2$, $+3$, $+4$, $+5$, $+6$; the highest oxidation state, $+6$, corresponds to the sum of the numbers of 3d and 4s electrons. The lowest, -2, $-1, 0$, and $+1$, are formal oxidation states displayed by chromium in compounds such as carbonyls, nitrosyls, and organometallic complexes.

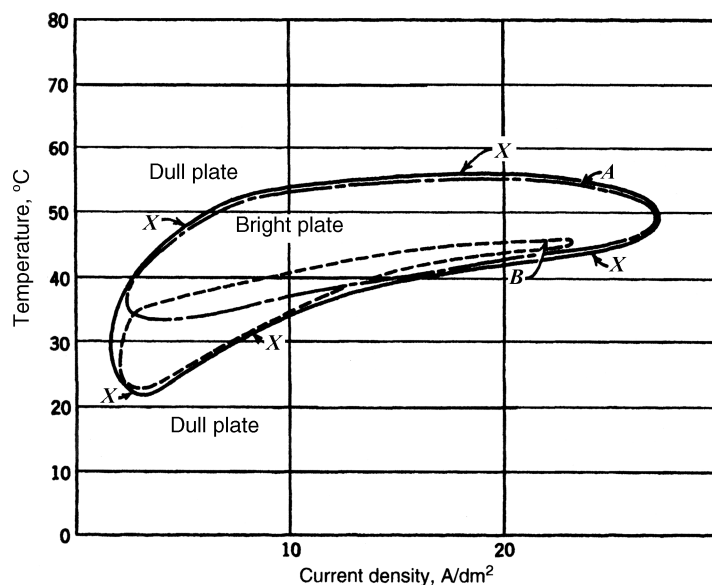**FIGURE 7.2** Bright plating range.

Divalent chromium in the oxidation state $+2$ was not considered in the past to be of particular interest for electrodeposition mechanisms. It does play a role, however, in the passivation of chromium. Recently it has been recognized that, probably, it plays a role in the deposition and dissolution mechanisms. The outstanding characteristic of the Cr^{2+} ion (sky blue in aqueous solution) is its strength as a reducing agent $Cr^{3+} + e \leftrightarrow Cr^{2+}$, $E_0 = 0.41$ V. Because it is easily oxidized by oxygen, preservation of the solution requires exclusion of air. Even under such conditions the Cr^{2+} ion is oxidized by water with the formation of hydrogen. The rate of oxidation depends on several factors, including the acidity and anions present.

It has been known for some time [12] that pure chromium (usually obtained electrolytically) dissolves in acids to form Cr^{2+} with no (or very little) Cr^{3+} if the solution is protected from air; impurities apparently catalyze formation of Cr^{3+}. Chromium $(+2)$ solutions may also be obtained [13, 14] by electrolytic reduction of Cr^{3+} chromium $(+3)$.

Chromium $(+3)$ is the most stable and most important oxidation state of the element. The E_0 values [15] show that both the oxidation of Cr^{2+} to Cr^{3+} and the reduction of Cr^{6+} to Cr^{3+} are favored in acidic aqueous solutions. The preparation of Cr^{3+} compounds from either state presents few difficulties and does not require special conditions [16].

The chemistry of Cr^{3+} in aqueous solutions is coordination chemistry. It is demonstrated by the formation of kinetically inert outer orbital octahedral complexes. The bonding can be explained by $d^2 sp^3$ hybridization; a great number of complexes have been prepared. The kinetic inertness results from the $3d^3$ electric configuration of Cr^{3+} ion [17]. The type of orbital charge distribution makes liquid displacement and substitution reactions very slow and allows separation, persistence, and/or isolation or Cr^{3+} species under thermodynamically unstable conditions.

Chromium $(+3)$ is characterized by a marked tendency to form polynuclear complexes. Literally thousands of Cr^{3+} complexes have been isolated and characterized and, with a few exceptions, are all hexacoordinate. The principal characteristic of these complexes in aqueous solution is their relative kinetic inertness. Ligand displacement reactions of Cr^{3+} complexes have half-times in the range of several hours. It is largely because of this kinetic inertness that so many complex species can be isolated as solids and that they persist for relatively long periods in solution, even under conditions of marked thermodynamic instability.

The hexaaqua ion $[Cr(H_2O)_6]^{3+}$, which is a regular octahedral, occurs in numerous salts, such as the violet hydrate $[Cr(H_2O)_6]Cl_3$, and in an extensive series of alums, $MCr(SO_4)_2 \cdot 12H_2O$, where M usually is NH_4^+ or K^+ ion. The aqua ion is acidic $(pK = 4)$, and the hydroxo ion condenses to give dimeric hydroxo bridged species.

On further addition of base, a precipitate is formed that consists of H-bonded layers of $Cr(OH)_3(H_2O)_3$, which readily redissolves in acid. Within 1 min, however, this precipitate begins "aging" to an oligomeric or polymeric structure that is much less soluble [18–20].

The Cr^{3+} ion may also polymerize, as a result of hydrolysis and associated reactions, to form bridged complexes with a certain composition whose existence is indicated by indirect but substantial evidence. Complexes of this type range from dimers through polymers of colloidal dimensions to precipitated Cr^{3+} hydroxide. Except under special circumstances, such reactions are inevitable in neutral and basic solutions and highly probable in slightly acid solutions,

What makes the chemistry of Cr^{3+} complexes interesting and often difficult for researchers is the large number of steps and mechanisms possible. The processes include aquation, hydrolysis, olation, polymerization, oxolation and anion penetration.

7.2.1   Aquation

Chromium salts (chloride, sulfate, nitrate, etc.) are aqua complexes characterized by ions such as $[Cr(H_2O)_6]^{3+}$, $[Cr(H_2O)_5Cl]^{2+}$, and $[Cr(H_2O)_4Cl_2]^{+1}$. In aqueous solutions the replacement of coordinated groups by water molecules (aquation) is a common reaction: $[CrA_5X]^{2+} + H_2O \leftrightarrow [CrA_5H_2O]^{3+}$, where A is a singly coordinated neutral molecule and X is a singly charge coordinated negative ion (e.g., Cl, CN, CNS).

The extent of aquation depends on several factors, including the relative coordinating tendencies of H_2O and X and the concentration of X. Accordingly every aqueous solution of Cr^{3+} is potentially a solution of aqua complexes. The Cr^{2+} ion (whose complexes are labile) catalyzes such reactions, which are usually quite slow otherwise. Electron-transfer reactions between Cr^{2+} and $[Cr(H_2O)_5]^+$ proceed predominantly through bridged intermediates $\{[CT-X-Cr]^{4+}\}$. Ligand transfer accompanies electron transfer. In the investigations establishing these conclusions, the reaction conditions have generally been characterized by relatively low $[Cr^{2+}]$ and relatively high $[H^+]$. With relatively high $[Cr^{2+}]$ and relatively low $[H^+]$, another pathway is available [21] with the rate determining reaction involving a hydroxy bridged complex: $[(H_2O)_4-X-CrOHCr_6]^{3+}$.

The role of Cr^{2+} is very important, however, in industrial "hard" chromium applications when plating thick layers of chromium or Cr–Ni and/or Cr–Ni–Fe alloys from trivalent chromium solutions, as an alternative for Cr(+6)-based solutions. Failure to control the transient levels of Cr^{2+} is recognized as the reason for Cr(+3)-based solutions not to sustain heavy deposition with an appreciable deposition rate. The problem is recognized as massive olation, catalyzed by a buildup of Cr^{2+} in the high-pH region in the vicinity of the cathode. Although the bulk of the electrolyte can be about pH 2, the diffusion layer can reach pH 4. At this pH and with Cr^{2+} promoted cata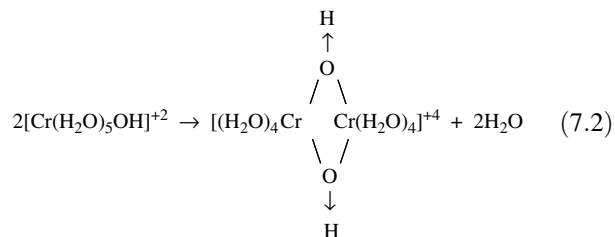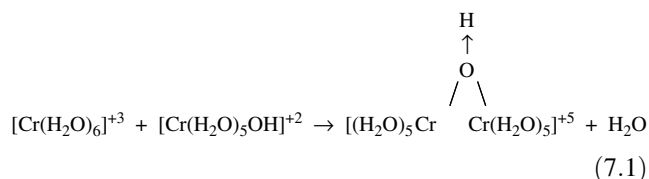lysis, oligomeric species are released into the bulk of the electrolyte, where they can build up and reduce the level of active species and, consequently, the deposition rate [22–25].

7.2.2   Hydrolysis

The behavior of aqua complexes as acids leads to far-reaching consequences. The acidity of such solutions arises because of the $[Cr(H_2O)]^{3+} \leftrightarrow [Cr(H_2O)]^{2+} + H^+$ reaction. The equilibrium can be displaced to the right by heating and, of course, by the addition of base. The order of magnitude of the first hydrolysis constant is $K = 10^{-4}$. As the pH of the Cr^{3+} solution is raised, the equilibrium is shifted, and more of the coordinated water molecules are converted to OH groups, which brings into the picture a new process called *olation*.

7.2.3   Olation

Olated compounds are complexes in which the metal atoms are linked through bridging with OH groups. Such a group is designated as an *ol* group to distinguish it from the *hydroxo* group (i.e., a coordinated OH linked to only one metal atom). The process of formation of ol compounds from hydroxo compounds is called olation. Olation results from the formation of polynuclear complexes consisting of chains or rings of Cr^{3+} ions connected by bridging OH groups. The first step of this process may be as follows [26]:

$$[Cr(H_2O)_6]^{+3} + [Cr(H_2O)_5OH]^{+2} \rightarrow [(H_2O)_5Cr\ \overset{\displaystyle \overset{H}{\uparrow}\ O}{\diagup \diagdown}\ Cr(H_2O)_5]^{+5} + H_2O$$

$$(7.1)$$

$$2[Cr(H_2O)_5OH]^{+2} \rightarrow [(H_2O)_4Cr\ \overset{\overset{H}{\uparrow}\ O}{\underset{O \atop \downarrow \atop H}{\diagup \diagdown \diagdown \diagup}}\ Cr(H_2O)_4]^{+4} + 2H_2O$$

$$(7.2)$$

Because the *diol* produced by reaction (7.2) is stabilized by the four-member ring, there is a driving force tending to convert the singly bridged to a doubly bridged complex. This diol is produced by polymerization of $[Cr(H_2O)_5OH]^{2+}$, oxidation of Cr^{2+} by molecular oxygen, warming an equimolar mixture of Cr^{3+} and NaOH, and boiling an aqueous solution of $[Cr(H_2O)_6]^{3+}$.

The diol and any other polynuclear products containing water molecules (or a group that can be displaced by, water molecules) can still act as acids, releasing hydrogen ions and leaving coordinated OH groups.

7.2.4   Polymerization

Instead of reaching a definite termination, reaction (7.2) may continue, with the formation of larger and larger molecules, the polymers, as a continued process of olation. This will occur if the product of each successive step contains aqua or hydroxo groups. The ultimate consequence is precipitation of chromium hydroxide, $Cr(OH)_3 \times H_2O$, a tridimensional olated complex [27]. Olation reactions are pH and time dependent. At moderate acidity they are quite slow. It can take days for higher oligomers to be formed after addition of the base to aqueous Cr^{3+} solution, but they will subsequently decay, contributing to pH stabilization after a few weeks [28].

The continued process of olation starts with the hydrolysis of salts of such metals as Al or Cr. The acidity of solution of such salts results from conversion of aqua to hydroxo groups: $[Cr(H_2O)_6]^{3+} \leftrightarrow [Cr(H_2O)_6OH]^{2+} + H^+$. The degree of hydrolysis increases as the temperature is raised, and this relationship depends on the nature of the anion, and especially on the pH of the solution. If alkali is added to a warm solution of hydrolyzed chromium salt, but not enough for complete neutralization, polymerization occurs instead of precipitation of the basic salt or hydroxide.

Because of the octahedral configuration of complexes of metals such as chromium, the bonds of a given metal occur in pairs, each of which lies in a plane perpendicular to the planes of the other two pairs. Accordingly such cross-linked polymers are three dimensional.

The process of olation is favored by an increase in concentration, temperature, and basicity. The process reverses slowly when the solution of olated complexes is diluted or when the solution is cooled (i.e., olation decreases the reactivity of coordinated OH groups).

7.2.5   Oxolation

Oxolation may accompany or follow olation, particularly if the reaction mixture is heated. This reaction converts bridging OH^- groups to O^- groups. Olation and oxolation account for changes in reactivity of chromium hydroxide as it ages. Freshly precipitated chromium hydroxide usually dissolves quite rapidly in mineral acids, but after standing some hours, it becomes difficult to dissolve. Presumably olation continues in the precipitate; because bridged OH^- groups react more slowly with acids than singly coordinated OH^- groups, the reactivity of the precipitated hydroxide progressively diminishes. If the hydrate is heated, there is a drastic decrease in reactivity as a result of oxotation, a process even more difficult to reverse than olation. While olation and oxolation are both reversible, the long times required for the acidity of solutions, which have been heated and then cooled, to return to the original values lead to the conclusion that deoxolation is extremely slow. In general, ol groups are more readily depolymerized than oxo compounds because protons react more rapidly with oxo groups.

7.2.6   Anion Penetration

It is well known that the addition of neutral salts to a solution of basic sulfate changes the hydrogen ion concentration. Coordinated water molecules, OH^- groups, OH bridges, or other ligands are replaced by anions in the solution. The extent to which anion penetration occurs with ol complexes is determined by the relative coordination tendencies of the entering anions and the groups that they replace and the length of time that the solutions are allowed to stand [29]. Anions that can enter the coordinated sphere easily and displace OH groups can effectively prevent olation. Penetration by anions into basic chromium complexes decreases in the following order [30]:

Oxalate > glycinate > tartarate citrate > glucolate > acetate > monochloracetate > formate > sulfate > chloride > nitrate > perchlorate

Consequently, if a solution of $[Cr(H_2O)]^{3+}$ is required, the only anion that should be weakly coordinated is nitrate or perchlorate because anions of greater coordinating tendency will displace one or more of the coordinated molecules. In a stock solution of basic chromium sulfate, Serfas et al. [29] found ionic species having molecular weights of 68,000.

7.2.7   Reaction Rates

In a system containing Cr^{3+} complexes, after a parameter is changed, the corresponding change in composition of the complexes generally occurs only slowly. Heating a solution (or dispersion) of such complexes promotes olation and oxolation, both of which reverse at a low rate when the system is cooled. Reversal of oxolation is much slower than reversal of olation. If the pH of a solution containing olated complexes is reduced to a value at which normally only monometric Cr^{3+} complexes would exist, it may take a long time for the state of aggregation corresponding to the new pH to be attained.

7.3   HEXAVALENT CHROMIUM

The mechanisms of the electroreduction of chromic acid are of great interest, not only from a theoretical point of view but also for their application in industry. The vast majority of decorative, and almost all hard, chromium plating is carried out using CrO_3 as the electrolyte. The fact that chromium can be deposited from Cr^{6+} solutions but not from simple aqueous solutions of lower valency salts is a disadvantage for the following reasons:

1. Because the electrochemical equivalent of Cr in a CrO_3 solution is $0.3234\,g\,h^{-1}$ and cathode current efficiency is typically 10–20%, the passage of current of 1 Ah yields only 0.032–0.064 g of metal. This is 15–30 times

less than for nickel, 18–36 times less than for copper from acid solution, and 63–126 times less than for silver. The only way to offset this is to increase the working current density via increase in mass transport and temperature and/or plating time.

2. The minimum current density at which electrodeposition takes place is two to three orders of magnitude larger than in the case of other metals (Zn, Ni, Sn, Ag, Au, etc.).

3. The electrodeposition of chromium is more sensitive to operating conditions (temperature and current density) than any other deposition process.

4. In contrast to other processes, the cathodic current efficiency varies inversely with temperature but is proportional to current density (which causes low throwing power).

5. Chromium will plate only in the presence of a catalyst (e.g., H_2SO_4), whose concentration influences the plating rate.

6. On the positive side, hexavalent chromium electrolytes are relatively less sensitive to the presence of impurities, and the anode material is lead or lead alloys, which can easily be made to conform to any shape.

Despite its paramount technological importance and with all the advances of modern science and instrumentation, the exact mechanisms of chromium electrodeposition are still open to considerable conjecture. The main difficulty is the necessary formation and presence of a cathodic film on the surface of the metal being plated. The argument of whether the reduction of Cr^{6+} ions to chromium is direct or indirect developed during the last decade into a discussion of whether or not the cathodic film is useful (and in what way it should be modified to improve the process, inasmuch as the existence of this film is no longer in question).

Because of the absence of complete understanding of the deposition mechanism, it is important to understand the chemistry of chromium with all its intricacies of condensation, polymerization, number of different valence states, ability to make anion/cation compounds [e.g., $Cr_2(Cr_2O_7)_3$], existence of a number of double salts (alums), isomers, oxyhydrates, and so on. Virtually all Cr^{3+} compounds contain a Cr–O unit.

7.3.1 Chromic Acid

The primary Cr–O bonded species is chromium (+ 6) oxide, CrO_3, which is better known as chromic acid, the commercial and common name. This compound is also known as chromic oxide and chromic acid anhydride. Chromium (+ 6) forms a large number and considerable variety of oxygen compounds, most of which may be regarded as derived from Cr^{6+} oxide. These include the oxy-halogen complexes and chromyl compounds, chromates, dichromates, trichromates, tetrachromates, and basic chromates. All these Cr^{3+} compounds are quite potent oxidizing agents, although kinetically they cover a wide range.

Chromic trioxide has a molecular weight of 100.01 and forms dark red prismatic crystals belonging to the orthorhombic system, the bipyramidal subclass. The density of the solid is $2.79\,g\,cm^{-3}$. It melts with some decomposition at 197°C. CrO_3 is very hygroscopic. Its solubility in water varies from 61.7% at 0°C to 67.5% at 100°C. Oxidation potentials of CrO_3 and chromate solutions are augmented by increasing the acidity of the solution. Chromic acid, H_2CrO_4, is not known except in solution, where it shows a marked tendency to form polyacids by elimination of water [31].

The change from $H_2Cr_2O_4$ to $H_2Cr_2O_7$ is rapid, but further polymerization takes measurable time. The color of CrO_3 indicates that it is itself highly polymerized, for it is redder than the di- or trichromates and is approached in color by the tetrachromates. De-polymerization of CrO_3 solution in water is very rapid. It also seems to depolymerize on heating.

7.3.2 Chromates and Dichromates

Chromates are salts of the hypothetical chromic acid H_2CrO_4. Salts of the hypothetical polybasic chromic acids, $H_2Cr_2O_7$, $H_2Cr_3O_{10}$, $H_2Cr_4O_{13}$, are known as dichromates, trichromates, tetrachromates, and so on.

The chromate ion and most of the normal solid chromates are yellow, but upon acidifying, the solutions change colors through orange to red. The dichromates are red in the solid state and in solution. The higher polychromates are even of deeper red than the dichromate in the solid state. Although the various ions, CrO_4^-, $Cr_2O_7^{2-}$, $Cr_3O_{10}^{2-}$, $Cr_4O_{13}^{2-}$, and so on, exist together in equilibrium in solution, the ions higher than dichromate exist only in the most concentrated solutions. Water is easily added to the higher polychromate ions, causing them to revert to the dichromate. On further dilution, even the dichromate ion adds water, forming the chromates. The $HCrO_4^-$ ion exists in quantity only in dilute solution, according to Udy [32], but more recently Raman spectroscopy proved nonexistence of $HCrO_4^-$ ions in dilute and concentrated solutions [33–36].

7.3.3 Polychromates

Polychromate ions are of particular interest because of their role in chromium plating from hexavalent solutions. It is recognized and accepted that chromium cannot be electrodeposited from Cr^{6+} solutions without the addition of a catalyst, usually in the form of the sulfate. Because the strength of commercial solutions is customarily 1–3 M, at this concentration, considering the low pH and taking into account the dark red color of the solution, at least the tri- and possibly the tetrachromate ions are present. It should be noted

that in the absence of electric current, the pH of the chromium plating solution is subject to considerable variation, depending on the initial concentration of chromic and sulfuric acids. If the amount of CrO_3 is increased from 10 to $300 \, g \, L^{-1}$ ($0.1–3 \, M$), the pH changes from 1.4 to 0.08. Martens and Carpeni [37] using radioactive chromium measured the auto-diffusion coefficients of isopolychromates at $25°C$ in aqueous solution as a function of concentration. They found that in the plating operating ranges ($1.5 < CrO_3 < 3.5 \, mol \, L^{-1}$), the predominant species are di- and trichromate ions.

The dominant role of trichromates in chromium deposition is advanced by Hoare [38]. According to his model, in the absence of the bisulfate ion (or sulfate, which at low pH dissociates to bisulfate) the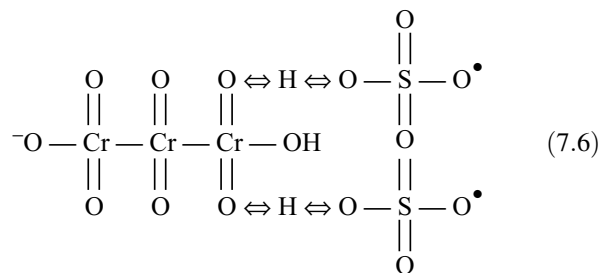 trichromate ion will in successive steps (of electron transfer and loss of oxygen and reaction with H_3O^+ ion) decompose to chromous hydroxide and dichromates, which in turn may undergo condensation with other chromates to regenerate trichromates. The process then includes an intermediate step of formation of chromic ($+3$), then chromous ($+2$) dichromates, finally discharging at the cathode as black chromium at very low current efficiency. In the presence of sulfates, the next step of the reduction mechanism is the formation of a complex between the Cr^{2+} hydroxide and the bisulfate through hydrogen bonding:

$$Cr(OH)_2 \Leftrightarrow Cr = O + H_2O \tag{7.3}$$

$$Cr = O + HSO_4^- \Leftrightarrow {}^{+\delta}Cr - OH \dots O - SO_3^- \tag{7.4}$$
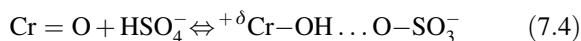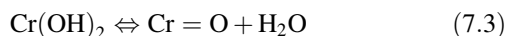
where the ellipses represent the hydrogen bond and $^{+}\delta$ represents a dipole generated on the chromium end (left side) of the complex. Now, the positively charged complex may be specifically adsorbed on the cathode, two electrons transferred to this end on configuration with formation of metallic Cr and regeneration of HSO_4^-:

$$^{+\delta}Cr - OH \dots O - SO_3^- \xrightarrow{2e-,2H^+} Cr^0 + HSO_4^- + H_2O \tag{7.5}$$
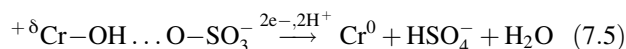
According to this model, the chromic–dichromate complex is necessary to protect the Cr^{3-} from forming stable Cr (3^+) aquocomplexes. As a refinement of this model, the HSO_4^- ion has a dual role—it also "blocks" other chromium atoms in trichromate ions from being reduced (leading to Cr^{3+} aquocomplex formation). The ideally protected trichromate ion would be

$$\begin{array}{c} O \\ \parallel \\ O \quad\quad O \quad\quad O \Leftrightarrow H \Leftrightarrow O - S - O^{\bullet} \\ \parallel \quad\quad \parallel \quad\quad \parallel \quad\quad\quad\quad \parallel \\ {}^-O - Cr - Cr - Cr - OH \quad\quad O \\ \parallel \quad\quad \parallel \quad\quad \parallel \quad\quad\quad\quad \parallel \\ O \quad\quad O \quad\quad O \Leftrightarrow H \Leftrightarrow O - S - O^{\bullet} \\ \parallel \\ O \end{array} \tag{7.6}$$

This would leave one end [the right side of (7.6)] protected, preventing formation of unwanted dichromatic chromate complex, decomposition of which would lead to unwanted $[Cr(H_2O)_6]^{3+}$ formation. This also explains the narrow range ($CrO_3 : HSO_4^- = 100 : 1$) of bisulfate concentration in the chromium plating solution. Too little HSO_4^- will cause insufficient protection of the Cr at the right end of the trichromate ion (undercatalization); too much will block the left-end Cr, which is necessary for reactions (7.3)–(7.6) and Cr deposition (overcatalization).

According to Hoare [39, 40] for fluoride-catalyzed CrO_3-based plating systems, almost the identical mechanism is proposed in which F^- plays the role of blocking agent and catalyst. Although not complete, this mechanism is the most accepted to date. The incompleteness of his remarkable theory is that it treated the chromium deposition mechanism without reference to the structure and influence of the liquid layer adjacent to the cathode (L-film), which is formed at the beginning of the cathodic process and is continuously forming and re-forming in the steady-state condition.

Research originating in Russia is extensive on the L-film formation and reactions that occur in the film. They recognized quite early its decisive importance for the deposition mechanism in general and for current efficiency in particular. On the other hand, it is a well-known fact that halide ions (X) such as Cl^- and F^- have a marked improving effect on the cathode current efficiency of chromium electro deposition as recently reported [41].

Because the hydration of halide anions is incomplete, they can penetrate the hydrogen layer and be absorbed onto the metal surface. X-ray photoelectron spectroscopy (XPS) results [41] show that F^- and Cl^- ions, which are stable in the chromic acid bath, may participate in the film formation. The probable activation steps of halides are the absorbed halide first penetrates the hydrogen layer at the chromium surface and then forms a bridged transition surface complex. The electrons on the cathode are transferred to Cr^{3+} through halides, and Cr^{3+} is reduced to metallic chromium. By the formation of the transition complex, the activation energy of the reduction of Cr^{3+} to Cr^0 is decreased. The overpotential of chromium deposition apparently is decreased, which facilitates chromium electrodeposition. The rate of reaction follows a first-order rate equation [42]. In case of a rotating cylinder, the specific reaction rate constant was found to increase with increasing rotation speed up to a limiting value which is reached with further increase in the rotation speed. A study of the reaction mechanisms has shown that at a relatively low rotation speed the reduction of chromium is partially controlled by diffusion; at higher speeds the reaction becomes kinetically controlled. Agitation (cylinder rotation) increases the rate of chromium reduction by decreasing the degree of cathode coverage by hydrogen bubbles, consequently increasing the effective cathode area [43, 44]. In this sense it seems that nonstationary currents can be of great

advantage, since the current interruptions and/or current reversal can promote hydrogen liberation [45]. In addition the use of current pulses interrupts the nucleation and resulting crystal growth. Each pulse enables a fresh renucleation with the net effect of refining the structure and size of grains. Grain consolidation appears to interfere with the accumulation of internal stresses and to act as an inhibitor of crack formation, as noted in earlier studies [46].

As reported in a recent paper [35], an X-ray diffraction study was done to identify the predominant species in an industrial CrO_3–H_2O system. Structural analysis showed that dichromate ions may have maximum likelihood, but that linear trichromate ions may also exist in significant concentrations. This study also concluded that formation of a complex shown in (7.6) can be hardly assumed because of steric hindrance and that it is more realistic that one HSO_4^- ion reacts with polychromate.

A recent paper [47] studied the existence of various chromium complexes in CrO_3/H_2SO_4 plating solutions for different $X = CrO_3$/H_2SO_4 ratios. They concluded that although five different chromium complexes exist, the reduction to metal proceeds only from the following type of complexes $[HSO_4]_n^- \cdot [Cr_2O_7]_m^{2-}$, where $n = 1$, $m = 1$, and $25 < X < 150$–200. They concluded that those complexes are characterized by a single hydrogen bond between two ions in the complex.

In another recent paper on chromium mechanisms [48], potentiodynamic and impedance measurements are used to further corroborate their mechanism of deposition, based on formation of a cathode film (with solid and liquid phases) consisting of oxide–hydroxide Cr^{3+} compounds. It is felt that an in situ method is needed to study the deposition mechanisms under both transient and steady-state conditions.

Pressure from environmentalists is leading to research regarding the issue of replacing Cr^{6+} solutions by the less toxic Cr^{3+}. At the same time it becomes obvious that mechanisms of deposition from trivalent and hexavalent solutions are rather intertwined and that in both cases chromium coordination chemistry is heavily involved.

Despite the flurry of research on chromium deposition mechanisms in the 1950s, 1960s, and 1970s, the flow of papers on chromium was later reduced to a trickle. The reason is the complexity of the problem and the difficulties involved in the highly colored, highly concentrated solutions of chromium salts, the number of different valence states involved, and general lack of in-depth information regarding chromium coordination chemistry.

What further complicated the matter is that at the onset of the deposition process one set of reactions occurs—formation of a compact film independent of the anions present with a rather thin profiles, 5 mg m^{-2}. Some Russian workers use the term "product of partial reduction of Cr^{6+} $\rightarrow Cr^{3+}$," and this film forms in the first branch of the chromium polarization curve, at potentials up to about 700 mV. Once this film is formed (the C-film, short for compact film), another cathodic film (layer) is formed on the surface of the C-film and closer to the bulk of the solution—the L-film (short for liquid film).

Yoshida et al. [49] studied the behavior and composition of a cathode film with the help of radioactive tracers in the form of ^{35}S radioactive-labeled sulfuric acid and over-the-counter, high-grade CrO_3 treated with radiation to obtain ^{51}Cr as a tracer. A special, rather simple plating cell was constructed with a rapid rinsing station. In essence, a steel cathode was plated for a short time, so that the C- and/or L-films were formed and could be analyzed. Because the L-film is liquid and soluble in either hot plating solution or hot alkali, by dissolution or simple brushing, its formation and influence on the deposition of metallic chromium was studied. By initially forming the C- and L-films with radioactive-labeled Cr or H_2SO_4 and plating in pure (unlabeled) solution, and vice versa, they came to these important conclusions:

1. The cathode film is composed of two layers with different forming properties in terms of thickness and composition. The outer layer, referred to as the L-film, and the inner layer, the C-film, differ in that the L-film contains sulfate ions and dissolves easily in the electrolyte and is about 10 times thicker than the C-film.

2. The C-film has a mass of about 5 mg m^{-2}, contains very few sulfate ions, and does not dissolve easily in the electrolyte.

3. The cathode film itself is not reduced to metallic chromium, which is deposited from a separate chromium complex compound that passes through the cathode films (C and L) from the bulk of the solution.

4. In the electrolyte, the L-film vigorously repeats the dissolving and forming cycles, while the C-film remains constant, once formed.

5. The cathode film may be a chromium hydroxy *aquo* complex or primarily an oxolated version of this compound. Assuming that the cathode film is formed from such chromium complexes, the authors suggest that the L-film is a compound with lower molecular Weight, while the C-film is a large complex with a high degree of polymerization.

Kimura and Hayashi [50] also used sulfates labeled with radioactive ^{35}S to overcome the difficulties of determining the amount of sulfate in the cathode film. They used standard analytical methods (because of the relatively small content) to study sulfate content in the cathodic film which is formed during potentiostatic polarization of 0.4, 1.5, and 2.5 M CrO_3 baths on Fe, Au, and Pt cathodes. They found that the sulfate content is directly related to the potential in the region of

−0.6 to −1.0 V, which in turn is controlling the state of the cathode surface (L-film formations) and the accompanying electrochemical reactions. In the region of −0.2 to −0.8 V, where current is increasing (C-film), sulfate content was negligible for Pt, Au, and Fe cathodes. In the region > −0.8 V, where current starts to decrease and L-film starts to form, sulfate concentration increases sharply. In the potential regions between −1.0 and −1.1 V (beginning of Cr deposit region), the sulfate concentration in the film drops as a result of liberation of sulfates from the complexes, At potentials more than −1.1 V, the sulfate concentration increases slightly again because of inclusion in the cracks and imperfections in metallic chromium deposits. They also found that as sulfate concentration in a 0.4 M CrO_3 bath is increased from 0.002 M (200 : 1) to 0.008 M (50 : 1), sulfate content in the L-film tends to increase. A temperature increase has a similar effect, while an increase in CrO_3 concentration at constant ratio has the opposite effect. At any given CrO_3 concentration, the maximum amount of sulfates in the L-film is predictably in a 100 : 1 ratio of sulfuric acid. The authors also investigated the influence of other anions in addition to H_2SO_4. Specifically, HCl or KBr (0.01 M) added to 1.5 M CrO_3 + 0.01 M H_2SO_4 solution considerably increased the sulfate content of the L-film, while 0.01 M Na_2SiF_6 addition had the opposite effect, demonstrating the substantial film dissolution effect of Na_2SiF_6. The effects of HCl, KBr, and Na_2SiF_6 on the film were also proportional to increases in their respective concentrations.

Nagayama and Izumitani [51] studied the coordination chemistry of chromium complexes as related to deposition mechanisms. They started with the observations made by Levitan [52] that during galvanostatic ($I = 75$ mA cm^{-2}) chromium deposition from a sulfate-catalyzed bath, a chromic acid dimer is formed together with a polymer of unknown structure as well as mononuclear $[Cr(H_2O)_6]^{3+}$, the stable aquocomplex. Rather than use the galvanostatic method, where current is kept constant and potential changes, they chose to keep potential fixed at −0.75 V [vs. the saturated calomel electrode (SCE)]. Here only $Cr^{6+} \rightarrow Cr^{3+}$ and $2H^+ \rightarrow H_2$ reactions are in progress (for the $Cr^{6+} \rightarrow Cr^{3+}$ reaction to happen, this potential is too positive). During electrolysis (0–60 min) they took samples at different time intervals, and with the use of anion and cation exchange chromatography, they separated the mononuclear, binuclear, and polynuclear Cr^{3+} complexes. They found that the complex formation rate for mononuclear complexes increases linearly with time, while for the other two complexes the rate increase is more gradual. They concluded that each complex is forming at its own constant rate.

They repeated the experiment at −1.10 V (Cr^0 formation region) and obtained similar results. The authors concluded that the cathode layer, made of the dense film of various Cr^{3+} complexes, is a necessary condition for the deposition reaction $Cr^{6+} \rightarrow Cr^{3+} \rightarrow Cr^{2+} \rightarrow Cr^0$ to happen. The catalyst

(e.g., H_2SO_4) promotes formation and dissolution of binuclear and polynuclear soluble Cr^{3+} complexes, thus maintaining a film of constant thickness where deposition proceeds via intermediate Cr^{3+} (inner orbital) complex rather than through the extremely stable $[Cr(H_2O)_6]^{3+}$ (outer orbital) complex.

Okada [53] holds that SO_4^{2-} ions will penetrate an olated compound to form a complex and that from this complex metallic chromium is deposited. According to Okada, reduced solubility of the L-film causes the OH cross-linking level to rise together with the increase in pH.

Yoshida et al. [54] used electron spectroscopy for chemical analysis (ESCA) to further elaborate their previous research, in which they noted that there are two layers, the L- and C-films, within the cathode film. They obtained a depth profile of these films and demonstrated that the C-film is a highly polymerized complex, with very few anions present, if any. The L-film appears to be mostly in the Cr^{3+} state, but the exact valence could not be established, suggesting the possibility of two- and four valence states, as well.

They suggested that Cr^{3+} complexes are the main constituents of L-film and that metallic chromium does not deposit from this cathode film but from the Cr^{6+} state. That contributes to the formation of the cathode film and also forms olated complexes, hydroxy aquocomplexes, and polymers of higher molecular weight. These olated complexes will penetrate the cathode film from the bulk of the solution before being reduced to metallic chromium [55].

7.4 METHODS OF OPERATIONS OF CHROMIUM PLATING SOLUTIONS

7.4.1 Constituents of Chromium Baths and Their Actions

The chromium plating bath, used for decorative and hard chromium baths, is still mostly of the type originally investigated by Sargent. It is the simplest plating bath to make up, and it consists of two essential ingredients: (1) a water-soluble salt of chromium and (2) a small but critical amount of an anion, which for want of a better name is called the catalyst. The catalyst is supplied in the form of sulfuric acid alone or in combination with another acid radical, or anion(s), usually fluoride or fluoroborate or a mixture of them. Relatively recently an organic acid radical in the form of alkene-sulfonic acid [e.g., methane disulfonic acid, $CH_2(SO_3H)_2$, or one of its alkali metal salts] has been successfully included in the high-efficiency etch-free, (HEEF®) formulation introduced by Atotech, Inc. (USA) [56].

Because chromium metal will not serve satisfactorily as an anode, owing to its close to 100% anodic dissolution efficiency, insoluble anodes are used generally as a lead alloy. The source for the chromium trioxide, CrO_3 (chromic anhydride), is commonly referred to as chromic acid. It is a deep

red to reddish-brown crystal that volatilizes at 110°C. It is highly soluble in water (165 g/100 g at 0°C and 206 g/100 g at 100°C), producing a solution containing a mixture of $H_2Cr_2O_7$ and polychromic acids. Many manufacturers are now aware of the effect of even small amounts of catalyst acid radicals, and they furnish a pure grade of chromic acid especially suited for chromium plating. This chromic acid is made to meet specifications that require it to contain not more than a small fraction of a percent of sulfate that is free from other catalysts such as chloride.

A most popular solution containing $250 \, g \, L^{-1}$ chromic acid contains about 50%, or $125 \, g \, L^{-1}$, chromium metal. With complete current utilization, which is never the case, and no losses, 200 g of chromium would be sufficient to cover an about $110 \, m^2$ surface with a deposit $0.156 \, \mu m$ thick.

The conversion of a pure chromic acid into a chromium plating bath requires the addition of a sulfate catalyst. With a given set of conditions of bath temperature, current density, and chromic acid concentration, too low amounts of catalyst will result in either no current flow, at first, or no plate or in an iridescent to brown oxide stain. Too high a catalyst content will result in an adverse effect: either partial plating with poor throwing power or, with great excess, no plate at all. The latter effect is due to depolarization action or easy formation of Cr(III) at the cathode. By increasing the current density and temperature to a sufficiently high value, plating can be accomplished with a very low ratio (up to 10:1). The essential criterion of bath composition for chromium plating from the congenital chromic acid–sulfate solution is the ratio, by weight, of chromic acid to sulfate. This ratio should be kept within the limits of 50:1 to 250:1 and preferably at about 100:1. A ratio of 90:1 is common; ratios of 70:1–80:1 are common in hard chromium baths, especially at higher temperatures.

A typical formula for chromium plating using a sulfate as the catalyst acid radical is presented in Table 7.1.

Although concentrations of chromic acid from about $50 \, g \, L^{-1}$ up to saturation (about $900 \, g \, L^{-1}$) can be used, most commercial baths are operated between 150 and 400 $g \, L^{-1}$. Still higher concentration gives very low current efficiencies. The important requirement is the proper ratio already mentioned.

Baths containing $200 \, g \, L^{-1}$ chromic acid have a slightly higher current efficiency than more concentrated solutions.

They also have a lower conductivity and therefore require a higher voltage for a given current density. The more dilute baths are also more sensitive to the changes of catalyst acid radicals from drag-in and drag-out. Hence they require more frequent and more careful adjustment for maintenance. Usually the more concentrated solutions are favored for decorative applications and the more dilute baths for heavy hard chromium plating.

Silicofluoride has had wide use as a catalyst in chromic acid baths since Fink and McLeese first proposed it in 1932 [8]. Such solutions were difficult to analyze and maintain. Yet those baths have definite advantages compared to sulfate-only catalyzed baths. They have inherently higher current efficiency, can be operated at higher deposition rates, and produce somewhat harder and brighter deposits. Fluorides or rare earth metals give better throwing and covering power. On the other hand, there are some important disadvantages. These metals are sensitive to changes in composition and to impurities such as iron and aluminum, and consequently more careful attention to bath purification, frequent analytical control, and housekeeping are required. Also analytical control of simple or complex fluorides are relatively more complicated, and finally, those solutions will attack or etch the base metal at low current density as well as unmasked areas such as blind holes. If masking is less than optimum, which sometimes cannot be avoided, proper attention must be paid to the possible etching effect. The solutions are aggressive toward plating equipment such as tank liners and heating/cooling coils.

7.4.2 High-Efficiency Chromium Plating Baths

The extra efficiency available from fluoride-containing baths still resulted in chromium deposition rates which, in relation to the high current densities employed, were much lower than for most other plating baths. However, in 1986, proprietary plating solutions were introduced that had higher cathodic efficiencies than obtainable from the fluoride-containing bath and these baths were established as viable industrial processes. They are based on chromic acid solutions which do not contain any fluorides or other halogens. Their chromic acid content is between 250 and $300 \, g \, L^{-1}$. The only other constituent of these solutions which is known is the primary catalyst, which is a sulfate ion, within the ratio of 100:1, and

TABLE 7.1   Basic Chromium Plating Baths

	Dilute Bath		Standard Bath		Concentrated Bath	
	$g \, L^{-1}$	Molarity	$g \, L^{-1}$	Molarity	$g \, L^{-1}$	Molarity
Chromic acid, CrO_3	100	1.0	250	2.5	400	4.0
Sulfate, SO_4^{2-}	1.0	0.001	2.5	0.026	4	0.042

Note: Ratio $CrO_3/SO_4 = 100$.

1–3% of alkene sulfonic acid as secondary catalyst. These proprietary solutions provide extra high cathodic efficiencies of up to 25%. These constituent catalysts have either been patented [56–59] or been kept secret. The properties of the deposits have been documented [60, 61], together with optimum operating parameters of these plating processes. The solutions are usually operated at temperatures between 55 and 60°C and typical cathodic current densities are 30–75 A dm^{-2}. Even at these high current densities, deposit distribution is superior to that obtained from conventional baths, with less edge buildup. The deposits have good hardness (1000–1150 KHN$_{100}$) and retain it better than conventional chromium when heated. The chromium plate always microcracked, having 200–700 cracks per centimeter.

One of the greatest benefits of these fluoride-free plating solutions is that they do not attack steel on those portions of the cathodes where the current density is too low for chromium to be deposited. This low-current-density etching is especially detrimental when complex shaped steel objects are hard chromium plated for a long period of time in fluoride-containing baths. The fluoride ion dissolves the protective oxide film off those portions of the substrate steel exposed to low current densities and thus the acid solution can then dissolve it with consequent iron buildup. This etching attack has been a limiting factor in the use of those baths for hard chromium deposit. Consequently many decorative and hard chromium platers prefer to use either conventional or nonfluoride high-speed chromium solutions despite their lower cathodic efficiency or the HEEF$^{®}$ bath. The ability to plate at higher current efficiencies without this detrimental attack at low-current-density areas has been the major feature of the HEEF$^{®}$ bath, which has resulted in these processes gaining a significant role in the hard chromium plating field.

In practice, relatively high concentrations of chromic acid are used, for example, from 250 to 400 g L^{-1} (33 and 53 oz gal^{-1}) of CrO$_3$. This increase in concentration increases the conductivity up to a maximum but decreases the cathode efficiency. In some cases these two factors, concentration and conductivity, may offset each other at the higher current density obtainable at a given voltage in a more concentrated chromic acid bath and may not yield a greater weight of deposited chromium.

Bright Plating Range   The wide use of decorative chromium coatings depends largely on the fact that under appropriate conditions it is possible to obtain bright smooth deposits at a fair range of current densities. The conditions under which bright deposits are obtainable are often defined as the plating range for bright chromium. This dependence of the appearance on the conditions of deposition makes it necessary in chromium plating to hold the temperature nearly constant. For example, if a decorative bath is operated at 45°C (113°F), this temperature should be kept,

preferably by automatic control, between 44 and 46°C (111 and 115°F).

It is also desirable to keep the current density as nearly uniform as practicable. On flat sheet cylinder rods, or nearly symmetrical articles, there is no difficulty in obtaining a nearly uniform cathode current density. However, on irregular shapes the ratio of the maximum to the minimum current density is usually at least 2, and it may be 5 or larger. The bright range for chromium deposits seldom covers a current density greater than about 3 to 1. Hence with more irregularly shaped articles, it is not possible to produce bright deposits or, in some cases, any deposit in the areas with low current densities without obtaining burnt deposits on the more exposed areas. In all such cases efforts must be made to make the primary current distribution more nearly uniform by (1) conforming anodes, (2) intermediate or bipolar anodes, (3) thieves to detract current from points or edges, or (4) shields to obstruct current to more exposed areas. Much of the success in chromium plating has resulted from ingenious applications of these methods. The acidity of chromium plating baths is very high; it is not ordinary controlled or measured. The measurements that have been made (with glass electrode) indicate values for acidity off the usual pH scale and in the range of small negative values of pH [62].

7.5   MIXED CATALYSTS AND SELF-REGULATING BATHS

If a fluoride, silicofluoride, or fluoroborate anion is added (mixed) into the sulfate-catalyzed bath, a *mixed-catalyst* bath is obtained. Although higher speed and other beneficial effects are obtained, the difficulty of controlling these baths, due to their reactivity analytical problems, speaks against their wider commercial use. Self-regulating high-speed, or simply SRHS, baths, developed by United Chromium, Inc. (now, Atotech), is an attempt to simplify the handling of the catalyst by automatically controlling the CrO$_3$/catalyst ratio by virtue of the solubility characteristics of the chemicals used. The advantages and results to be obtained were described by Stareck, Passal, and Mahlstedt [4, 63, 64]. The influence of cryolite [65], fluoroborate [66], magnesium [67], calcium [68], and ammonium fluoride [69] is presented in the literature. Little is available in the literature regarding the theoretical aspects of the role of the fluorides in electrochemical reactions related to the deposition mechanism [70, 71].

The main advantage of SRHS baths is their higher current efficiency. In addition they are less sensitive to current interruptions, less subject to chemical control, have a wider plating range, yield brighter and slightly harder deposits, and exhibit better ability to activate passive nickel surfaces.

Moderate disturbances of the bath balance, as by drag-in or contamination, are minimized by the nature of the system.

If a fresh catalyst is needed, a reservoir is normally present on the bottom of the tank in the form of undissolved salts, which can be readily dissolved, as desired, by heating and stirring.

When a bath gives low-catalyst results such as good coverage but a dull or rough deposit and it is desired to increase the catalyst concentration, it is only necessary to dilute a little and then stir to reestablish saturation. This yields a slightly higher catalyst concentration, which together with the lower chromic acid concentration gives the desired adjustment.

Similarly, if a bath gives poor coverage and is overcatalyzed, it can be adjusted by increasing the concentration a little and stirring to establish equilibrium. This will lower the catalyst and increase the chromic acid concentration,

Increasing the temperature of a self-regulating bath has two simultaneous effects: (1) The warmer solution has a wider bright range and less tendency to burning, as with ordinary baths, and (2) the increased solubility of catalyst gives a pronounced decrease in ratio. In general, these effects are of about the same magnitude or the latter may be greater. If it is desired to operate at a higher temperature, it may be necessary to maintain a higher concentration so as to balance the increased catalyst content. Conversely, when operating at a lower temperature, some dilution of the bath may be in order.

The first self-regulating bath to be introduced [63] was a simple combination of chromic acid with an excess of low-solubility catalysts, which gave bath systems with a proper catalyst concentration in the range of about 350–400 g L^{-1} CrO_3. In order to produce bath systems with good catalyst balance in lower concentration ranges as 200 to 250 g L^{-1} CrO_3, the solubility of the catalyst salts was suppressed by means of the common-ion effect [64]. Thus, if the sulfate was furnished by saturating the bath with strontium sulfate, the solubility was suppressed by adding strontium chromate or strontium carbonate. Similarly, if silicofluoride was furnished by saturating with potassium silicofluoride, the solubility was suppressed by addition of potassium dichromate. Postins and Longland [72] have briefly discussed the operation of self-regulating solutions containing suppressants.

While formulas are sometimes given in the literature for self-regulating solutions, it should be realized that these are not simple formulations where all the constituents are completely soluble. Generally, the formulas include an excess quantity of catalyst which only partially dissolves.

Romanowski and Brown [73] have patented the use of fluorides and complex fluorides of lanthanum, neodymium, and praseodymium and their mixtures. These rare earth fluorides, especially the silicofluorides, are only slightly soluble in the chromic acid baths and therefore are self-regulating with respect to the complex fluoride ion. The ratio of CrO_3 to SO_4 generally used with these fluorides is about 160 : 1.

A self-regulating bath system was adapted to the production of crack-free chromium deposits by Dow and Stareck in 1953 [74]. This process involves the use of rather high temperature (65°C) and gives smooth, satiny deposits that can be buffed to a higher luster. They are used where a combination of corrosion and wear resistance is required, as on washing machine shafts [75], high-temperature-resistant coatings [76, 77], gun barrels [78], and gas turbine buckets [79]. They have been employed for the decorative plating of zinc die-cast parts without undercoating [80], and two-tone, brushed finishes may be obtained by buffing part of the surface through a mask.

Seyb et al. [81] have developed a self-regulating bath for thicker decorative coatings for bright crack-free chromium plating up to a thickness of 1.3–2.5 μm, compared to the maximum of about 0.5 um which had been used previously. This process was of interest in the search for more corrosion-resistant decorative coatings and had the added advantage of better throwing or covering power than had been obtained previously [82]. Similar procedures were advocated with sulfate-catalyzed baths [83]. Similar procedures were found by Safranek and Faust [84] to give substantially improved corrosion resistance to decorative deposits on zinc die castings when the bright crack-free chromium deposits were 2 μm thick. Wiener [85] confirmed the improvement obtained with bright crack-free chromium.

Complex fluoride catalysts have the advantage of giving higher current efficiencies at higher temperature of operation, whereas sulfate-catalyzed baths decrease markedly in efficiency at higher temperature [86–89].

Bilfinger [90] and Hood [91] discussed the operating characteristics of mixed catalyst baths. Bilfinger's curves of the current efficiency due to sulfate, fluoride, and silicofluoride catalysts are given in Figure 7.3. The best bright plate range is indicated by featherlike markings on each curve.

It should be noted that simple fluoride is a much "stronger" catalyst than sulfate and silicofluoride is much "weaker," thus making its effect easier to control because of the larger quantities required [92, 93].

Fluoride is not only a very powerful catalyst; it is also a very reactive one. The hydrofluoric acid, which it generates in the strongly acid chromic acid bath, is unstable as a catalyst. It will etch glass and dissolve silica in any form, thus converting to the weaker silicofluoride. It combines readily with boric acid, which may be dragged in from nickel baths, and the list of other "complexing agents" is long. A method of determining the relative strength of complex fluoride catalysts by means of the rate of solution of aluminum has been patented [94].

An unexpected behavior of solutions catalyzed largely with fluoride or silicofluoride is that the current efficiency increases with increasing chromic acid concentration in the usual commercial range, whereas in sulfate-catalyzed baths the reverse is true. This behavior is portrayed in Figure 7.4. The main disadvantages of the SRHS solution are its corrosive nature, which shortens the life of the plating equipment
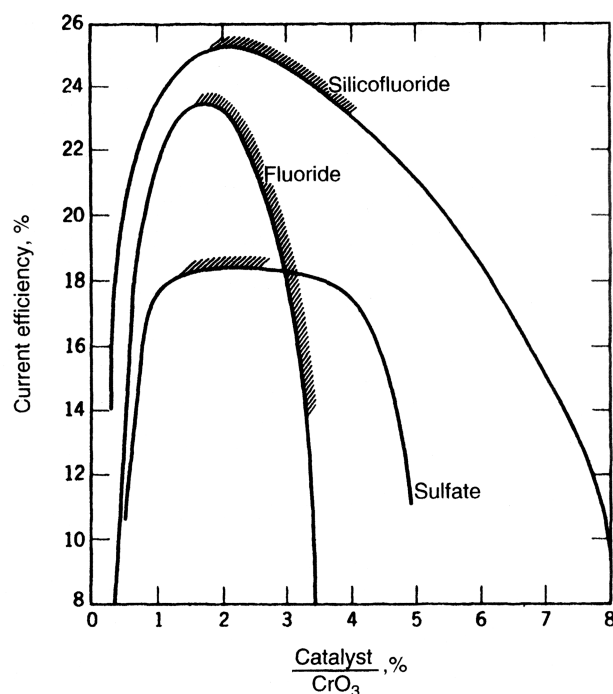
FIGURE 7.3 Chromium plating speed in $250\,g\,L^{-1}$ 100 : 1 solution ($25\,\mu m = 1$ mil).

(e.g., heating/cooling coils), and its sensitivity to the iron, aluminum, boric acid, and chloride contaminations.

7.6 CHROMIC ACID BATHS: OPERATING CONDITIONS

In general, bright plate is obtained by keeping temperature and current density within definite limits, taking into account the chromic acid concentration of the bath and the catalyst ratio. A convenient chart [2] showing the conditions for bright plating is given in Figure 7.2. In that figure the semidashed line A circumscribes the bright plate area for solutions containing about $250\,g\,L^{-1}$ CrO_3, and the dashed line B circumscribed by the line X is typical of the behavior of most chromium plating baths. Thus, to produce bright deposits from a solution containing $250\,g\,L^{-1}$ chromic acid and
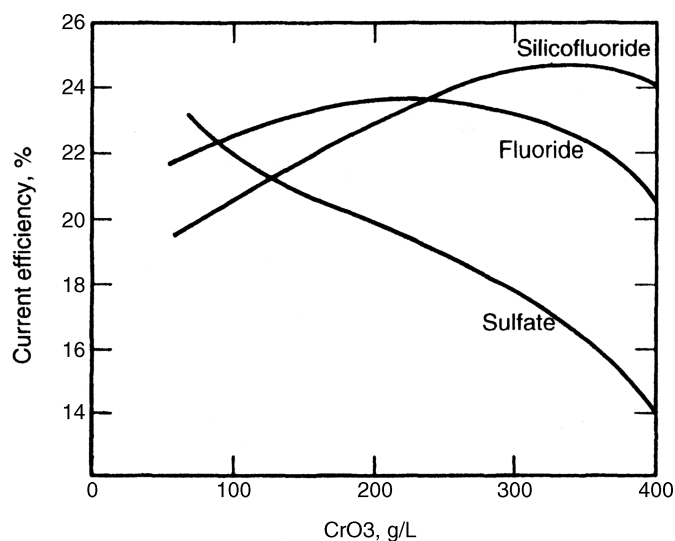
FIGURE 7.4 Chromium plating speed in $400\,g\,L^{-1}$ 100 : 1 solution ($25\,\mu m = 1$ mil).
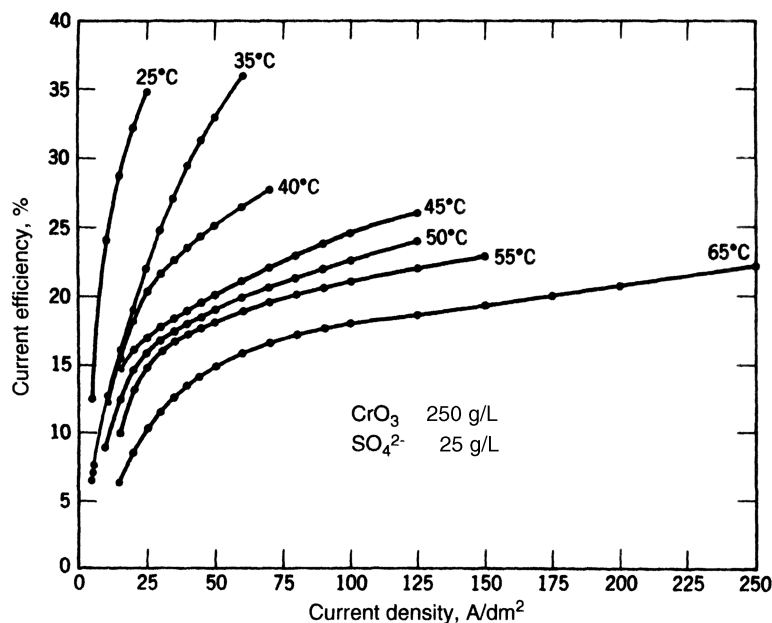
FIGURE 7.5   Current efficiency in $250 \, g \, L^{-1}$ CrO_3 bath with sulfate, fluoride, and silicofluoride catalysts.

$2.5 \, g \, L^{-1}$ sulfate at a temperature of $40°C$, cathode current densities between 3 and $16 \, A \, dm^{-2}$ must be used; at $45°C$ the current densities must be 50% higher.

If faster plating is desired and sufficient dc power is available, the temperature is often increased to about $55°C$ and the current density to about $30 \, A \, dm^{-2}$. These conditions, when used with the $250 \, g \, L^{-1}$ solution for building up a heavy plate for industrial purposes, result in a plating speed of almost 25 μm of chromium per hour. Higher plating speeds

can be obtained at higher current densities at $80:1$ ratio, but the deposits are prone to become slightly rough and nodular, which presents no problem if the parts are going to be ground.

Figures 7.5–7.8 [95] show the current efficiencies and plating speeds of two chromium plating solutions as determined in the laboratory. Actual speeds in production plating will not conform with these exactly because shop conditions never exactly duplicate laboratory conditions. Other current efficiency data were published by Griffin [96].
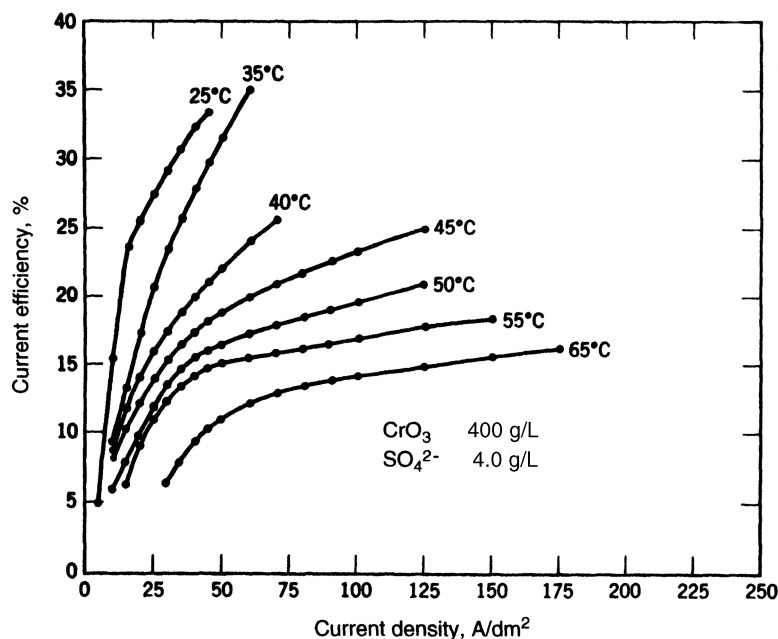
FIGURE 7.6   Current efficiency versus CrO_3 concentration.
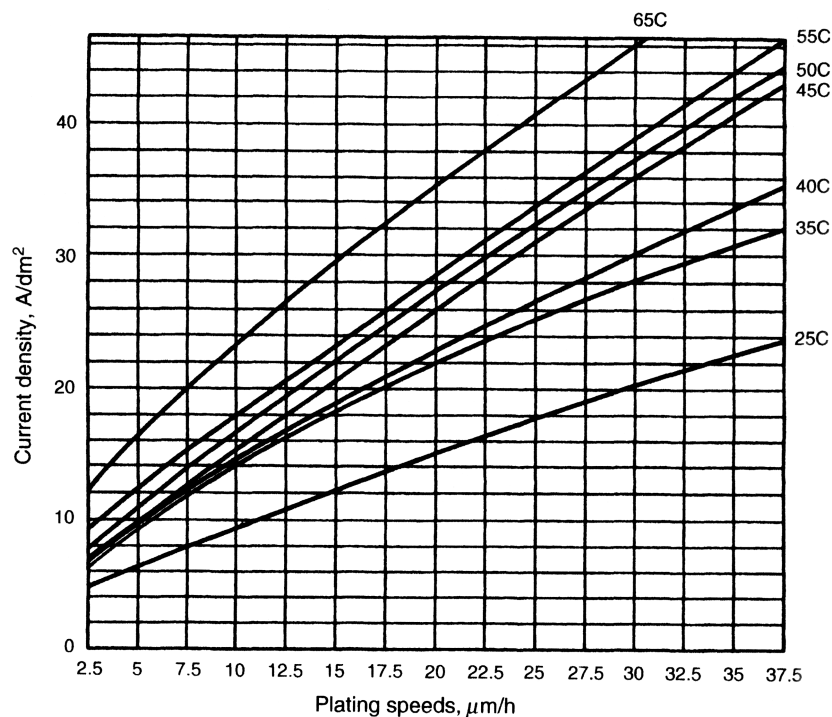
FIGURE 7.7 Current efficiency in $250\,\text{g}\,\text{L}^{-1}$ CrO_3 bath.

The current efficiency increases regularly as the concentration of CrO_3 decreases down to $75\,\text{g}\,\text{L}^{-1}$. The average increase in efficiency on diluting the solution, with a $100:1$ ratio, $55°C$, and current density $30\,\text{A}\,\text{dm}^{-2}$, was about 0.25% per $10\,\text{g}\,\text{L}^{-1}$ decrease in concentration of chromic acid [97]. These figures are useful in calculating the plating speed variation with small changes in chromic acid concentration.
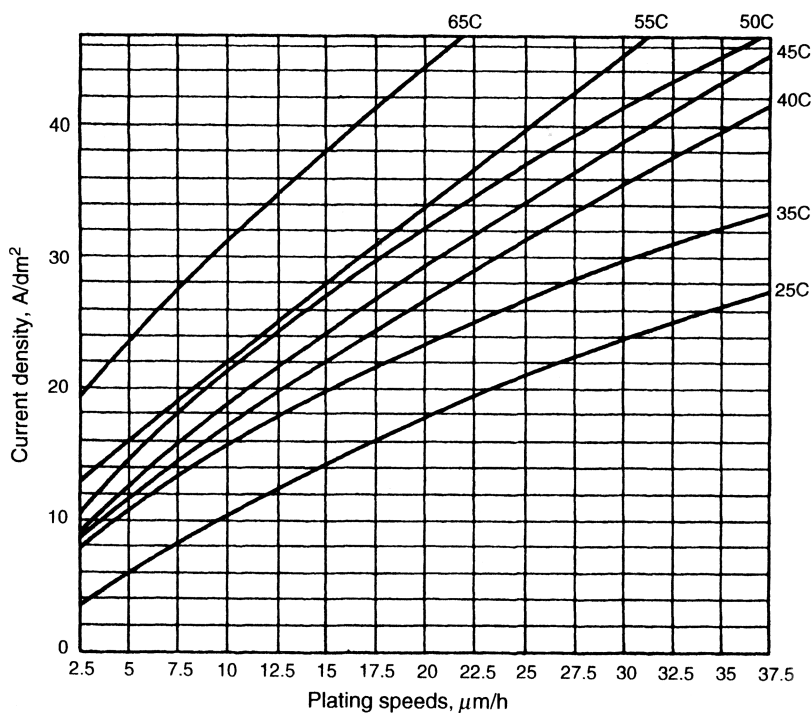
FIGURE 7.8 Current efficiency in $400\,\text{g}\,\text{L}^{-1}$ CrO_3 bath.

The acidity of chromium plating baths is very high; it is not ordinary controlled or measured. Those measurements that have been made (with glass electrode) indicate values for acidity off the usual pH scale and in the range of small negative values of PH [98]. (See Fig. 7.1.)

7.7   THROWING POWER

The poor throwing power of chromic acid plating solutions frequently refers to three different but related phenomena: (1) covering power, (2) throwing power, and (3) bright plating range, previously discussed. By virtue of their effectual interrelation, the terms "covering" and "throwing" power are at times erroneously used synonymously, perhaps because plating baths with poor throwing power generally exhibit poor covering power and vice versa.

7.7.1   Covering Power

The covering power (CP) of chromium plating solutions refers to the ability to initiate deposition over the entire cathode surface at varying current densities (CDs). While other plating baths may permit metal deposition at very low current densities, chromium will not generally deposit below $1\,A\,dm^{-2}\,(10\,A\,ft^{-2})$, depending of course on specific plating conditions. Below the critical density, a manyhued nonmetallic deposit is sometimes formed. It has the appearance of a rainbow—a pleasant name for a troublesome phenomenon. According to Pan [99], angle cathodes with different angles and various side lengths, slotted cathodes, and slit cells are normally used to determine the covering power.

The covering power depends on the electrolysis conditions and on its nature, any pretreatment, and the surface condition of the base metal. CP improves with increasing CD, and this fact is used particularly for chromium plating. Thus for a short time the plating is carried out at higher than normal CD ("strike" or "covering" current). Then plating is continued at normal CD, as soon as the part has been completely covered with a thin chromium layer. The CP of the chromium bath is less on aluminum and aluminum alloys, for example, than on copper or iron, although it can be improved by the use of an appropriate intermediate layer. On iron, it is better than on copper or nickel.

7.7.2   Throwing Power

The ability of a plating bath to uniformly deposit metal on the cathode surface is a measure of its throwing power (TP). The major factors influencing TP in a chromium plating bath are the primary current distribution, polarization, secondary current distribution, and cathode efficiency. The primary current distribution is a function of the geometrical properties of the system, that is, the shape and distance of the anode to the cathode. The electrochemical properties of the system trans-form the primary current distribution into the secondary current distribution, which is determined by all the factors that influence the polarization during chromium deposition. Polarization is the change in potential on the cathode, which is mainly due to concentration gradients and the rates of electrochemical reactions, and in the case of chromium it is fairly constant. In general, polarization increases with an increase in CD. As the polarization becomes greater at the projected (higher CD) areas, the net result is a more uniform secondary current distribution. Unfortunately, in chromium plating, the cathode efficiency increases with the CD, and its effect on metal distribution can counteract any benefit of polarization. In the operation of a chromium plating bath the TP is generally improved by increasing the bath temperature and plating CD. As opposed to covering power, higher ratio baths have a tendency to improve TP. Increasing the anode-to-cathode gap is helpful, but this usually requires higher operating voltages; an initial high strike current may be necessary in order to obtain adequate coverage. On irregular cathodes, the CD varies widely, being highest on corners, edges, and areas closest to the anode; it is lowest in recesses, reentrant angles, concavities, and areas farthest from the anode. It is then evident that cathode efficiencies being highest at the high-CD areas result in heavier deposition, whereas the low-CD areas have thinner deposits.

Consequently the major variables connected with throwing power in bright chromium plating are the current efficiency and the bright plating range. If a certain set of conditions gives the widest possible bright plate range, and the plating is done at an average cathode current density near the upper limit of current density for this bright plate range, optimum throwing power will be attained.

In the conventional throwing power cell, cyanide copper plating baths with good throwing power generally have a rating of around 20–40%, whereas most nickel plating and acid copper plating baths have a rating near zero. The throwing power in chromium plating has been found to vary from around -13% under the best conditions to -100% and even lower [7, 97, 100]. The relative throwing power of chromium plating baths is often estimated by an empirical test as the Hull cell test, described in the next section.

7.8   METALLIC IMPURITIES

They are two general classes of impurities in a chromium bath: (1) inorganic impurities such as chlorides, excess of sulfates or fluorides, boric acid, and organic matter and (2) metallic impurities. The former are most common in the form of detrimental impurities such as iron, copper, and zinc. These metals enter the solution from parts accidentally dropped into the bath and not recovered, attack of the solution on racks and fixtures, attack on anode or cathode bars, and corrosion of plating tanks through pinholes in the tank

linings. The maximum acceptable concentrations of these metals will depend somewhat on the overall bath composition and the type of work being processed. However, approximate limits are $15\,g\,L^{-1}$ for iron and $0.2\,g\,L^{-1}$ for copper. At or near these concentrations, copper and iron will restrict bright coverage in low-CD areas. It should be noted that harm done by metallic impurities is very much synergetic; while one impurity alone even at high concentrations is not necessarily highly damaging, a combination of impurities even with less total concentration certainly is.

Other cations that may commonly be present in chromium plating baths include Cr(III), which usually results when baths are operated with too large a cathodic area and too small an anode area or when organic matter is introduced. The Cr(III) content can be kept down by increasing the area of the lead anodes used relative to the cathode area or, where this is not practical, by electrolyzing the solution for a time with a relatively large anode area and a small cathode area.

Of all the impurities that can be present, Cr(III) is particularly detrimental, although contrary statements have been made [101]. The tradition has emerged that a small amount of Cr(III) is beneficial when added to a new bath. This is due to making such additions in the early days in the form of chromic sulfate or chromium hydroxide precipitated from chromic sulfate and containing some sulfate, thus affecting the catalyst content of the bath. A number of investigations have failed to indicate any improvement in new baths with the addition of small amounts of Cr(III), and there is no need to electrolyze a properly made up new bath for this purpose.

Buildup of metallic impurities can be corrected only by two procedures: discarding a portion of the bath (only as a last resort) and sending it to the authorized landfill or purification through a properly selected method [102]. The rapidly growing problem of chromium waste disposal has both helped and aggravated the problem of metallic contamination. Extensive use of drag-out tanks or the use of closed-loop systems accumulates and concentrates the impurities in the bath that might otherwise reduce itself in normal drag-out. On the other hand, the incentive for the plater to install chromium recovery and reclamation units has given many plants the facilities for electrolytic, selective membrane, or ion exchange treatment of contaminated baths.

Periodic checks with a magnet and, if nonferrous parts are processed, periodically pumping out the bath should be performed on any chromium installation to determine and remove fallen or broken anodes, processed parts, racks, tools, sludge, and the like.

7.9 MAINTENANCE AND CONTROL

Chromium plating baths are very stable in use, and their composition can be readily maintained by physical analysis or by more accurate chemical or instrumental analysis. If the bath is meant to be operated faultlessly, continuous correction in the control of bath composition is inevitable. Since chromium deposition is sensitive and controlled by such small amounts of catalyst, it was recognized even in the early times that maintaining the proper catalyst ratio is of utmost importance.

Analysis of the catalyst concentrations in such small range, while routine to the fully equipped analytical laboratory, are complicated and of debatable accuracy for the average electroplating plant setting. Even if this were not the case, the validity of such tests is often subject to questions, in view of the fact that a bath's operating characteristics depend on the effect of the concentrations of the total catalyst content in the bath. Analysis for sulfate alone may neglect traces of chlorides, fluorides, and so on, which mole for mole have a much more marked effect on the bright electroplating characteristics from a similar bath using high-chloride-content tap water.

Analysis for sulfate content can be a complicated procedure. The simplest procedure is to use the centrifuge method. This method is adequate for routine control and, if desired, may be checked occasionally by the classic but more elaborate gravimetric method given in the literature [103–106]. Since gravimetric methods require equipment that may not be available in the average electroplating plant laboratory, the straightforward titrimetric method may be of value [107]. It requires no special equipment and it is relatively fast. The most accurate is the ion chromatographic (IC) method [108, 109].

Analytical testing methods for radicals other than sulfate are quite complicated, which is one of the drawbacks of these solutions. Data on these testing methods can be found in the literature or in the process manuals of a particular solution supplier. Organic catalyst determinations, as in the case of HEEF®-25, need an accurate, reliable, and rather specialized equipment, which is the ion chromatograph. This elegant instrumental technique can simultaneously determine many common ions. The attractive feature of the IC method is for process control, where in a matter of a fraction of an hour, CrO_3, sulfates, fluorides, silicofluorides, and chloride anions can be determined in a single experiment [110]. The separation mechanism is based on differential absorbency and affinities toward the material used in the anion-separating column. Concentration of each anion is determined with highly selective conductivity detector. Trivalent chromium is determined in the cation separation column using an ultra-violet detector. For determination of alkenesulfonic acids, which are constituents of modern high-speed baths, this is the only practical method. These analyses are usually performed by the supplier.

Chemical analysis for the chromic acid content is not an excessively complicated procedure, and typical methods can be found in the literature. Hydrometer readings based on the

density of the solution are a common and quite accurate method of chromic acid determination in new and relatively pure baths. A wide difference in hydrometer compared with analysis readings is not inevitable. Unfortunately, this is the case in most baths which, with age, build up in trivalent chromium, metallic, and organic impurities. Thus daily or at least weekly hydrometer checks, coupled with a periodic analytical determination, will form an acceptable and reliable control procedure for a chromium bath if done frequently enough. The standard hydrometer, calibrated to read solution density or, better, to read directly in ounces per gallon of chromic acid at the normal bath operating temperatures, is an essential tool and can be placed directly in the bath. The specific gravity is a good indication of the chromic acid content with new baths, but it may show considerable deviation as the bath is used and accumulates metallic impurities. Sulfate is often determined centrifugally, but this method is not always reliable. Excess sulfate is commonly precipitated by the addition of barium carbonate, but it can also be counterbalanced by the addition of chromic acid, if convenient.

In the absence of silicofluoride-containing chromium, plating baths were found difficult to analyze and control. Many methods were proposed, but they were not generally dependable for the total fluorine content. There is considerable confusion and inaccuracy in the literature about fluoride- and silicofluoride-containing chromium baths. Despite the difficulties, present-day silicofluoride-containing baths with or without self-regulating features still have more than compensating advantages. The estimation of fluorine can be done in a comparatively simple method with the aid of a fluoride-sensitive electrode [62].

Probably in no other electroplating solution, except perhaps that of bright nickel, is the value of electroplating tests greater than in chromium baths. In most electroplating baths, control tests (e.g., the Hull cell) are important additions to chemical analysis. In chromium baths, when properly employed, control tests can supersede and often eliminate some of the routine chemical analysis. The reason for this is the extreme sensitivity of the bath to relatively minute changes in catalyst content. A standard bath with of $2.5\,g\,L^{-1}$ of sulfates will exhibit detectable narrowing or widening of the bright electroplating range when this concentration is altered 10% $(0.25\,g\,L^{-1})$ or a mere $250\,ppm$. The interpretation of the Hull cell or other electroplating cell panels requires only a moderate amount of experience and average amount of skill. It is an invaluable toot for day-to-day solution control, especially for troubleshooting.

Hull cell electroplating tests are fast, effective, and rather simple [111–114], On the other hand, the chromium electroplating operations that thrive on excellence should also employ advanced versions of electroplating cell tests like hanging Hull cell, jiggle cell, and rotating cathode cell [16–20]. The ultimate testing cell accomplice is the hanging Hull cell, which eliminates the major drawbacks of the regular Hull cell, namely a lack of correlation with actual bath agitation, preplating cycle, and possible rectifier ripple, bipolar effects, and stray currents. Since the hanging Hull cell operates directly in the electroplating solution, a much closer picture of the actual electroplating range present in the bath is obtained from these test panels than from the laboratory-type Hull cells.

Some of the chromic acid is reduced to Cr(III) concentration at a relatively low figure under usual operating conditions, especially if the area of the lead anodes is sufficient [115]. If iron or other nonlead anodes are used for special purposes, they do not reoxidize the Cr(III) to chromic acid as well as do lead anodes, and a higher equilibrium concentration of Cr(III) is reached after the bath has been used for some time. Furthermore these other anodes, unless highly insoluble as lead, introduce contaminating metals such as iron into the solution and therefore should generally be avoided. A rise of Cr(III) content can be seen by darkening of the color of the solution.

Wetting agents are frequently used to suppress the mist of solution carried into the atmosphere by the hydrogen evolution at the cathode, rather than to prevent pitting as in other plating baths. A great variety of wetting agents have been developed to minimize the fumes evolved during plating; the prospective user of such compounds should satisfy himself about their stability under his or her particular conditions. If they are used, surface tension measurements may become desirable for control, although visual observation of the fume suppression or amount of foaming may be sufficient.

Due to the high oxidizing power of chromic acid, plating baths are seldom filtered, although filtering has been recommended [116, 117]. If some clarification is desired, it can be accomplished by settling overnight and decanting. If desired, a chromium solution may be filtered through a pad of glass or through a fiber glass filter cloth. Filtering cloths of Vinylite (Vinyon) and Saran are also available and have substantially complete resistance to chromic acid.

7.9.1   Anodes

While it is possible to use anodes made of solid chromium, there are four serious objections; (1) Chromium anodes are much more expensive than chromium purchased in the form of chromic acid. (2) Chromium metal dissolves with much higher anodic efficiency (85–100%) than the prevailing cathode current efficiency (12–24%) and hence rapidly increase the chromium content in the bath. (3) Unlike lead anodes, there may be reoxidation of Cr(III) to Cr(VI), an unfortunate reaction that proceeds in parallel with the main, chromium deposition reaction. (4) No metal can match ease of lead for forming and joining together ("burning") when making conforming anodes.

While many anode materials such as iron, steel, stainless steel, nickel, and titanium can be used for special purposes, as auxiliary or conforming anodes, they are unsatisfactory for extended use, since they dissolve and contaminate the solution and also increase the Cr(III) content. Although pure lead can be used for its ease for conforming, platers generally prefer more corrosion-resistive anode material, such as lead alloyed with silver, tin, or antimony. Many anode materials other than lead alloys have been tried, but nothing better has been found [119]. Recently, it was revealed that bismuth-doped lead anodes can triple the anodic reoxidation of Cr(III) [120]. Pure iron, such as Armco or electrolytic iron, dissolves less when used as an anode than steel, nickel, stainless steel, or similar alloys. Iron anodes have occasionally been used, particularly in industrial chromium plating, in special instances where greater strength and rigidity than are obtainable with lead are desired. Their continued use, however, leads to the accumulation of iron and Cr(III) in the bath. Small platinum wire anodes can be used for special purposes, such as plating the insides of very small openings, such as those of wire-drawing dies. Antimonial lead anodes are preferable to chemical lead due to the greater corrosion resistance and strength, but they do not eliminate the formation of copious amount of lead chromate sludge. Lead–tin alloys have higher corrosion resistance but less rigidity than antimonial lead anodes, and these are widely used. A good compromise is achieved by using Pb–Sb–Sn ternary alloy. The best are silver containing lead and lead alloys [121], but they are more expensive. Those anodes not only have the advantage of increased durability but also give quick or immediate startup after downtime without special reactivation.

Lead and lead alloys serve two key functions in the chromic acid plating bath: (1) They provide effective current distribution and (2) reoxidize Cr(III) to Cr(VI). Lead peroxide film, which forms on these anodes during use, causes continuous reoxidization of the Cr(III), forming chromic acid and thereby keeping its concentration at a low, acceptable value [122].

Lead and lead alloy anodes of varying shapes and cross sections have been proposed and used from time to time. They have to be thick enough to conduct the high currents required. Anodes that are too thin will overheat in use and will corrode and warp excessively. This difficulty can be avoided by the use of solid round copper core in the center of lead anodes. The copper core aids in rigidity and securing good current distribution because considerable current can come from the back as well as the front.

Auxiliary conforming anodes are sometimes used in hard chromium plating or through the complete cycles of decorative plating. Improved coverage is obtained on difficult shapes, and more uniform plate distribution is achieved on large surfaces where a minimum plate thickness is required, as for the production of microcracked chromium. Pure nickel anodes are perhaps the best for this service, and cast nickel is sometimes used to produce a number of anodes of a special shape. Platinized titanium anodes are also used for this service, but they have the disadvantage of a limited life and insufficient indication of when they are becoming inoperative, except for increasing rejects. Nickel dissolves slowly in use and can be replaced when visibly worn away.

Lead anodes used in chromium plating cannot have too heavy or irregular a coating of lead dioxide on them or the current distribution may be affected. It is beneficial to clean the anodes regularly, especially those used in heavy hard chromium plating that conform closely to the article being plated. The cleaning is done by acid dips and scratch brushing, but the process is difficult and time consuming; frequently not all the semi-insulating coating is removed. Hyner [123] developed the method of electrolytic reduction of the coating to metallic lead by cathodic treatment in an alkaline pyrophosphate solution. Lead anodes coated with lead dioxide tend to become somewhat passive after standing idle for some time. Some platers would electrolyze the bath with full tank voltage from several minutes to an hour for reactivation in order to reestablish the original conductivity. However, other platers found it unnecessary to do this. This passivation tendency, investigated by Hardesty [124], is presumably due to the insulating effects of insoluble lead compounds such as lead chromate and lead fluoride. The only way found to avoid this effect, aside from recleaning as described, is to remove the anodes from the tank promptly after use and to permit the solution to dry on them rather than rinsing it off. This gives good results but is not always practical. Platinized titanium anodes with thermally deposited indium dioxide are proposed [125]. Titanium anodes coated with PtO_2 are recently recommended for chromium plating [126]. Practical experience with platinum-plated titanium anodes in chromium plating solution is described [127].

7.9.2 Materials of Construction

Most tanks for chromium plating are made from steel and lined with some kind of acid-resistant material. In the past, chromium plating tanks were made of lead or antimonial lead-lined steel. Acid-proof brick linings have also proved very satisfactory for chromium plating tanks made of steel [128], although they are seldom used any more. The type of lining now used, which gives satisfactory service, consists of flexible synthetic resin sheets (plasticized polyvinyl chloride, PVC) cemented to the steel tank and welded at seams and corners. This type of lining saves space compared to a brick lining but is generally not recommended for temperatures above 60°C. Special insulating materials of the vinyl type (Corroseal) haw; been developed [129] to withstand the action of hot chromium plating solutions and thus have good mechanical properties. These insulators are used in sheet, rod, tube, tape, and other solid forms in the construction of composite racks and in liquid

form for coating ordinary racks or for stop-offs. The use of insulated racks results in a saving of power and chemicals and gives much better plating. Microcrystalline, high-melting paraffin wax and still higher melting chlorinated naphthalene wax compounds are also used for stopping off in industrial chromium plating.

Tanks can be heated and cooled by lead alloy coils submerged in the solution. Titanium, columbium, tantalum, Teflon, or Teflon-coated stainless steel coils and heat exchangers have come to be used extensively for their extremely long life and efficient operation. More durable than titanium, tantalum is probably the most suitable material. Its high initial cost can be justified by a long period of trouble-free operations. Titanium coils are not the best choice for fluoride-based solutions.

Owing to the relatively high current densities used in chromium plating, it is necessary for all compounds of the circuit to be of sufficient size to carry the amperage required without overheating or excessive voltage drop. The plating tanks have to be of such a size that the parts can be positioned 10–25 cm (4–10 in.) from the sides and the bottom of the lank as well as from the surface. When designing the tank and the rectifier's capacity, consideration should be given to an ideal current loading of l–1.5 AL^{-1} of the tank volume. This will save energy required for heating and cooling in improperly designed tanks.

7.9.3   Safety and Health Considerations

The chromium metal and trivalenl chromium compounds are nontoxic in comparison with the much more hazardous sixvalent compounds. The chromic acid is sharply irritating and corrosive to the mucous membranes of the nose and throat. This spray therefore requires removal or suppression to protect the workers and equipment, and adequate exhaust facilities must be provided for the purpose. Carcinogenic factors are also suspected. Skin contact can cause ulcers and dermatitis; different persons may react differently to dermatitis effects. Chromium plating solutions emit mist as they are used. The mist contains, in addition to hydrogen and oxygen gas, basically the same ingredients as the plating solution and therefore presents a health hazard to the workers and the community. The mist must therefore be captured and removed from the air and the tank to protect the workers and equipment, and adequate exhaust facilities must be provided for the purpose. The U.S. Environmental Protection Agency (EPA) regulates the amount of chromium that may remain in the air discharged from hard chromium plating facilities with different levels for large new facilities and for small facilities.

Many measures have been proposed to replace or supplement the necessary exhaust hoods and to prevent some of the chromic acid and heal losses these entail. The proposed use of a layer of floating plastic beads [130, 131] or of stable wetting agents may in some cases offer a partial solution to the problem, but they may not make it possible to dispense with an adequate exhaust system. The development of completely stable perfluorinated sulfonate wetting agents [132, 133] made an important difference. They are effective in reducing the emission between 93 and 98% depending on the operating conditions and the type of foaming/wetting agent used. These wetting agents would not induce but may accentuate basis metal pitting in thick, hard chromium plating deposits [117, 134–137]. Their use is quite widespread in decorative baths and permit economies in chromic acid and heat losses, among other advantages. Floating balls pose the problem of traveling from tank to tank and also can become stuck in the crevices of the parts.

Studies of industrial dermatitis arising in workers exposed to chromates or chromic acid have been published [138, 139]. The remedies suggested include avoidance of contact with the irritating chemicals, cleanliness, thorough washing, use of protective and healing salves and ointments, and visits to a physician when necessary.

The disposal of wastewaters containing chromic acid is a problem of increasing importance [140, 141]. Chromic acid-based plating solution also presents a fire hazard when in contact with organic matter such as paper.

7.9.4   Bulk Chromium Plating

Chromium plating barrels of both the batch and continuous types have been described [142–145] and are operating successfully in a number of plants. The barrel plating time, for decorative purposes, is about 5–10 min, but heavy hard chromium plates can also be reduced in the barrel by using longer plating times [146]. Deposition from trivalent baths has been recently described [147]. Round or cylindrical articles, which roll easily, that are not too light lend themselves best for barrel plating. The lower limit is about 3 g, although the most important aspect is the ratio between area and weight. The preferred solution is sulfate-free chromic acid baths containing silicofluorides as a catalyst. This solution has the lowest threshold current density requirement (as low as $0.6\,A\,dm^{-2}$), has relatively the best activating properties, and can withstand short current interruptions, which occur repeatedly when plating in a barrel. Small parts such as screws, nuts, bolts, and rivets can be chromium plated in wire mesh baskets or by stringing them on wires. Stringing on wires or racking is convenient for articles of moderate size, perhaps 25 mm long or longer. For basket plating, horizontal copper wire mesh trays are generally used with a rim about 13 mm high soldered to a frame for suspension from the cathode rod. The small parts should be spread in a thin layer on a tray so that they do not cover each other. They are typically plated, at as high a current density as possible without burning, for 5–10 min. Generally the entire basket is shaken or jarred a little a few times during plating or even rotated to cause the parts to shift position and avoid contact

marks. Flat articles, which fit closely on top of one another, do not lend themselves readily to basket plating.

7.9.5   Preparation of Basis Metals

In order to ensure the satisfactory adhesion of chromium deposits, the parts must be almost perfectly clean and free of any grease. If parts are transferred from nickel or other baths to the chromium bath without unmerited delay, only an acid dip and a water rinse may be enough. On the other hand, if the nickel is buffed or the parts are handled or stored for a time, further treatment may be necessary before chromium plating.

The cleaning of work to be chromium plated for bright or decorative finish (as distinguished from work for thick deposits or for industrial applications) may be divided into tree general classifications—solution cleaning, dry cleaning, and vapor degreasing. Typical solution-cleaning procedures are detailed in the chapter on preparation for plating. Dry cleaning consists of wiping the work on a buff wheel or by hand with pumice powder without dipping it in solutions of any type.

Where solution cleaning is feasible, it generally gives better results than dry cleaning. It helps to remove any oxide or tarnish on a nickel surface, whether visible or invisible, and results in ''activating'' the nickel or making it easier for chromium plate. Nickel surfaces are considered ''passive'' if they are oxidized and difficult to cover with bright chromium plate. Cathodic alkaline cleaning is quite effective in removing this condition if it is not too severe. Acid dipping is even more effective. Typical acid immersion procedures for maximum nickel activation are as follows:

1. Chemical activation in 30–50% (volume) HCl for 30–60s
2. Chemical activation in 5–20% (volume) H_2SO_4 for about 2–5 min
3. Cathodic activation in 5% (volume) H_2SO_4 at 4–6 V for about 15 s

Where wet cleaning is not feasible, the plater must sometimes resort to dry cleaning. Success of this procedure depends on the fact that the chromium plating solution itself serves to some extent as both cleaner and acid dip. The vigorous evolution of gas during plating, together with the strong cleansing action of the hot chromic acid, tends to remove light soil films. If the dirt, grease, and oxide are excessive, the cleansing action of the plating solution is overtaxed, with the result that the chromium plate is defective.

The importance of a satisfactory wet cleaning procedure for nickel surfaces has been confirmed by Tucker and Flint [148]. They reviewed some of the previous work in the field. Cathodic electrolytic cleaning is also helpful, and special solutions and procedures are sometimes used [149].

Mandich recently discussed the practical and theoretical aspects of nickel and chromium activation as well as chromium reverse etching [150]. Anodic cleaning in the usual alkaline cleaners must be scrupulously avoided, since it tends to oxidize nickel surfaces and make them impossible to chromium plate.

Plating over stainless steel also requires wet cleaning and activation. The surface should be freshly buffed and not be permitted to stand from one day to another. Often it can be placed after a short dwell time, particularly if a silicofluoride-type solution is used under conditions of higher than normal catalyst concentration or low ratio and high temperature. Heavy chromium deposits used in industrial or hard chromium plating usually require extraordinary good adhesion to the basis metal because the plated articles are often subject to severe stress in service. A high degree of adhesion of chromium to steel is the normal result of plating in a hot chromic acid bath, but adhesion tendencies can best be treated using electrolytic cleaning or etching of the steel surface before chromium plating. A satisfactory etch for steel parts is obtained by setting the anode at 6 V for about 1 min in chromic acid solution or in the plating bath. Anodic etching in sulfuric acid (sp. 1.53g) at about 25°C for about 1 min gives the highest adhesion. Similar results are obtained by electropolishing [151]. Additional details for the preparation of steel for heavy chromium plating are given in a recommended practice of the American Society for Testing and Materials (ASTM) [152], Greenwood [153], Morisset [154], Guffie [155], Peger [156], and Mandich [150]. Levy [157] and Johnson Dini [158] give procedures for plating on some special alloys.

Zmihorski [159] has investigated the adhesion of heavy chromium deposits on steel by means of a shear test; he found that an adhesion of about 40 to 45 kg mm^{-2} is obtained by the usual hard chromium plating procedures. He also found that etching in sulfuric acid gives somewhat better adhesion than etching in chromic acid, that a low current density gives somewhat better adhesion than high current densities, that thin deposits are better than thick, that deposits from pure solutions containing no iron and Cr(III) are better than those from contaminated solutions, that silicofluoride solutions are better than sulfate solutions, and that heat treatment appears to have no effect on adhesion.

The adhesion of thick chromium deposits is difficult to measure because it is commonly greater than the tensile strength of the coating, which will fail before it can be pulled off the base metal. Williams and Hammond [160] made direct measurements on the range of 16–32 kg mm^{-2}. Beams [161] used a centrifugal force method. Chessin and Poor [162] first used an indentation method for adhesion and later [163, 164] developed a ''push-out'' test in which a 6-mm-diameter hole was pushed out of the basis metal from underneath the coating, and the nature of the fracture around the hole was examined. Dini and Johnson [165] described a

"flyer plate" test for measuring the adhesion under dynamic conditions. Methods for measuring adhesion have been critically reviewed by Davies and Whittaker [166] and Ploog [167].

High-carbon cast irons and steels may be difficult to chromium plate directly if acid pickled before plating. Pickling apparently develops a low-overvoltage surface which makes it easy to deposit hydrogen and difficult to plate chromium. It is therefore recommended that acid pickling be avoided in such cases and that sandblasting or other methods of cleaning be used.

Zinc and zinc-based die castings are commonly chromium plated for decorative purposes after previous copper and nickel plating. If the castings are satisfactorily nickel plated, the chromium plating is the same as for any other nickel-plated basis metals. If the nickel plate, directly applied on a zinc-based article, does not completely cover it or is too thin, it will be difficult or impossible to deposit chromium at or near the bare or thin points. A remedy for such a difficulty is to plate a substantial thickness of copper under the nickel. There is a certain amount of chromium plating directly on zinc die castings, generally for wear purposes.

7.9.6 Hard Chromium Plating

Dubpernell's book treats the behavior of the sulfate- and fluoride-type catalysts [168]. Morriset [6, 169], and Weiner and Walmsley [170] have published some general books on the subject. Practical plant manuals have been published by Greenwood [171, 172], Guffie [155], and Peger [156]. Dennis and Such [174] covered both nickel and chromium plating in their book. Racking for hard chromium plating is well elaborated by Logozzo [175] and Peger [156]. Mandich treated practical problems in hard chromium plating in a series of papers [176].

The success of the chromium plate in industrial applications may be attributed to its unique combination of properties not possessed by any other single material available commercially. The most important of these are hardness, adhesion, corrosion resistance, nongalling and nonwetting qualities, low coefficient of friction, and high melting point. These properties make hard chromium invaluable for industrial and engineering purposes. The hardness alone, although approaching that of diamond, would not be sufficient to secure widespread use, because a number of other hard materials or hardening processes are available. It is the combination of very high degree of hardness with extremely good corrosion resistance (equal or even superior under most conditions to that of gold or platinum) and very low coefficient of friction or unique surface qualities which has given remarkable results in many applications of the chromium plate. To these should also be added the relative ease of application and control, which ensures maintenance of fixed standards of quality and durability, together with moderate cost. There is also the ease of stripping and replanting for repeated salvage in cases where the plate wears beyond suitable limits.

The benefit of the harness of chromium deposits is not efficiently obtained unless the coating is deposited on a sufficiently hard basis metal and to satisfactory thickness. Generally, hardened steel is used for the basis metal. Even a relatively heavy deposit of chromium may be crushed or indented if applied over a soft basis metal such as copper. The best possible adhesion is also important in many uses where the surface may be subjected to severe stress or shock and any chipping of the deposit would be injurious.

The low coefficient of friction and desirable surface properties of chromium are realized for the most part only on relatively smooth surfaces, although the advantages of certain types of interrupted surfaces are also described in Section 7.12.4. Frequently chromium deposits are ground or lapped to size. The deposits are easily ground but are sensitive to the heat generated and usually need to be ground with very light cuts [177, 178].

Sometimes a bright deposit is applied to a smooth surface and used without further mechanical treatment. By means of careful operation it is possible to plate to size within very close limits. Worn machine parts are salvaged by chromium plating oversize and grinding back to size.

Some outstanding applications of the industrial chromium plate include gages, tools, and machine parts generally, both new and worn parts, which are plated or replated for salvage purposes. Taps, reamers, drills, saws, milling cutters, burnishing tools, and so on, have all been successfully plated. Molds for plastics and rubber are plated to reduce wear and sticking and to improve appearance. Drawing dies and mandrels, coinage dies, rolls for cold-rolling metals to high luster, calendar rolls for various materials, and printing and engraving dies are other examples of common uses. Oswald [179] reported an increased life of over 4 times for rolls used for the cold rolling of steel and 8–10 times for printing cylinders. Wilson [180] mentions sometimes getting 3,000,000 copies from rotogravure cylinders without apparent wear.

Gun barrels are frequently plated for the maintenance of accuracy over a long period of use [181–186]. It is reported that the life of machine gun barrels is increased 30 times by chromium plating [187]. Oil drilling rods, pump shafts, and the cylinders of internal combustion engines have been plated with good results. The list of special uses could be greatly extended [128],

In each application the most desirable thickness of chromium and hardness of the basis metal have to be determined empirically with the aid of previous experience. If high corrosion resistance is desired in addition to wear resistance, as with rotary dryers for corrosive chemicals and paper mill machinery, relatively thick deposits are required. Sometimes

substantial undercoats of nickel or copper are used in such applications.

A hard chromium plate has been found useful on basis metals of widely varying hardness, although the basis metal should generally be as hard as possible. Thus, on one end of the scale, good results have been obtained by chromium plating cutting tools tipped with tungsten carbide [188]. On the other hand, zinc alloy dies for autostamping have been chromium plated for longer life [189, 190], and the hard chromium plating of aluminum has been developed [191–193], especially in connection with small internal combustion engine cylinders [191, 194, 195].

Additional information on hard chromium plating is given in other sections of this chapter.

7.9.7 Etch Prevention in Hard Chromium Plating

The biggest disadvantage that self-regulating baths have in common with all baths containing fluorides or complex fluorides is a tendency to etch the areas where cathodic current density is low or areas not covered with chromium. Because of this risk, fluoride-containing baths are often discouraged. This tendency to etching is especially noted on steel; conversely, the ordinary baths with sulfate catalyst have a strong tendency to etch copper, bronze, and brass. This etching tendency is especially marked in overcatalyzed baths and can be overcome to a considerable extent by keeping the bath in proper balance or operating at as low a catalyst concentration as possible. In addition this tendency results in the increase of the iron content of the bath, which when it reaches a certain level may slow down the plating rate, produce roughness, and if not checked make the bath unusable. Stareck and Dow [196] overcame etching by prefilming the surface to be plated as a cathode in a plain chromic acid solution. This procedure is effective only in higher ratio baths.

Etching and pitting of the basis metal are sometimes encountered in hard chromium plating even when using only sulfate catalyzed processes. If stray current is permitted to leave nonplating areas such as the exterior of cast iron diesel cylinder liners, it will plate only on the inside. This can be prevented by greater care in maintaining full insulation on racks and fixtures or by insulating the protected surface [150, 197, 198].

Bedi [199] found that immersion deposits of noble metals such as platinum and palladium on steel would prevent the etching that occurs in low-current-density recesses, particularly in baths containing fluoride catalysts. Such immersion deposits of noble metals create a low-overvoltage condition on the steel surface, which favors hydrogen evolution and tends to prevent other reactions. They may even prevent chromium deposition at higher current densities, and Bedi and Dubpernell [200] demonstrated the possible use for stopping-off purposes.

7.9.8 Black Chromium Deposits

Black chromium plating now has reached the stage where it is a completely practical plating operation that can be conducted in any existing plating plant. This process received the proper amount of attention in the last few decades. Black chromium selective surfaces have held the promise of being the most suitable coating for a wide range of low- to medium-temperature applications as solar selective coatings because of their excellent optical properties and apparent high degree of stability under diverse operating conditions. Mcdonald [201] reported that black chrome is not susceptible to degradation in humid atmospheres and possesses excellent selectivity. Mattox [202] reported excellent selectivity and thermal stability in air and in vacuum up to 350°C, and these authors have reported similar characteristics for black chrome.

The ideal selective absorber will have a high absorbency to incident solar radiation with wavelengths below 3000 nm and a low emittance beyond 3000 nm; this means that it will absorb solar radiation but simultaneously will emit little long-wave thermal radiation. Black chromium comes close to this ideal and will retain more heat energy than other types of black coatings.

The coating has good thermal stability. At temperatures below 480°C (900°F) there is no effect by the coating; at temperatures up to 590°C (1100°F) there is a slight graying of the deposit but the color reverts to black on cooling. The use of black chromium is not recommended on components subject to temperatures in excess of 700°C (1300°F).

Black chromium deposits have a high degree of microporosity, and this produces a corrosion resistance that is better than standard bright chromium. The same porosity gives it the ability to absorb and retain oil and paint films, which make it useful for the machine tool and electronic industries, and these properties are retained even after such operations as stamping, forming, drawing, and welding. An early "black" deposit was produced by using high current density in a cold bath principally containing chromic and acetic acids [203–205].

Modifications of this process for black chromium plating were proposed [206–211]. Current interruption [212] and nitrate, borate, and fluorosilicate [213] sulfate-free acid with a fluoride or complex fluoride catalyst [214] have been used. Mechanisms and structure of black chromium were studied [215–217]. There is some controversy among authors in the area of surface structure and composition, with the only real agreement being that black chromium is a homogeneous deposit of chromium metal and its compounds. The coating is generally believed to consist of particular chromium metal and chromium oxides and compounds. Baths based on trivalent chromium [218] and tetrachromates have been proposed [219, 220].

7.9.9 Postplating Treatments

Postplating treatments are not commonly used on chromium plate, since the great passivity and tarnish resistance of the metal usually make them unnecessary for most commercial parts. The normal "air passivity" of the metal, however, can be increased considerably by treatment with an oxidizing agent such as nitric acid, where this is practical. Flasch [221] treated thick chromium deposits with hot nitric acid, chromic acid, or permanganate solutions for many hours. He found that the passive chromium would no longer dissolve in hydrochloric acid and was nobler than platinum. Except for nitric acid, such treatments tend to discolor the chromium surface.

Willson [222] found that electrodeposited chromium foils 250 μm or more thick (produced by stripping the brass basis metal from them in concentrated nitric acid and then baking overnight at 165°C) resisted corrosion for 2 h in concentrated hydrochloric acid. It should be noted, however, that this is a metastable condition, and any slight disturbance or handling may result in a sudden violent attack of the chromium by the hydrochloric acid with the evolution of hydrogen gas.

Although treatment in a sodium hydroxide–sodium nitrite solution has been recommended for improving the corrosion resistance of thick chromium deposits on steel, other workers have disputed the efficacy of this procedure. Electrolytic polishing of the steel before chromium plating was effective in giving hard chromium deposits greater corrosion resistance [223].

Giesker and Britton [224] improved the corrosion resistance of chromium-plated steel surfaces by treating them cathodically in $50 \, \mathrm{g \, L^{-1}}$ sodium dichromate solution of pH 4.5 at about 95°C and $0.3–0.5 \, \mathrm{A \, dm^{-2}}$ for 1–2 min. Similar results were obtained by simple immersion in the same solution for about 2 h [225].

Safranek and co-workers [226] improved the corrosion resistance of chromium-plated parts with supplementary surface films applied by cathodic treatment for about 1 min in a solution of $50 \, \mathrm{g \, L^{-1}}$ sodium dichromate and $1 \, \mathrm{g \, L^{-1}}$ chromic sulfate at 85–95°C and pH 2.0–2.5 using $0.32–0.64 \, \mathrm{A \, dm^{-2}}$. The extent and permanence of the improved corrosion resistance are not certain. There are indications that the effect tends to be lost after a year or two of outdoor exposure. Occasionally chromium plate is used as an undercoat [227, 228]; for example, chromium is about the only undercoat that readily bonds to molybdenum [229]. In such cases, or whenever it is desired to deposit another metal over chromium, special precautions are necessary, owing to chromium's passive surface condition. This can be readily overcome by dipping in strong hydrochloric or other strong acid until the chromium starts to etch and hydrogen is briskly evolved. Quick rinsing and plating will then result in an adherent electrodeposit of almost any metal.

This etching procedure has the disadvantage of removing more chromium than is permissible or results in greater dulling and roughening of the surface than is desired. In such cases the chromium can be activated without etching by cathodic cleaning in alkali and followed by a short dip in mild acid such as dilute sulfuric at about 25°C or else by cathodic treatment in weak acid. One may follow with a strongly acid nickel strike [227, 228], and no difficulty should be experienced in obtaining a good bond to the chromium. A strongly acid copper chloride strike was used to obtain adherent copper coatings on chromium many years ago [230].

If the current is interrupted even briefly during hexavalent chromium plating, the subsequent layer of chromium may peel from the first due to the intervening passivity. The subsequent layer of chromium is also likely to be dull. This difficulty of plating one layer of chromium on another can be decreased by using a high catalyst or low ratio composition of the chromium bath, silicofluoride along with the sulfate catalyst, and high bath temperatures. If a current interruption occurs, chromium can be plated on the first layer of chromium by permitting it to come up to the temperature of the bath while submerged without current in the bath. The current can then be applied slowly in increments over a period of 1–2 min, starting with less than the plating current [231]. The hot, strong chromic acid solution has considerable activating action that only needs to be assisted by gentle gassing at just below the current density for the beginning of chromium deposition.

Current interruptions during trivalent chromium electroplating will not passivate the chromium deposit. Removing the part from the plating solution, rinsing, inspecting, and then returning it to the tank and continuing with the plating process can be done. Thus activating the surface before plating is not typically required. There will also be no loss of appearance. Trivalent chromium processes typically plate over passive deposits much easier than hexavalent chromium processes. The activation steps developed for plating hexavalent chromium deposits might not be necessary when trivalent chromium processes are used.

Occasionally organic coatings need to be applied over chromium, and once again obtaining good adhesion is of major concern. In general, organic coatings baked at a high temperature will adhere to chromium, whereas air-dried coatings will not. A detailed investigation of the adhesion of organic coatings to chromium plate was published by Safranek and Milter [232]. Practical experience is reported by a number of workers [234], One requirement appears to be to apply the organic coating to the fresh clean chromium surface before it can become contaminated with grease, dirt, or other foreign matter. Waiting even a few hours after chromium plating to apply organic coatings increases the degree of difficulty of application. Additional experience with the application of lacquer to chromium-plated surfaces can be found in the section on tin-free steel (TFS).

7.9.10 Stripping

Every chromium plater is eventually faced with the necessity of stripping chromium plate. Chemical, electrochemical, and mechanical methods are used to remove chromium plate.

In view of its passivity and usefulness, chromium is remarkable for ease of stripping. The metal dissolves readily as an anode in almost any aqueous solution to form chromic acid (Cr^{6+}) with close to 100% efficiency. It is only necessary to select a solution in which the basis metal suffers little attack from anodic action or in which the action is not too injurious for the purpose at hand. The most common strip is a dilute alkaline solution, such as an alkaline cleaner used with reverse (anodic) current. The cleaner becomes contaminated with chromate, and it is therefore best to use separate solutions for cleaning and stripping. A solution containing 70–100 g L^{-1} of sodium carbonate or 50–100 g L^{-1} of caustic soda can be used. It is important that the solution is free of chloride to prevent attack on the basis metal. For chromium thicknesses above 0.010 in. (250 μm) is more economical to grind the chromium deposit rather than to use any stripping method. A soft grinding wheel with a lot of coolant is required.

Chromium deposits from trivalent chromium processes containing metallic contamination might not strip completely in alkaline solutions. Activating the deposit in hydrochloric acid prior to the anodic alkaline strip is effective if dissolving it completely in hydrochloric acid is not desirable.

Simple immersion in hydrochloric acid from 10% (vol) to the concentrated acid of about 1.18 specific gravity, at 25°C, will dissolve a thin decorative chromium coating with hydrogen gas evolution in a few seconds and will generally leave the underlying nickel in condition for immediate replating. Care must be taken to rinse thoroughly to avoid contaminating the hexavalent chromium solution with chloride. Stareck [235] developed an alkaline pyrophosphate strip for chromium and other metals. This has the merit of leaving the steel, cast iron, or other basis metal clean and ready for further finishing operations. An alkaline strip tends to oxidize or passivate the underlying nickel and to make it difficult or impossible to replate with chromium. If, however, the strip is used cold at low concentration, low current density, and for the shortest possible time, replating is sometimes possible.

Thick chromium deposits are sometimes stripped in hydrochloric acid, but the action tends to slow down or stop where the deposit is thickest and to be too corrosive to the basis metal. Reverse current in a plain chromic acid solution of about 100–400 g L^{-1} is a better and safer stripping method for heavy chromium deposits on steel.

Another useful thickness test for thin decorative coatings is the anodic solution method [236].

7.10 TESTS OF DEPOSITS

7.10.1 Porosity and Cracking

Dubpernell [168] reported that acid copper plating over chromium up to about 25 μm thick could detect pores and cracks. Under the conditions of the test, acid copper does not deposit on chromium, owing to the passivity of the surface, and the copper deposits only in pores or cracks of sufficient magnitude to permit the solution to penetrate them to the basis metal. This makes the pores and cracks visible to the naked eye and easy to study at low magnifications.

Baker and Pinner [237] used this test to study the porosity and cracking of decorative chromium coatings. An important precaution is to apply it only to articles completely covered with chromium or to insulate all areas not chromium plated. Otherwise, all the copper will deposit on the areas not covered by chromium, and none will plate on the pores or cracks in the chromium plate. Another way of treating this difficulty is to increase the voltage during the acid copper plating step until some copper is deposited on the chromium-plated areas. However, too much voltage will plate copper directly on the chromium, thus hiding the pores and cracks. Masking off the unplated areas is preferred over increasing the voltage.

Another important precaution is to rinse the chromium plate in hot water to establish the equilibrium amount of cracking for the particular plate being tested. If this is not done, the deposit may appear relatively crack free and yet develop cracks with time, and the test will fail to give reproducible results. A certain amount of low-temperature heat treatment is necessary to stabilize the crack structure. Chessin and Seyb [238] used a 2-min immersion in boiling water. Some inconsistencies in the literature may possibly be due to the use of a hot-water rinse by some workers and the drying of specimens after a cold-water rinse under laboratory conditions by others.

Additional studies of the porosity and cracking of chromium plate were reported [5]. The cracks in thicker deposits were made evident by Gebauer [239] by anodic etching in 10% caustic soda solution followed by microscopic examination. Anodic treatment in chromic acid solution has been used by Dubpernell as a test for cracks in heavy chromium deposits. Almost any brief treatment is sufficient, a typical one being 60 A dm^{-2} for 15 s. These tests are of much shorter duration than the anodic treatment described below for the production of porous chromium deposits. A very fast method usable on some deposits, involves covering the surface with the ink from a solvent-based, dark felt pen, wiping off the excess surface ink, and examining the ink retained in the cracks under low magnification (100–150×).

Wyllie [240] used the copper plating test to show the cracks in chromium deposits after tensile testing. Cohen [241] studied the film of chromium compounds found

in the crack network of heavy chromium deposits, particularly after heat treatment of the metal.

7.10.2 Corrosion Resistance

The need in recent years for more durable decorative chromium deposits has led to something of a revolution in the specification and testing of such deposits. This in turn has led to several new developments to help meet the new requirements with thicker bright copper, nickel, and chromium coatings.

Until about 1960 decorative chromium deposits were generally confined to thicknesses of 0.5 μm or less since macrocracking would begin at this thickness. Under normal service conditions, macrocracks in thick deposits would contribute to a reduction in corrosion resistance [237]. Since the development of bright macrocrack-free chromium plating [242, 243], it has been demonstrated that if the undercoating of nickel or copper and nickel is of adequate thickness (generally more than 25 μm), a thicker decorative chromium plate adds substantially to the corrosion resistance. This is evidenced by accelerated corrosion and outdoor exposure tests. This development was foreshadowed as early as 1934 [244, 246], but it remained for the development of better accelerated tests and intensive testing to demonstrate the usefulness of thicker chromium coatings.

An electrolytic corrosion (EC) test was developed by Saur and Basco [247]. This test is highly accelerated and permits the examination of decorative chromium-plated parts in a few minutes as compared with many hours in other tests such as CASS (copper-accelerated acetic acid-salt spray (FOG) testing). Even though this test is fast, it has not received wide acceptance.

Seyb and Rowan [248] showed the improvement that could be obtained by means of thicker decorative chromium deposits, whether cracked or crack free. This demonstration was followed by the recommendation of duplex chromium coatings [249–252] for greater corrosion protection of both steel and zinc die castings. Because of the color change and the difficulty of plating decorative duplex chromium, this approach lost importance for extended corrosion resistance. The use of decorative microporous chromium over two or more layers of nickel is now preferred.

7.10.3 Microcracked and Microporous Deposits

A substantial improvement in the corrosion resistance afforded by thicker decorative chromium deposits was made with the introduction of "duplex" or "dual" chromium plating procedures in 1959 [249]. By first plating with "crack-free" chromium with good throwing or covering power and then with a second layer of highly cracked or microcracked chromium, a convenient means was found for applying heavier decorative coatings with good corrosion

resistance. Seyb [250] has explained the corrosion resistance of duplex chromium coatings as depending on many small electrochemical cells with a relatively low rate of corrosion of the nickel undercoat and decreased tendency to basis metal corrosion. Lovell and co-workers [251], who detailed the same explanation, also report their experience with dual chromium systems and emphasize the need for a substantial copper layer under the nickel and chromium for best results.

The duplex chromium plate provides a convenient means of increasing the thickness and obtaining a microcracked plate with existing equipment, as well as combining the properties of different types of coatings. The most commonly used duplex system is a first plate of bright crack-free chromium with good coverage and adequate thickness in recesses followed with an ordinary cracked or microcracked chromium plate. The total thickness of the two deposits generally ranges from 0.75 to 2.5 μm. Specifications usually call for a minimum of 0.8 μm [252, 253].

Even with the improvements in duplex chromium plating, this system was difficult to consistently produce. Crack-free chromium deposits quickly develop cracks in service, thus reducing their corrosion resistance. It was also found in practice that it was difficult to plate two layers of chromium and that the color of the deposits changed because of the two layers of chromium. This approach has almost been completely replaced by 0.25 μm thick of microdiscontinuous chromium over two or more layers of nickel [254–257]. Another development is the use of an undercoat of chromium [228, 258, 259].

The need for a minimum thickness, about 0.75 μm, to obtain microcracking brings with it a need for good plate distribution into recesses in order to avoid unduly prolonged plating times. This need was lessened by Chessin and Seyb [238], who produced low-current-density microcracking by programming the current density during plating.

Microcracking of chromium in conventional thickness (0.25–0.75 μm) was obtained by several workers using a thin substrate of highly stressed nickel over the bright nickel layer before chromium plating [260, 261]. Du Rose et al. [260] also used hot-water treatment and the addition of selenium compounds to the chromium bath to increase microcracking in thinner chromium deposits.

The use of thin microporous chromium plate to improve corrosion resistance originated through the work of Brown and Tomaszewski [262]. They produced decorative, satin-finished nickel–chromium coatings by means of particle inclusion in the bright nickel undercoat. Chromium did not plate where the inclusions were on the nickel surface. Odekerken [263] and Chessin [264] have described other methods for producing microporous and thin microcracked chromium deposits. Improvement in the corrosion resistance of microporous chromium plate can also be effected by a low impact impingement of fine hard particles onto the brittle chromium-plated surface [265, 266].

Du Rose [267], Ogburn and Schlissel [268], and Willson [269] reported that chromium may be anodic or cathodic to the nickel depending on exposure conditions. Willson further suggested that residual stresses in the chromium–nickel system may be a factor in determining the type of corrosion that occurs.

The large number of papers that have appeared dealing with the general subject of improved corrosion resistance indicates the intense interest in these developments. The copper undercoat, the nature and thickness of the nickel, and the nature and thickness of the chromium as well as the galvanic effects between the dissimilar metals have all been discussed, and it appears that all play a part in the final result [261]. These improved decorative chromium deposits are being used more widely on a commercial scale and are included in recent specifications [220, 221]. Beacom [271] points out that the same kinds of systems that are used on die castings and steel are also desirable for plating over plastics.

The importance of the potential difference between adjacent nickel layers has been demonstrated in actual service. Microdiscontinuous chromium is now required by most decorative exterior automotive specifications, with microporous chromium being preferred. Harbulack developed an easy-to-use STEP test that simultaneously measures nickel thickness and adjacent electrode potential on completed parts [272]. ASTM Standard B764 details the operating conditions of the test [273].

7.10.4   Structure of Deposits

Chromium deposits are somewhat unique among the commercially used electroplated metals due to the deposit structure's influence on its performance. Many variations in structure and physical properties can be obtained by proper adjustment of the plating conditions and postplating treatments.

Chromium deposits 0.5 μm or less thick are normally crack free but porous, whereas thicker deposits are generally cracked after rinsing in hot water or after time in service. Up to a certain thickness, which varies depending on the plating conditions, the surface of the deposit is usually smooth and bright appearing to the unaided eye. When viewed under the microscope, however, the surface is revealed as having numerous domelike projections. Figure 7.9 shows a typical hard chromium surface. These projections become more prominent as the thickness increases, up to the point that they become visible to the unaided eye.

Figure 7.10 shows ordinary bright chromium deposit built up over the usually decorative thickness. The crack pattern is clearly shown, along with vestiges of "plated-over" cracks. All conventional bright plates more than 0.5 μm thick are cracked in this fashion. Figure 7.11 shows a crack-free, slightly "milky" type of plate such as is produced by the Mahlstedt process [274], plating at high temperature and low
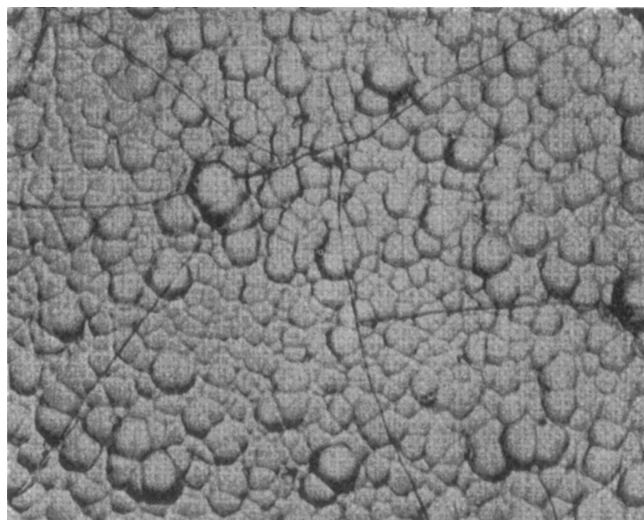
FIGURE 7.9   Semibright hard chromium plate, 100×.

current density. Such deposits crack readily when heat treated, however.

Although other causes have been suggested, the basic cause of the cracks in deposits was believed by Snavely [275] to be related to the formation of unstable chromium hydrides of variable composition during the plating operation. Hydrides can be electrodeposited in either the hexagonal crystal form (formula Cr_2H to CrH) or the face-centered-cubic (fcc) crystal form (from CrH to CrH_2). The hexagonal hydride is most likely the one formed under normal plating conditions. It decomposes to body-centered-cubic (bcc) chromium and free hydrogen, even at 25°C. Some of the hydrogen escapes during the deposition process; the remainder is included in the deposit.

Data on the structure of the chromium hydrides were reported by Snavely and Vaughn [276]. The normal structure

FIGURE 7.10   Thick bright chromium plate, 100×.

FIGURE 7.11 Crack-free "milky" low current density chromium plate, 100×.

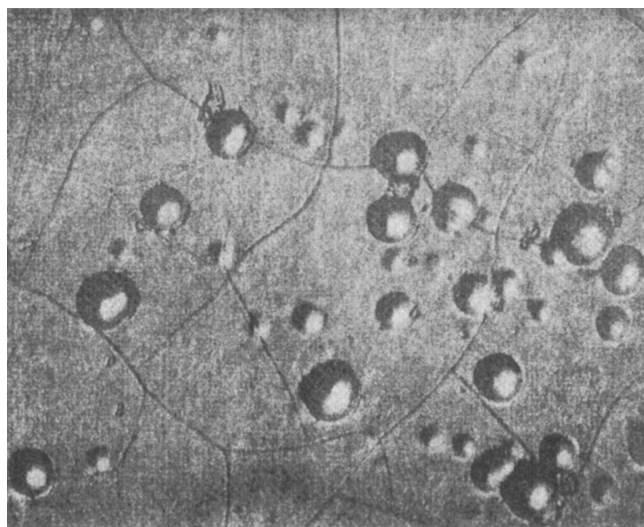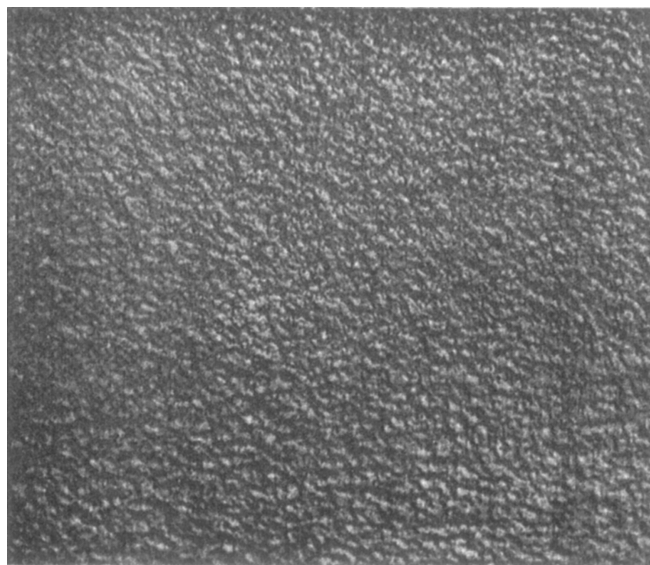of hexavalent chromium electrodeposits is bcc and is typically formed through deposition from warm solutions. Trivalent chromium electrodeposits are microporous under 0.8 μm and microcracked over this thickness. The structure is amorphous as plated but becomes bcc if heated. The amount of heating required is time and temperature dependent, but 1 h at 200°C is sufficient.

The decomposition of either hexagonal or fcc chromium hydrides to bcc chromium may involve a volume shrinkage of over 15%. Because the deposit is restrained in the plane of the basis metal, surface cracks form normal to that surface. The chemical constituents making up the cathode film are drawn into these cracks and may be bridged over by newly deposited chromium. These crack-filling constituents are the inclusion films studied by Cohen [241].

In addition to the oxide film inclusions in the cracks, which are readily detectable by metallographic examination of as-deposited chromium, experimental evidence indicates that there may be additional quantities of oxide or oxide-forming compounds finely dispersed through the plate. This dispersed oxide appears to be agglomerated on heating and then may be detected by the microscope [86, 277, 278].

Wood [279] measured the grain size of various chromium deposits by X-ray diffraction and arrived at a figure of 14×10^{-6} mm for bright plate made at 50°C. As a comparison, the smallest grains producible by cold-working metals are about 10^{-3} mm in average diameter. The extremely fine grains in chromium plate have been explained as resulting from the hydride decomposition [275].

Hardesty [280] reviewed cases of epitaxial chromium deposition in crystalline form. By working at over 80°C in a solution containing $250\,g\,L^{-1}$ CrO_3 and $5\,g\,L^{-1}$ fluoride ions with 500–700 mA cm^{-2}, he demonstrated the continued

growth of the crystals of an electropolished nickel basis metal in the cross section of a thick chromium deposit.

Structural changes taking place on beading chromium plate are those normal for a highly stressed, fine-grained metal [277, 281]. Recrystallization takes place on prolonged heating in the temperature range 300–500°C or on shorter exposure at higher temperatures. The new grains are elongated normal to the basis metal. On prolonged exposure at temperatures of about 1100°C, large equiaxed grains are formed. During this heating the inclusion films remain in their original positions, although they are agglomerated into lines of spheroidal particles.

Brittain and Smith [282] examined the grain size of annealed chromium plate under the electron microscope and concluded that it increased to about 10^{-4} mm at 450°C in 1 h and to about 2×10^{-3} mm in the same time at 1000°C.

Bright hexavalent chromium plate is strongly grain oriented, with the (111) plane parallel to the basis metal [283]. This preferred orientation persists even after recrystallization [281]. The initial layer of plate is unoriented, and the preferred orientation is achieved as plating continues. Chromium plates on polished brass or electropolished steel attain the preferred orientation rapidly, whereas plates on a machine-ground basis metal receive a relatively thick layer of unoriented plate before the preferred orientation appears.

The laminations or striations in chromium deposits parallel to the basis metal [281] were found [284] to have an important connection with the crack structure; many cracks start and stop in the striations. Cracking occurred periodically, corresponding to the striations in deposits [285].

X-ray and other work on the structure of hexavalent chromium deposits were reviewed in 1967 [286]. Chromium generally has a bcc structure (α-chromium). Hexagonal chromium (β-chromium) was shown [266] to be an unstable chromium hydride rather than an allotropic modification. These hydrides decompose into the normal bcc chromium at 25°C in three to eight weeks, but decomposition is complete in 1 h at 150°C. Snavely [275] gives the best conditions for plating the hexagonal close-packed (hcp) hydride in dull gray form as $600\,g\,L^{-1}$ chromic acid, $3\,g\,L^{-1}$ sulfate, and $10\,g\,L^{-1}$ sugar to reduce some chromic acid to Cr(III). The temperature was maintained below 12°C and current densities were 4.6–9.3 A dm^{-2}. These were essentially the conditions reported earlier by Wood [287].

"Cold" chromium plate, deposited from solutions of widely varying composition at 25°C or less, has a distinctive, velvet-smooth, mouse-gray appearance and is obtained at current efficiencies up to about 35–40%. Such cold chromium plate is generally crack free and has an entirely different aspect from ordinary bright plate from warm solutions. Nevertheless, both cold chromium and bright plate were said to be entirely of the normal bcc structure [275]. Cold chromium plates significantly slower than regular chromium

processes. One would think that cold chromium plate would be formed by the decomposition of the hexagonal hydride, and the results of a number of workers [288, 289] have confirmed chromium plate to consist primarily of it.

Shluger and Kazakov [290] reported a thick cathode film on deposits of the hexagonal type made at 20°C but a thin film on cubic deposits made at higher temperatures. Okada and Ishida [291] found mixed crystals of hexagonal and cubic chromium in black chromium deposits. Matsunaga [292] obtained hexagonal chromium from Wood's solution at lower temperatures and higher current densities and cubic chromium under other conditions. He observed the oxide film on all of his deposits on X-ray examination, unless they were first etched with hydrochloric acid.

Cold chromium plate has the disadvantage of poor adhesion, in addition to being relatively soft and expensive to buff to a high luster. The poor adhesion can be partially overcome by special care in the preparation of the basis metal, as by electro polishing [293].

Cold chromium has been used to a limited extent commercially, particularly in Europe and North America. A common method is the Bornhauser process [294, 295], often called the tetrachromate or D-chromium bath (direct chromium plating).

Snavely [275, 296] also found some fcc chromium hydride in his hexagonal hydride deposits. By using a bath containing $1020\,g\,L^{-1}$ chromic acid, 300; 1 ratio of chromic acid to sulfate, and $20\,g\,L^{-1}$ sugar, at 0–4°C and $12.4\,A\,dm^{-2}$, Snavely produced a black plate which was the fcc hydride. This deposit was stable for about a week before X-ray tests showed appreciable decomposition. Dubpernell [119] studied such black deposits in 1942 but found the current efficiency to be extremely low, and thick deposits were difficult to produce by prolonged plating. The hardness was about 600 Brinell.

The dull deposits produced with interrupted current from single-phase rectification were partly hexagonal [297]. X-ray results [298] showed that dull deposits from interrupted current and from periodic reverse current were cubic but the current from a half-wave rectifier gave a mixture of cubic and hexagonal chromium.

Metallographic investigation of deposits of different structures showed that the hexagonal or β modification could be identified in the unetched cross section by means of polarized light [291]. Some deposits were found to be partly hexagonal and partly cubic. It was necessary to increase the Cr(III) content of Wood's [279] bath by adding $32.4\,g\,L^{-1}$ sugar instead of $10\,g\,L^{-1}$ in order to get completely hexagonal chromium [300]. The hydrogen overvoltage was considerably lower on hexagonal than on cubic chromium, although the same source later reported the opposite [301, 302]. Stress measurements [289] indicated that cubic chromium absorbs hydrogen and converts to hexagonal at least partly when treated as a cathode in $71\,g\,L^{-1}$ Na_2SO_4.

7.11   PHYSICAL PROPERTIES OF CHROMIUM PLATE

A number of convenient summaries of the physical and chemical properties of hexavalent chromium and of chromium deposits are available [286, 303–305].

7.11.1   Hardness and Wear Resistance

The hardness and wear resistance of chromium deposits are generally quite good in service, regardless of moderate variations in the conditions of plating. This is true as long as a satisfactory thickness is applied for the intended use. There also has to be good coordination between the hardness of the basis metal and the pressures encountered [306]. Frequently service is at elevated temperatures, and some of the as-plated hardness is lost. On the other hand, relatively soft deposits produced from hot solutions have often given especially good service, possibly owing to freedom from cracks or to greater strength and cohesion of this type of plate. Trivalent chromium deposits become harder when heated. Chrome carbides are thought to form by a reaction between the chromium and the codeposited carbon.

Hardness measurements are difficult to make and not very rewarding, since so many other factors are involved in service life. Unfortunately, hardness is not a simple elementary property; it depends on other properties in a little-known manner [307]. For these reasons the hardness measurement is not often used in chromium plate specifications.

Generally, the hardness of bright hexavalent chromium deposits is given as about $900–1000\,kg\,mm^{-2}$. Approximately the same values are obtained whether on the Brinell, Knoop, Vickers, or diamond pyramid scale [6]. Organic-catalyzed hexavalent chromium deposits can reach 1100 Knoop or Vickers with a 50–100-g load. As-plated trivalent chromium deposits fall into the same hardness range. After heat treatment the hardness can reach 1500 Knoop or Vickers (50–100-g loads).

The microhardness number depends to some extent on the test load used, and the deposit must be thick enough to withstand it or be conducted on a thick enough cross section. On a soft basis metal, a thin chromium deposit will show only the hardness of the basis metal; it would have to be extremely thick to indicate its full hardness. Chromium deposits 25 μm or more on a hardened steel base are thick enough for satisfactory measurement of the hardened metal with 50–100-g loads. It is recommended that the plate thickness should be at least 14 times the depth of penetration of the indenter [308]. Low loads often result in a considerable increase in the hardness number. Tests are sometimes made on the cross section of the deposit if it is thick enough and well supported [281]. If the deposit cracks around the indention, a smaller load should be used.

Brenner et al. [86] reported Knoop hardnesses for as-deposited chromium ranging from 300 to 1000, the softest deposits being from boiling solutions. Hosdowich [309] converted scratch hardnesses to the Brinell scale and reported figures from 640 to 1165 Brinell. The softest deposits were dull plates obtained at 15°C, and the hardest were burnt nodules. The hardness of the deposits was closely correlated with the appearance. All the bright deposits had a hardness of about 1000 Brinell.

Eilender and co-workers [310, 311] also made an extensive investigation. Wahl and Gebauer [312] determined Vickers hardnesses of 390–1280 with a 50-g load on deposits from 250 g L^{-1} solutions at 20–80°C and 10–200 A dm^2.

In tests with fluoride-catalyzed baths at 85°C Brenner et al. [86] found that the deposits were harder than corresponding ones from sulfate-catalyzed baths. Wahl and Gebauer [312] found slightly higher hardnesses for deposits from solutions containing silicofluoride catalyst. In general, deposits from solutions containing fluoride or complex fluoride catalysts seem to be about 100–200 units harder than corresponding deposits from solutions containing only sulfate catalyst. There also seems to be definite evidence of better retention of hardness by such deposits when exposed to heat.

The wear resistance is perhaps even more difficult to measure than the hardness. Two types of measurement have been used: abrasive wear with relatively light load similar to grinding [309, 312] and rubbing or frictional wear under higher pressures against a harder material such as a tungsten carbide wheel. There is considerable evidence that the hardest deposits do not necessarily give the greatest wear resistance. Thus Hosdowich [309] found the bright or slightly frosty deposits around 1000 Brinell to have the greatest wear resistance, and the burnt deposits up to about 1165 Brinell had somewhat less, perhaps because of brittleness. Likewise deposits of medium hardness around 750–800 Vickers were found to have the best frictional wear resistance, whether obtained as deposited or by moderate heat treatment of still harder deposits [310, 311].

Radioactive chromium plate is used to follow the wear of chromium-plated piston rings and to check the chromium transferred to the cylinder walls [313] or the lubricating oil [314, 315]. See Section 7.3 on porous chromium plating.

7.11.2 Coefficient of Friction

The low coefficient of friction of chromium plate against other metals is an important factor in its use on shafting, piston rings, internal-combustion engine cylinders, and similar applications. Table 7.2 illustrates the superiority of chromium in terms of this property.

Bright chromium plate against cast iron gave a lower coefficient of friction than mat or burned plates [318]. The coefficient of friction of chromium plate against steel or cast

TABLE 7.2 Coefficient of Friction for Various Metal Combinations

Metal	Static Coefficient	Sliding Coefficient
Reference [316]		
Chromium-plated steel on chromium-plated steel	0.14	0.12
Chromium-plated steel on babbitt	0.15	0.13
Chromium-plated steel on steel	0.17	0.16
Steel on babbitt	0.25	0.20
Babbitt on babbitt	0.54	0.19
Steel on steel	0.30	0.20
Reference [317]		
Bright chromium plate on cast iron		0.06
Bright chromium plate on bronze		0.05
Bright chromium plate on babbitt		0.08
Hardened steel on cast iron		0.22
Hardened steel on bronze		0.11
Hardened steel on babbitt		0.19

iron increases rapidly with temperature [319]. The increase may be avoided by final polishing after heat treating.

7.11.3 Coefficient of Expansion

Hindent [320] found an average coefficient of expansion of 6.8×10^{-6} °C^{-1} for annealed electrolytic hexavalent chromium in the temperature range of 20–100°C. The coefficient of expansion at any temperature t between -75 and $+650$°C was shown to be expressed by the formula $a_t = (5.88 + 0.01584t - 0.00001163t^2) \times 10^{-6}$. Within the temperature range -100–700°C, the length of a chromium plate specimen is expressed by the formula $L_t = L_{0a} [l + 5.88t + 0.00774t^2 - 0.00000388t^3) \times 10^{-6}]$. Hindent also noted a linear shrinkage of approximately 1.1% during heating the deposits to 500°C for the first time. During subsequent heating and cooling cycles, the expansion and contraction were normal. Snavely [275] ascribed the initial shrinkage to relief of internal stress and closing up of voids between crystallites. These voids are a result of the decomposition of chromium hydrides.

Because of this unusual behavior, there is little hope that a basis metal can be found that will match the expansion and contraction characteristics of the chromium plate from chromic acid baths during heating cycles.

7.11.4 Melting Point

Sully and Brandies [286] tabulate measurements ranging from 1560 to 1920°C. Udy [303] selects the high value of 1930 ± 10°C based on results in [321] and [322]. Currently the American Society for Metals [304] has adopted the value of 1875°C after work at the National Bureau of

Standards [305]. Sully and Brandies [286] discuss much of the work in this area and state that it is not possible to come to any final conclusion but that a value close to $1878 \pm 22°C$ seems to be the most likely.

7.11.5 Density

The density of chromium plate varies according to the amount of inclusions in the plate, the number and size of cracks, and the magnitude of internal strain. Brenner and co-workers [86] reported a systematic study of the density of chromium deposited under various conditions. Values from 6.90 to 7.21 $g\,cm^{-3}$ were obtained. The oxide content decreased as the density increased. After annealing at 1200°C the density of the deposits increased to within the range 7.09–7.22 $g\,cm^{-3}$. The density of pure chromium is 7.20 $g\,cm^{-3}$, as calculated from its lattice parameter. Therefore the reported values over 7.20 can be considered anomalies related to the precision of the measurements. Hindent [320] reported a density of 6.93 $g\,cm^{-3}$ for as-deposited chromium, and this value is considered representative of most commercially deposited chromium.

Knoedler [288] reported a density of 6.143 for cold chromium or hexagonal hydride as deposited at 12–15°C, compared to 7.017 for as-deposited cubic chromium and 7.148 after annealing 2 h at 900°C.

7.11.6 Reflecting Power

Coblentz and Stair [323] studied the reflectivity of hexavalent chromium plate over a light range from ultraviolet to infrared. For the visible range of light, 4000–7000 Å in wavelength, they obtained reflectivity values between 62 and 72%. For ultraviolet light, the reflectivity ranged from 55 to 70%, and for infrared from 62% at 7000 Å to 88% at 40,000 Å. These high reflectivity values are usually retained over prolonged periods of exposure of chromium plate because of its corrosion and tarnish resistance. The reflectivity may be seriously reduced when the plate is exposed to highly corrosive atmospheres.

7.11.7 Electrical Resistivity

Electrical resistivity, like density, is a measure of the continuity, purity, and general soundness of a metal. The number, distribution, and size of the inclusion-filled cracks in chromium are related to the plating conditions. Therefore the electrical resistivity varies according to these conditions. Brenner and co-workers [86] reported electrical resistivity values for a wide range of deposition conditions. They showed that a resistivity of about 50–60 $\mu\Omega$-cm at 28°C may be expected for conventional chromium plate, with much lower values down to 14 $\mu\Omega$-cm for deposits from hot solu-

tions. After annealing at 1200°C, the oxide film inclusions are spheroidized, and the cracks in which they originated are no longer continuous. As a result the resistivity of annealed electrolytic chromium approaches a common value of 13 $\mu\Omega$-cm at 28°C, regardless of conditions of deposition [119].

7.11.8 Internal Stress

According to the theory of chromium hydride formation and decomposition during chromium plating [275], the cracks in the plate result from internal stresses that exceed the cohesive strength of the metal. Cracking relieves these stresses to the point where they are no longer of sufficient magnitude to extend the cracks. Most thick plates are cracked and contain residual internal stress. Thin plates may contain even higher stress because they are restrained from cracking by the basis metal and transfer their stress to it.

Brenner et al. [86] reported stress values as high as 56 $kg\,mm^{-2}$ for very thin chromium deposits which were not cracked. Conventional plating practices produced thicker cracked plates having internal stress of about 12 $kg\,mm^{-2}$. Plates from a dilute bath at 85°C were crack free but contained stresses of 45 $kg\,mm^{-2}$.

Stareck et al. [324] investigated deposits up to 100 μm thick and found that the stress in highly cracked deposits might become negative or compressive with increasing thickness. Compressive stress as high as $-12\,kg\,mm^{-2}$ was found. This was explained as due to a wedge effect of chromium plated into previously formed cracks. Williams and Hammond [325] confirmed the presence of moderate compressive stress in some thick chromium deposits in the as-plated condition.

Nishihara et al. [289] showed that the stress was lower in the hexagonal hydride but that cathodic treatment of ordinary bcc deposits in 71 $g\,L^{-1}$ Na_2SO_4 at 40°C and 1 $A\,dm^{-2}$ decreased the stress in less than 1 h to less than that of the cold chromium (hexagonal hydride). Additional work on stress in chromium deposits has been reviewed [326, 327].

7.11.9 Effect on Fatigue Strength of Basis Metal

The stress in various hexavalent chromium deposits was correlated with the crack structure and thickness [324], and it was found that because of a wedge effect of chromium deposited in previously formed cracks the stress frequently decreased with thickness, and heavy deposits even developed compressive stress. This was in turn correlated with the effect of the deposits on the fatigue strength of steel [328]. Two types of deposits that had a minimum effect on the reduction of fatigue strength were found: highly cracked deposits with low stress as plated and deposits from high-concentration baths that could cause stress damage as plated but could be heat treated with good results.

Chromium plate generally reduces the fatigue strength of steel markedly [329–331]. Stareck et al. [324, 328, 330] found that the decrease in strength was due to the stress in the deposits that weakened the basis metal. They found several ways to overcome or minimize the effect, such as by producing deposits of low or compressive stress or by heating to high temperatures to eliminate the stresses as far as possible. These results were confirmed and extended by Williams and Hammond [332].

Shot peening [333], roller burnishing [334], and grit blasting [335] of the basis metal have also been shown to be helpful. In this way there is introduced into the surface before plating a compressive stress which tends to counterbalance any tensile stresses in the deposit.

Continuing investigations of these matters are quite extensive. German work has been reviewed [336–339]. Effects of surface finishes in gun barrel manufacture were investigated by Greco and Penned [340]. The detrimental effect of chromium plate on other basis metals and methods of overcoming it have also been investigated for aluminum [341–344] and titanium [345].

7.11.10 Ductility

No ductility was found in chromium deposits from aqueous solutions by Wyllie [240] or Brenner et al. [86], although the latter found tensile strengths of 6–56 $kg\,mm^{-2}$. Deposits from fused salt baths have, however, been found to be ductile [304].

Klopp [346] reviews progress in improving the ductility and strength of chromium and chromium base alloys. Brandes and Whittaker [347] reported a tensile strength of 20 $kg\,mm^{-2}$ and an elongation of 17% on electrolytic chromium at room temperature after annealing in hydrogen at 1600°C.

7.12 CHEMICAL PROPERTIES

7.12.1 Oxidation and Tarnish Resistance

Chromium plate normally has a very thin oxide film on its surface. This film is so stable, tenacious, refractory, and self-healing that it protects the metal underneath from further oxidation. The plate remains bright at temperatures up to 260°C. On prolonged heating of chromium plate to temperatures of about 315°C in air, the oxide film thickens and darkens. At higher temperatures, temper colors are produced, and a black or green-black oxide layer is finally formed. At temperatures around 1000°C, an oxide layer forms on the surface and an extremely hard chromium nitride layer forms between the oxide and the chemically unaffected portion of the plate [281]. Pure trivalent chromium deposits undergo similar color changes due to heating. Deposits containing metallic codeposits such as iron and copper darken faster and to a greater degree.

The thin oxide film on chromium plate forms quickly when plating is completed or is present during plating, so tarnishing of the plate is not likely to be encountered. The chromium oxide is a satisfactory protection against sulfides, which cause serious tarnishing of silver, copper, or nickel.

7.12.2 Chemical Resistance

The chemical resistance of chromium plate is not so great as might be supposed from its performance in the atmosphere. Chromium is readily attacked by mineral acids and by reducing solutions in general. It is resistant to nitric acid, which heals the protective oxide film, and nitric acid may be used to dissolve other metals such as copper or nickel away from chromium plate. Smith and Dubpernell [348] found it possible to improve the acid resistance by anodizing.

Christov and Pangarov [300] found their cold chromium plate (β or hexagonal chromium) to be more passive and corrosion resistant than bright α cubic chromium plate deposited at 45°C. Thus a pH of about 1 was required to dissolve hexagonal chromium, while cubic chromium dissolved at pH 2; cubic chromium stopped dissolving when the pH was increased to about 2.6, while hexagonal chromium stopped dissolving around pH 1.7–1.8.

The chemical resistance of chromium plate may be used to the best advantage only if the underlying metal is completely covered [349]. For that reason hard or industrial chromium plates for corrosive service should be at least 25–50 μm thick to ensure that the cracks are not continuous to the basis metal. Otherwise, a crack-free type of deposit should be used. Many trivalent chromium deposits tend to have more substrate exposed than hexavalent chromium deposits. Many thin (under 0.8 μm) trivalent chromium deposits are microporous as plated. Over 0.80 μm the deposits are microcracked. Over about 2 μm the deposits tend to develop macrocracks, many of which extend to the substrate.

In general, hexavalent chromium plate may be used in the same types of corrosion-resistant service as the high-chromium stainless steels at ordinary temperatures, depending on the physical properties required of the basis metal. Even though trivalent chromium deposits contain the same type of oxide film, these deposits may not have the same chemical resistance. Codeposited metals with chromium from trivalent chromium can have a significant influence on chemical resistance.

Resistance to corrosion and wear in high-purity water at high temperatures in atomic reactors is a field where hexavalent chromium plate appears to have some utility, but many special application problems are involved [340]. Suss [351] found contradictory results on chromium-plated stainless steel, probably because of electrochemical effects. The general behavior of chromium exposed to corrosion in aqueous media at 25°C has been comprehensively outlined

on a thermodynamic basis by means of potential pH diagrams [352, 353].

A considerable number of specific corrosion tests on chromium and chromium plates were made [8, 245, 329]. These tests included a wide variety of acid and salt solutions, and organic compounds and acids as well, at 12 and 58°C.

7.12.3   Chromium-Plated Strip Steel–Tin-Free Steel

Chromium-plated strip steel for the production of "tin cans" originated commercially in Japan in 1962, as described by Uchida and co-workers of the Fuji Iron and Steel Company [354–356]. The process originally consisted in chromium plating for 10 s to get a thickness of 0.05 Å followed by a chemical dip treatment in 1% chromic acid or 2–3% sodium bichromate to improve the corrosion resistance and finally lacquering with a high-temperature baking lacquer.

Some further developments in the United States as well as in Japan have been reviewed [357–362]. Commercial production began in the United States in 1967. The resultant tin-free steel (TFS) has been used for the manufacture of beverage cans, a large proportion of which is now made from this material. The tin-free steel lacks the easy solderability of tin plate for high-speed can production and has necessitated the use of processes for cementing or welding the seams of cans. The resulting cans are more readily recyclable because they contain no tin.

In newer procedures the chromium thickness has been cut down to 0.005–0.0075 Å (35–54 mg m^{-2}) [363] but is sufficient to prevent filiform or underfilm rusting in the corrosion tests used [359] when combined with the oxide coating produced in a final cathodic posttreatment solution compatible with the plating bath [359]. The latter oxide is about five times the thickness of the natural oxide film present on most chromium plate, which is about 3.75 mg m^{-2} [357, 359, 365] in terms of weight of chromium in the oxide. Not much more than 16 mg m^{-2} of chromium as oxide can be applied without getting a colored coating instead of a transparent one.

In plating the steel strip moving at 300–550 mm^{-1}, Seyb and co-workers [366] found it necessary to use fluoride or complex fluoride containing electrolytes, and they formulated the first practical baths for this application, which have become the standard in commercial use. Current efficiencies of about 25% are obtained in practice. Typically the moving strip passes between four pairs of 38-cm-long sections of anode placed vertically, or six pairs counting the somewhat longer cathodic posttreatment. This gives a plating time of about 0.05 s in front of each pair of anodes, or a total plating time of about 0.30 s to produce the finished product, which is then rinsed, dried, oiled, and lacquered.

The reception of this product has been good, and its use has grown rapidly, resulting in the saving of substantial quantities of tin for other purposes. Tin-free steel is less expensive than comparable tin plate [362].

7.12.4   Porous Chromium Plate

This name has been given to modified chromium deposits with oil-retaining properties used on internal-combustion engine cylinders and piston rings. Such deposits were used especially on aircraft and diesel engine to make the engines last longer. Today most parts plated with hard chromium benefit from the cracks.

Three main types of "porous" chromium plate have come into common use. The first is the "mechanical" type produced by grit blasting the basis metal, chromium plating, and finally finishing to size by grinding, honing, or polishing [367]. The second and third types of plate are those with "pitted" and "channel" porosity. Both of these are obtained by treating the chromium deposit in an etching solution. The type of porosity obtained depends on careful control and regulation of the conditions of deposition. Numerous publications and patents describe the production of all these types of porous chromium plate and the results obtained with them [368–376].

Another variation is to etch pits into the surface of the deposit through a plastic mask [371] or a photoresist [372]. Etching by ion bombardment through a screen [372] and with alternating current [379] is proposed. Raymond [380] plates at extremely high current densities from 232 to 1160 A dm^{-2} at 30–55°C to produce a porous deposit directly. Still another variation is to impregnate the porosity with Teflon to provide the possibility of dry lubrication [381], but this does not seem to have become important commercially. Patents were issued to Forestek [382] and Letendre [383]. Zubrisky [384] patented the final grit blasting of polished or honed porous chromium surfaces to provide better breaking in qualities.

The "pit" type of porous chromium may be produced, for example, by plating under ordinary hard chromium plating conditions. Baths containing 250 g L^{-1} chromic acid and 2.5 g L^{-1} sulfate at 50°C are used. Plating took place at 46–54 A dm^{-2} for a minimum of 2–3 h to get a deposit at least 100 Å thick. They were then treated as an anode or cathode in a suitable etching solution or by simple immersion in acid. A typical anodic treatment [365] is about 150 A-min dm^{-2}, but this may be prolonged or repeated if it is desired to remove more metal or to obtain deeper porosity. After the deposit has been heavily attacked, numerous cracks are found to be eaten away, and a surface crust of undermined metal remains. When this crust is ground, honed, or polished away to the extent of 25–50 Å, numerous pits remain in the chromium plate.

Good conditions for producing the "channel" type of porous chromium plate are 60°C and a ratio of chromic acid to sulfate of 115 : 1. The usual current densities of 46–62 A dm^{-2} are employed for a deposit thickness of at least 100 or 125 μm. After treatment in the etching solution, the deposit does not have a loose surface crust but only a

network of fissures so that grinding, polishing, or honing off about 25 μm leaves channels, with dense chromium " plateaus" or "lands" between. This type of porous chromium has been largely used for aircraft engine cylinders, whereas the pit type has been more extensively employed in diesel engines and on piston rings.

Several specifications have been issued on porous chromium plating [385]. It is a well-established procedure conducted on a large scale in a limited number of plants. The merits of the product are confirmed by carefully controlled tests. Thus Kishi et al. [386] with radiotracer techniques determined that the wear on porous chromium and ordinary hard chromium was about equal under low loads. The ordinary hard chromium showed a rapidly increasing weight loss; the porous chromium showed very little wear.

7.13 TRIVALENT CHROMIUM BATHS

7.13.1 Trivalent Chromium Processes

Historically trivalent chromium baths have always been the first and favorite approach to chromium plating because of the increased safety and health properties [387]. It was not until the mid-1970s [388] that a commercial process was available and increased productivity became more important than health and safety in choosing this process.

The U.S. Bureau of Mines developed a process for electrowinning of pure chromium metal from the ore or from ferrochromium using a mixed bivalent and trivalent chromium sulfate solution [389–391], but the process has not been adapted successfully for plating purposes. A two-compartment cell has been used at the Union Carbide Corporation, Marietta, Ohio, plant. Continuous operation on a large scale seems necessary for good results [392]. In another review of the operation [392a], Bacon mentions that low efficiencies always prevail during the startup of a cell.

Success was very limited in efforts to use such baths for plating [393–403]. A chromium ammonium chloride solution was used for brush plating [399, 400]. Better results in brush plating were obtained with Gregory's salt, ammonium chromium oxalate [406–409].

More recent efforts were made to commercialize the use of chromium chloride solutions in, or containing, organic solvents. Bharucha and Ward [410] of the British Non-Ferrous Metals Research Association obtained several patents and published several articles [411, 412]. Diamond Shamrock Chemical Company has offered a similar process [413]. The deposits are darker than those from chromic acid solutions and some chlorine gas is generally evolved at the anode. Levy and Momyer of Lockheed [414] reported tests with chromium thiocyanate and chromium format dissolved in organic solvents. Brown and Tomaszewski also give a brief report of their work with trivalent baths [262].

In recent years, there has been many references on trivalent chromium research [415–419]. Snyder [420] reviewed the deposit's physical properties of one commercial formulation. Corrosion, a concern with decorative deposits, has also been extensively studied. The same author [421, 422] published corrosion data showing that, except for thin nickel applications, trivalent chromium deposits have equal or better corrosion resistance than hexavalent chromium deposits. Trivalent chromium processes do not contain hexavalent chromium ions that can react with unplated metal and offer short term corrosion protection. This makes trivalent chromium less corrosion resistant over thin nickel or bare steel. Carter and co-worker [423] also reviewed trivalent chromium corrosion studies using a different formulation to produce the deposits. One major advantage of some trivalent chromium formulations is that metallic impurities can be easily removed by directly passing the plating solution through an ion exchange [424].

7.13.2 Chromium Alloy Plating

One major advantage of trivalent chromium chemistry versus hexavalent chromium chemistry is the ability to easily produce chromium alloys. Chrome iron [425, 426] and chrome nickel–iron [427, 428] are the most typical alloys produced.

Chromium alloy plating can be considered a subheading under trivalent baths; there is almost no alloy plating possible from hexavalent solutions. There has been a great deal of work, and some reviews are available [429–431], but nothing of commercial importance seems to have been developed. Now that trivalent chromium processes are commercial, it is expected that there will be more research of chromium alloys. It is very easy to alloy metals such as nickel, iron, copper, and zinc from a trivalent chromium electrolyte.

One exception to the rule of no alloy plating from chromic acid baths is the work of Vagramyan and his collaborators [430]. Alloys of up to 37% selenium, 15% manganese, 2% molybdenum, and 1% rhenium were obtained with cold chromium deposits at about 20°C. These alloys are, on the whole, no longer obtained as the temperature is raised, so presumably they are alloys produced with the dull hexagonal hydride at low temperatures and not with the bcc deposits which form ordinary bright plate.

Snavely and co-workers [432] reported the physical data for chromium alloys containing iron, molybdenum, nickel, phosphorus, or tungsten from trivalent chromium baths. Alloys containing 6–10% iron were harder after heating to 800°C than hexavalent chromium from conventional baths. However, they were softer than conventional deposits prior to heating. Alloys containing 6% iron retained their hardness of 600–700 kg mm^{-2} after heating to 600°C [433]. Alloys with 15% iron exhibited a hardness of 1000–1025 kg mm^{-2} prior to heating [434]. Chromium alloys with up to 60% iron

exhibited stress of 36,000–38,000 psi [435], even though they had many cracks. Coefficients of expansion for chromium alloys containing 6–18% iron were slightly higher than those for conventional chromium [436].

Much work has been done, mainly in France, to investigate claims of improved wear resistance of chromium–molybdenum alloys produced from chromic acid solutions [437, 438]. It appears that bright deposits generally contain less than 1% molybdenum, and this could possibly result from solution contamination of the deposit instead of alloying. Hard chromium plating baths are frequently deficient in catalyst due to too strict adherence to the 100 : 1 ratio of chromic acid to sulfate. The improved wear resistance of deposits from solutions containing molybdenum compounds might in fact be due to the catalytic imbalance.

Chromic acid plating baths containing molybdenum salts have been employed for obtaining deposits requiring high abrasion resistance and wear [439–442]. Abrasion resistance was improved 200–300% over conventional deposits with the inclusion of molybdenum. A deposit containing 3% molybdenum had a reported hardness of 1000–1300 kg cm^{-2}. The hardness increased as the concentration of molybdate increased to 100 g L^{-1} [434]. X-ray diffraction studies showed the presence of molybdenum trioxide indicating a dispersion [439].

Chromium–ammonium sulfate solutions containing sodium hypophosphite produced deposits with increasing hardness as the phosphorous content increased up to 15% [444]. Hassion and co-workers studied formulations containing magnesium oxide, zirconia, and thoria and found that dispersions were produced [445]. The hardness of the deposits increased in every case. Additions of sodium tungstate or magnesium oxide [446] increased hardness. The same was reported for the addition of titanium oxide [447].

7.14   OTHER SPECIAL TYPES OF CHROMIUM PLATE

A "frosty" or satin-finish plate in between cold chromium and bright plate was found desirable for press plates [448]. Such smooth-bubbly or natural rounded nodular plate has been found useful for handling textile materials. Trist [449] used a special cold chromium plate produced in refrigerated electrolytes for printing plates.

Carveth [450] obtained a black color on chromium deposits by immersion in molten cyanide. The carburizing of chromium deposits for greater hardness has also been frequently attempted [451–453]. Although the plate is first softened by the heat, it does appear possible to obtain very hard chromium carbide coatings.

Bohlman [454] was successful in spot plating with a jet of ordinary chromic acid solution and achieved extremely high local rates of deposition. Chessin and Walker [455] developed a bath with organic additions to give a uniformly iridescent chromium plate, and Chessin and Gempel [456] obtained similar results with additions of molybdenum compounds.

7.15   REGULATIONS

In many developed nations, plating is one of the most regulated industries with hexavalent chromium plating one of the most regulated processes. Hexavalent chromium is a suspected or confirmed carcinogenic agent depending upon the regulator. It is also a strong oxidizer. Even the classical wetting agent used in hexavalent chromium electroplating, PFOS (perfluoro-octanesulfonic acid), which was almost universally used to improve the safety of the process by reducing the misting generated during plating, is being banned in many countries because it is extremely stable and does not break down. This stability is what is required to exist in a hexavalent chromium solution but is bad for the environment.

The plater must contend with regulations controlling the amount of hexavalent chromium ions inside the workplace, the amount discharged in the air outside of the plant, and the potential residual presence in the discharged waste. There are even tight controls on the disposal of precipitated trivalent chromium produced in the waste treatment process. Even the European Union's End-of-Life Directive, which was developed to regulate passivates for zinc and zinc alloy, impacts hexavalent chromium platers. Although the chromium metal on the plated part is not regulated, insufficient rinsing after hexavalent chromium plating leaves enough hexavalent chromium ions on the part to fail the End-of-Life leaching test. However, using good plating practices and the correct control mechanisms, most hexavalent chromium platers can meet the regulations, but in some locations only trivalent chromium plating is permitted.

Trivalent chromium processes are much less regulated because trivalent chromium ions are not strong oxidizers and are not even suspected carcinogenic agents. Under most regulations, if a wetting agent is used, trivalent processers are regulated similarly to nickel electroplating processes. Since in most trivalent chromium processes the wetting agent is also a required additive for producing bright decorative deposits, wetting agents are used. Trivalent chromium wetting agents are not in the PFOS family and remain unregulated.

Because regulations can be very different in different countries, different states/regions, and even different local communities, chromium platers must be very diligent in understanding and following the regulations that their operation must meet. Regulations also have a tendency to change because of the evolving understanding of the effects that chromium ions have on our environment/health/safety. This means platers must investigate their individual requirements and not solely use general literature cited values. Also, as in

the case where insufficient rinsing puts hexavalent chromium plating under the End-of-Life directive, all regulations should at least be considered even if they do not appear to be relevant.

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