HARD CHROMIUM PLATING—SOME ASPECTS OF ITS PRACTICE

H. V. K. Udupa and S. R. Natarajan

Central Electrochemical Research Institute, Karaikudi.

(Presented at the Conf. Industrial Metal Finishing, Bangalore, Oct. 1976)

Chromium deposit is characterised by its attractive appearance, hardness, wear resistance, low coefficient of friction, corrosion resistance and other useful properties, and its industrial applications are well established now.

Chromium plating solutions : Chromium deposits are obtained from chromic acid solutions with small quantities of sulphate or a combination of sulphate and fluoride or fluosilicate. Baths containing sulphate only as the minor constituent are notorious for their low cathode current efficiency. Those with a combination of sulphate and a fluorine-containing salt have about 30% higher cathode efficiency. Use of the Self-Regulating High Speed (SRHS) chromium bath dispenses with the need for analysis of minor constituents, making possible greater speeds of chromium deposition.

The conventional bath for hard chromium plating contains 250 g/l CrO_3 and 2.5 g/l H_2SO_4 and is operated around 50°C. This solution has slightly better cathode efficiency and throwing power than the more concentrated one usually employed for decorative plating. Use of baths with a combination of minor constituents is advantageous for production plating, because plating may have to be extended up to quite heavy thicknesses in certain cases.

Etching of substrate : In hard chromium plating, different kinds of substrates are always encountered. The substrate is to be anodically etched before plating in order to produce a metallurgically sound surface to which the deposited metal will adhere well. Heavier etching of substrate is necessary for thick, than in the case of light deposits. Typical sequences are given in Table 1[1].

Table 1 – Sequence of treatment of different substrates for hard chromium plating

Substrate		Heavy deposits	Light deposits
(i)	Mild steel	Anodic etch in 250 – 400 g/l H_2SO_4 for 3 – 5 min at 22–27 ASD; warm up in dead vat and plate at 27 32 ASD.	Warm up in dead vat; anodic etch at 27–32 ASD for 15–30 sec. deposit at 27–32 ASD
(ii)	Hardened steel	As above. Overetching leads to appearance of hardening cracks.	Anodic etch for 5–10 sec; warm up in dead vat, and plate.
(iii)	Nickel and stainless steels	Anodic etch in 250–400 g/l H_2SO_4 for 10 min at 22 ASD; cathodic flick for 1–2 sec; deposit immediately.	——
(iv)	Brass, bronzes, and copper	Anodic etch in 200 g/l NaOH and 6 g/l NaCN for 5–10 min at 5.5–11 ASD; dip in 10% HCl; Deposit immediately	Load in dead vat; commence plating within 10 – 30 seconds.
(v)	Cast iron and meehanite	Anodic etch in 250-400 g/l H_2SO_4 for 15-20 sec; load in dead vat to warm up; commence deposition at 38 ASD for 2-3 min; drop to normal C. D.	——
(vi)	Chromium and stainless steels.	Anodic etch in 250 - 400 g/lH_2SO_4 for 2 min; anodic etch for 15-20 sec in vat; bring up plating C. D. in 30 min.	Proceed as for heavy deposits but omit H_2SO_4 etch.
(vii)	Light alloys and aluminium	Anodic etch in 200 g/l NaOH – 6 g/l NaCN; etch in dilute HF or HCl for 2–3 min. dip HNO_3; immerse in zincate solution for 1 min; cyanide copper plate 3-5 min; load in vat and deposit.	As for heavy deposits

Anodes : Lead alloy anodes are commonly used in view of their mechanical strength and corrosion-resistance. Lead-tin alloy anodes (tin content 7-10%) have greater resistance to corrosion than lead-antimony alloy anodes in chromium plating solutions, especially those containing fluoride or fluosilicate. The anodes can be prepared by melting together the requisite metals and casting to required shapes.

Control and maintenance of plating solution : The solution should be analysed for all constituents at regular intervals and suitable additions made so that it conforms to the recommended composition. In the case of SRHS solutions, analysis for CrO_3 and meaurement of specific gravity are both helpful, replenishment of minor constituents being made on the basis of specific gravity change or ampere hours of current passed.

As different types of substrates are treated in chromium plating solutions, which are generally corrosive, various metal ions like ferric, zinc, copper, aluminium, find their way into solution. Also there is a build-up of trivalent chromium due to reduction of hexavalent chromium near the cathode by gaseous hydrogen, though to some extent, there occurs a re-oxidation at the anode. Table 2 lists the effects of some cations on solution and deposit[2]. When their amounts exceed certain limits, a portion of the solution is replaced with a fresh solution, or, when the bath is heavily contaminated, it is discarded. Trivalent chromium, however, can be brought down to a permissible level by electrolysing the solution at a high temperature with large anodes and quite a small cathode so that the anode-cathode area ratio is about 30 : 1. Recently electrodialysis of solutions containing trivalent chromium and ferric or aluminium ions in excessive amounts has been found to be useful as a method of continuous purification of baths[3].

Table 2 – Effects of some cations in chromium plating solutions

Cation	Effect
Trivalent Chromium	In excessive quantities, gives rise to increase in deposit hardness and production of pitted deposits ; also together with considerable amounts of ferric ions, brings about sudden increase in solution resistivity, and in the case of decorative plating solutions, restricts the bright plating range.
Ferric	In large amounts, affects solution conductivity; the already poor throwing power may be further reduced and deposit brittleness raised ; together with trivalent chromium restricts bright plating range in the case of decorative plating solutions.
Cu, Ni, Al, Zn.	Solution conductivity is affected or deposit hardness increased.

Formation of spray in chromium plating solution : Only a small fraction of the current passed through the solution is effectively utilised in metal deposition. The gases evolved at the cathode and anode create a fine spray of chromic acid which, when not contained, will become a health-hazard. Fume - suppressants appear to be incompatible with solutions used for obtaining highly thick deposits. as, under those conditions, hydrogen gas bubbles formed tend to stick to the cathode surface for a much longer duration than when no fume-suppressant is used and this causes excessive pitting of deposit. Not infrequently pitting of deposits is also encountered, when a solution with small polythene balls floating (in order to suppress spray) is used for very long durations. Installation of fume extraction equipment offers the best solution in this regard. Recently, however, a product under the trade-name Foam-lok, which can be used in solutions for obtaining very thick deposits, has been brought into the market by Udylite Corporation, USA[4].

Heat—treatment of components : A proportion of hydrogen gas evolved both during preplating treatments like pickling and electrocleaning and during chromium deposition may be occluded by components especially of hardened steel leading to embrittlement and loss of strength and even failure. Stresses induced during machining or similar operation before plating, may give rise to flaking of chromium deposit ; cracks caused by hardening stresses can, in conjunction with occluded hydrogen, lead to complete failure of the component. Parts that are particularly affected are (1) of highly hardened steel, (2) of steels work-hardened by machining (3) those of thin sections, (4) those subjected to sudden stresses, eg. high-speed steels and carbon steels, and (5) those treated at 500°C or a higher temperature.[5] All these parts require heat treatment before and/or after chromium plating in order to relieve stress and/or to ameliorate the effects of hydrogen embrittlement. Post plating heat treatment is preferably carried out within 15 minutes of plating. Parts of steel with hardness less than 40

Rockwell C do not require any heat-treatment. Chromium plating should not be carried out on parts of steel with hardness more than 62 Rockwell C. Conditions of heat-treatment of parts are given in Table 3.

Table 3 – Conditions of Heat treatment

Parts	Before plating	After plating
(i) Parts of steel	Stress-relieving heat-treatment at 150°-230°C for 30 minutes	De-embrittling heat-treatment at 175°-200°C for 3 hr.
(ii) Parts heated to 500°C during tempering or nitriding.	—	Heat-treated at 440°C for not less than 1 hr.

Uses of chromium deposits: Hard chromium plated parts find use in a number of engineering industries. The applications are based on the following properties of chromium deposits: (i) hardness and resistance to wear; (ii) resistance to corrosion and heat; (iii) low coefficient of friction and prevention of sticking of pasty materials; (iv) attractive appearance; and (v) paramagnetic properties.

The various fields of application include mechanical, electrical, chemical, fluid-power, and plastic engineering, agriculture, air-craft, food, metal, motor, optical, paper, photographic, printing, textile, building, leather, mining and armament industries and railways. The hard chromium deposit applied may be light, or a heavy ground deposit, grinding being necessary only when the thickness is more than about 50 μm. Salvaging of worn-out parts is an important application of hard chromium plating. Morisset et al[2] and Greenwood[2] give exhaustive lists of application of hard chromium plating in various industries. Typical uses[6] with required deposit thickness are given in Table 4. From many experiments and observations, it has been deduced that a 8–10 μm thick deposit can give protection for parts subject to light corrosive conditions in service, and a 12–18 μm thick deposit can withstand both wear and corrosive atmospheres while a thickness of 50–75 μm provides protection against liquid corrosive attack. Heavier deposits are required to withstand heavy wear and for salvaging of parts.[2]

Table 4–Typical applications of hard chromium deposits

Parts (base metal)	Thickness(μm) of chromium plate
Lock cases (brass)	5–7.5
Cylinders (cast iron)	250
Crankshafts (steel)	250–3750
Forming and drawing dies (steel)	25
Gear (steel)	200
Gun barrel 30-calibre (steel)	25
Hydraulic cylinder (steel)	12.5
Relief valve plunger	100
Ring gauge (steel)	200
Rolls (steel)	25
Shaft (steel)	250
Shaft (soft steel)	12.5
Valves (steel)	50

SRHS Chrome Salt Additive Mixture: An SRHS Chrome Salt Additive Mixture, when used during chromium bath preparation, not only helps dispense with chemical analysis of the minor constituents, but substantialiy increases the speeds of metal deposition at different current densities. The bath can be maintained by analysing for chromic acid, measuring specific gravity of solution and making additions of chromic acid and SRHS Chrome Salt Additive Mixture respectively, as required. Typical data on the rates of deposition[7] are included in Table 5.

Table 5 – Comparison of SRHS chromium bath and conventional[7] chromium bath (both at 55°C)

Deposition	Rate of deposition (μm/hr)	
C. D., ASD	SRHS bath*	Conventional bath
31.0	33	24
46.5	48	38
62.0	67	54

*Values for a 90 litre bath; deposit micro hardness 940 – 960 VHN

REFERENCES

1. J.D. Greenwood, Heavy Deposition, Robert Draper Ltd, Teddington (1970) 174.
2. P. Morisset, J. W. Oswald, C. R. Draper and R. Pinner, Chromium Plating, Robert Draper Ltd, Teddington (1954); J. D. Greenwood, Heavy Deposition, Robert Draper Ltd, Teddington (1970).
3. L.E. Lancy, 8th Congress of the International Union for Electrodeposition and Surface Finishing, Basle (1972) 435.
4. D. R.Millage, European Metal Finishing Congress, Amsterdam (1971)
5. J. D. Greenwood, Heavy Deposition, Robert Draper Ltd Teddington (1970) 143; Metals Handbook, American Society for Metals, Ohio (1964) 473.
6. Metals Handbook, American Society for Metals, Ohio (1964) 463.
7. A. G Gray, Modern Electroplating, John Wiley & Sons, Inc., New York (1953) 143.

ASHOK INDUSTRIES

Kakad Chambers, 132, Dr. Annie Besant Road,
WORLI, BOMBAY–18.

Manufacturers of :

Metallic Surface Treatment Chemicals

such as

ASFOCLEAN	—	For Degreasing
ASHTREAT	—	Heat Treatment Salt
CHEMIKLIN	—	Metal Derusting
ASFOCOAT	—	For Phosphating
COROBIT	—	Corrosion Inhibitors
ASFOSIL	—	Rust Preventives
SCALGUN	—	For Descaling
ASWASOF	—	Water Conditioning Chemicals

Gold Medal Academy Award Winners of International Trade Fair of 1973-74

Approved Suppliers to D. G. S. & D. Various Govt. Defence Units, Railways
HAL Units, Navy, Public Undertakings Etc.

Technical Services Available At :
POONA, HYDERABAD, BANGALORE, BARODA
MADRAS, KOTTAYAM & COCHIN

MCIC
THE METTUR CHEMICAL AND INDUSTRIAL CORPORATION LIMITED

The Mettur Chemical & Industrial Corporation Limited

METTUR DAM–636 402 (TAMIL NADU)

Large Scale Manufacturers of :

CAUSTIC SODA
STABLE BLEACHING POWDER
METHYL CHLORIDE
METHYLENE CHLORIDE
CARBON TETRACHLORIDE
CHLOROFORM
ETHYL SILICATE
SILICON TETRACHLORIDE
LIQUID CHLORINE
CHLORINATED PARAFFIN WAX

HYDROCHLORIC ACID
POTASSIUM CHLORATE
CALCIUM CHLORIDE
SULPHATE OF ALUMINA
CHEMICAL LIME
COMMON SALT
VANASPATI
REFINED VEGETABLE OILS
AND
TOILET & WASHING SOAPS