

Short Communication

Cathodic Efficiency of Industrial Chromium Plating

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Abstract. Current efficiency of hard chrome plating bath was studied. Experiments were carried out using industrial grade chromic acid. The best results were obtained from the chrome plating bath comprising chromic acid 300-350 g/l, sodium silicofluoride 5-6 g/l, $\text{CrO}_3/\text{H}_2\text{SO}_4$ ratio of 125 : 1, at current density 12 A/dm² and temperature 30-35 °C. The current efficiency of the bath was $\approx 32\%$.

Keywords: chrome plating, copper coulometer, sodium silicofluoride, cathode efficiency

A chromium plating bath was recommended to produce bright electrodeposits at a high current efficiency, and high microhardness with less porosity. The bath contained chromic acid (250 g/l) and potassium sulfate (2.5 g/l) at 325 K and the cathodic current density of 15.5-31.0 A/dm² (Krishnan *et al.*, 1999). Chrome electrodeposition bath with improved throwing power was discussed in an earlier report (Haque *et al.*, 2003). The role of activators, such as sodium silicofluoride and sulfuric acid, in bright chrome electroplating, has been also discussed (Haque *et al.*, 2002).

Composition of an electrolyte for hard decorative chromium electroplating has been proposed. The electrolyte for hard decorative chrome plating, at the temperature of about 50 °C and current density of 15.0-50 A/dm², contained 250-400 g/l chromic acid and 2.5-4.0 g/l sulfuric acid. Shiny mirror-uniform microcrystalline electroplates were obtained in this electrolyte on the addition of 10-15 g/l boric acid, 1-1.5 g/l strontium sulfate and 0.2-2.0 g/l sodium fluoride (Grunwald *et al.*, 1998). Results of experiments carried out with nonetching electrolytes, but containing sulfate and potassium iodate have been reported. Different concentrations of chromic acid, sulfate and potassium iodate were used and current efficiency, rate of build-up, throwing power, deposit nature, and microhardness have been evaluated (Kennedy *et al.*, 1996). Decorative or hard chromium plating was possible from a bath containing chromic acid (250 g/l) and ammonium fluoride (30 g/l) at 50 °C and current density 25-60 A/dm². The bath produced brighter deposits even up to 50 μm thickness (Sriveeraraghavan *et al.*, 1996).

The present study reports the current efficiency of hard chrome plating bath. Experiments were carried out using industrial grade chromic acid. Chemicals used were chromium trioxide

(Oxychem, USA, industrial grade, containing 0.2% sulfate maximum), sulfuric acid (BDH, England, analytical grade), and copper sulfate (Merck, Germany, analytical grade). Other chemicals used were: sodium hydroxide, sodium carbonate, sodium silicate, trisodium phosphate and ethanol, all of laboratory grade and used as received. In all experiments, the electrolytes for chrome plating were prepared from chromium trioxide (Haque *et al.*, 2003). The cathode efficiency was measured by placing the copper coulometer in series with the bath (Canning, 1971). The composition of the solution of copper coulometer is given in Table 1.

Brass pieces, 1.45 x 0.9 in², were used as the cathode for chrome plating. The sheet was polished, mechanically buffed, degreased with ethanol, and electrolytically cleaned before plating. The copper cathodes of area 2.7 x 1.4 in² were employed. For chrome plating, 6% tin-lead alloy (Dr. Hesse and Cie, Germany), were used as anodes. For copper coulometer, copper pieces, 6 x 1.75 in², were employed as anodes. The experiments were carried out in glass cells, containing the electrolytes.

The nature of the deposits over a wide range of current density was ascertained from Hull cell experiments using brass panels of 20 gauge, 2.5 x 4.0625 in². The 6% tin-lead alloy (Dr. Hesse and Cie, Germany), 2.5 x 2.5 in² was employed as the anode. The effect of various concentrations of chromic acid and sodium silicofluoride on cathode efficiency of the hard chrome plating bath was studied and results have been summarized (Fig. 1, 2).

Table 1. Composition of the solution for copper coulometer

Chemical	Concentration
Copper sulfate	100-125 g/l
Sulfuric acid	25-35 ml/l
Ethanol	25-35 ml/l

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Influence of sodium silicofluoride on cathode efficiency of hard chrome plating bath was studied in six sets of experiments, in which the concentrations of sodium silicofluoride was varied from 1-8 g/l, while the concentrations of chromic acid were: 200, 250, 300, 350, 400, 450 g/l, respectively, for sets 1-6 (Fig. 1). Other conditions, namely, $\text{CrO}_3/\text{H}_2\text{SO}_4$ ratio of 125 : 1, temperature 30-35 °C, and current density of 12 A/dm² were kept constant for all sets of experiments. Chromium cannot be deposited from a solution containing only chromium trioxide and water. The solutions that were used contained chromic acid with sulfate as the catalyst (Dennis and Such, 1986; Lowenheim, 1967). Sodium silicofluoride (5-6 g/l) gave the best results in terms of cathode efficiency. The cathode efficiency was \approx 32% at the chromic acid concentration of 350 g/l. The ratio of the chromic acid to the catalyst is most important. It may be noted from Fig. 1 that for successful continuous operation, the ratio of the chromic acid to sodium silicofluoride must be maintained within definite limits. This ratio fell within the range of 50 : 1 to 70 : 1; with 60 : 1 giving the best efficiency.

The concentration of chromic acid usually used is within the range of 150-550 g/l. The concentrated solutions are more expensive to use than the more dilute solution bath, and a higher drag-out rate is incurred during the operation. At high chromic acid concentrations, the cathode efficiency, 25% maximum, was obtained at the sodium silicofluoride concentration of 7-8 g/l. The effect of chromic acid on the cathode efficiency, in the absence and in the presence of sodium silicofluoride (5-6 g/l), has been summarized in Fig. 2. The presence of sodium silicofluoride in the bath was found to produce higher cathode efficiency. The cathode efficiency of chrome plating was noted to increase from chromic acid concentration range of 200-350 g/l. Maximum current efficiency was obtained from chromic acid concentration range of 300-350 g/l. High chromic acid concentration bath (400-450 g/l) had lower cathode efficiency (Fig. 2). The results reported here have good agreement with those reported in literature (Dennis and Such, 1986; Lowenheim, 1967). Bath comprising chromic acid (300-350 g/l), sodium silicofluoride (5-6 g/l), and $\text{CrO}_3/\text{H}_2\text{SO}_4$ ratio of 125 : 1 at the current density of 12 A/dm², and temperature 30-35 °C, gave the cathode efficiency \approx 32%.

Hull cell tests were carried out on mechanically buffed, polished, and electrolytically cleaned brass panels degreased with ethanol to examine the appearance and the adhesion of the deposit. Plating was carried out for the duration of 30 min at temperature of 30-35 °C, and the cell current of 6 A. The bath

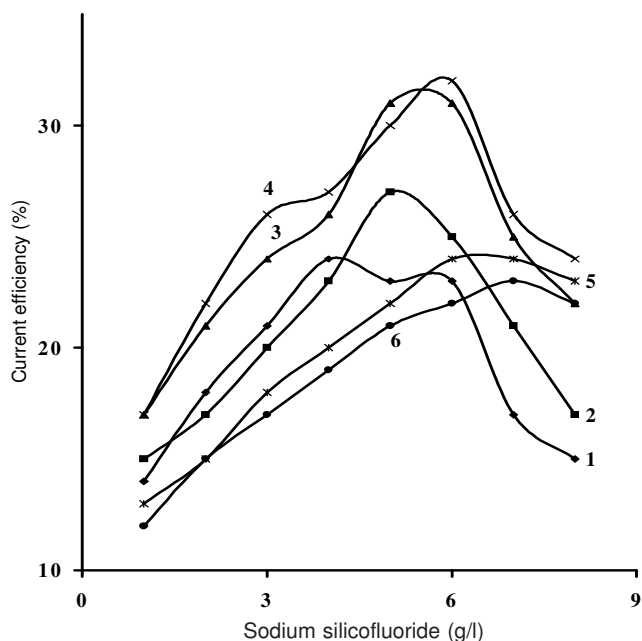


Fig. 1. Influence of the concentration of sodium silicofluoride on cathode efficiency; $\text{CrO}_3/\text{H}_2\text{SO}_4$ ratio of 125 : 1, temperature 30-35 °C and current density 12 A/dm²; 1 = chromium trioxide 200 g/l; 2 = chromium trioxide 250 g/l; 3 = chromium trioxide 300 g/l; 4 = chromium trioxide 350 g/l; 5 = chromium trioxide 400 g/l; 6 = chromium trioxide 450 g/l.

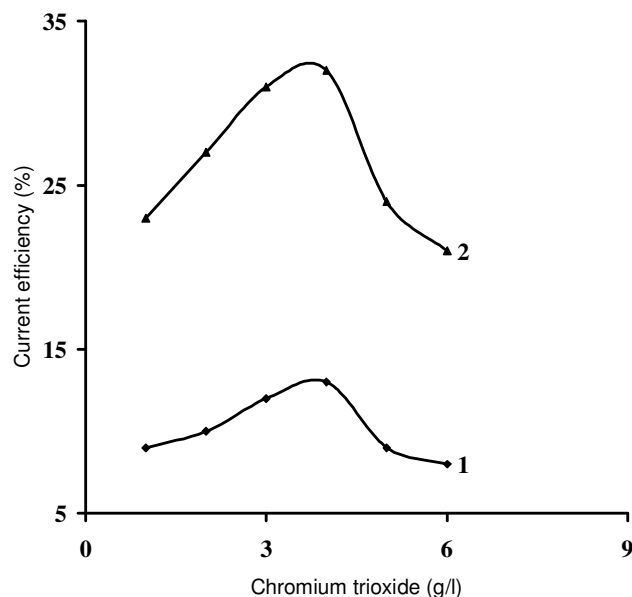


Fig. 2. Influence of the concentration of chromic acid on cathode efficiency; $\text{CrO}_3/\text{H}_2\text{SO}_4$ ratio of 125 : 1, temperature 30-35 °C and current density 12 A/dm²; 1 = in the absence of sodium silicofluoride; 2 = in the presence of sodium silicofluoride (5-6 g/l).

gave satin grey deposit over a wide current density range. The adhesion of the deposit was good. Results showed that sodium silicofluoride (5-6 g/l) gave good results in terms of cathode efficiency. Higher concentration of chromic acid baths had lower cathode efficiency than the low concentration chromic acid bath. The bath contains 300-350 g/l chromic acid and 5-6 g/l sodium silicofluoride, and the $\text{CrO}_3/\text{H}_2\text{SO}_4$ ratio of 125 : 1 at 30-35 °C and 12 A/dm² gave the current efficiency of $\approx 32\%$. The appearance and adhesion of the deposits were good.

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