# Role of Activators in Bright Chrome Electroplating

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**Summary:** Role of activators such as sodium silicofluoride and sulfuric acid in bright chrome electroplating was investigated using technical grade chromic acid, $CrO_3$, containing 0.15% sulfate, maximum. It was found that bath comprising $CrO_3$ 300-350 g/L, $Na_2SiF_6$ 2-3 g/L, $H_2SO_4$ 1-2 ml/L at temperature 30-35°C and current density 8-10 A/dm$^2$ can be recommended as a self-regulating one for bright chrome plating.

## Introduction

Chrome electroplating was carried out on brass panels in Hull cell using technical grade chromic acid. A bath for bright chrome electroplating was reported. The throwing power of bath was good. It is found that sulfate is an effective catalyst for the chrome electrodeposition [1]. A chromium plating bath was recommended to produce bright electrodeposits at a high current efficiency, high microhardness and with less porosity. The bath contained chromic acid 250 g/L and K sulfate 2.5 g/L at 325K and cathodic current density 15.5-31.0 A/dm$^2$ [2].

Effect of type and concentration of foreign acid anions on the course of stepwise reduction of chromium(VI) oxide was reported. When two types of chromium electroplating catalytic agents were applied: sulfate anions and hexafluorosilicate(IV) anions, the reduction rate of the cathode layer was twice larger than in the case, when only one type of catalytic agent was applied [3]. It was found that improved throwing power was achieved with enhanced concentrations of $CrO_3$, with leveling observed at higher chromic acid concentrations [4]. $C_1$-$C_{12}$ alkanesulfonic or alkanedisulfonic compounds and aminoalkanesulfonic acids or salts thereof, were used as additives in chromium plating baths to reduce anodic corrosion, improve the covering and penetrating power of the bath, reduce the surface tension and gave a bright deposit [5].

The bath comprising $CrO_3$ 250-350, $H_2SO_4$ 2.5-3.5, $SrSO_4$ 2-4, and $SiO_2$ 0.5-1 g/L was used. The current density was 10-20 A/dm$^2$. The lead anode was alloyed with 10% Sn or 7% Sn and 1% Ag. Alloying the anode decreased its potential and the rate of lead peroxide formation and $Cr^{3+}$ oxidation [6]. Experiments were carried out with varying concentrations of chromic acid from 50 g/L to 250 g/L in the presence of 1% sulfate by means of Hull cell tests in order to determine the basic solution composition. Current efficiency and rate of build-up were also determined in the case of selected compositions. The effect of boric acid or lanthanum oxide was investigated [7]. 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/dm$^2$. The bath produced brighter deposits even up to 50 μm thickness [8].

The electroplating of chromium on bright nickel-electroplated brass was carried out from baths containing halo carboxylic acid-rare earth compound mixture as an additive. The throwing power and cathodic current density were improved, the Vicker's hardness of the electroplate was 980-1100, and the adherence was good [9]. The current efficiency of chromium electrodeposition and cathodic polarization curves were determined in halide-chromic acid-sulfuric acid systems.The composition of the cathodic films formed was determined by XPS and AES. The results show that the sulfate is an effective catalyst for the deposition of bright chromium and that the current efficiency of the chromium deposition increases remarkably when $F^-$

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and $Cl^-$ were added to the bath, and also that $F^-$ and $Cl^-$ participated in the formation of the films [10].

**Results and Discussion**

All experiments were carried out on brass panels in a Hull cell. Five sets of Hull cell experiments were carried out and the results are summarized in Tables. Bath comprising, $CrO_3$, 150-500 g/L, $H_2SO_4$ 1-2 ml/L, $Na_2SiF_6$ 2-3 g/L, at temperature 30-35°C, plating duration 2-3 minutes, running voltage 3.75-4.0V and current density 8-10 A/dm$^2$ was used in first set. Influence of chromic acid concentration on the throwing power is shown in table 1. Brightness of the plates was good at higher chromic acid concentrations.

Table 1: Influence of chromic acid concentration on throwing power

| Plates No | $CrO_3$ (g/L) | Throwing power (cm) | Quality |
|---|---|---|---|
| 1 | 150 | 1.7 | Slightly smoky |
| 2 | 200 | 2.1 | Slightly smoky |
| 3 | 250 | 3.0 | Slightly smoky |
| 4 | 300 | 5.3 | Greyish white |
| 5 | 350 | 5.7 | Greyish white |
| 6 | 400 | 6.4 | Greyish white |
| 7 | 450 | 6.6 | Semi-bright |
| 8 | 500 | 7.0 | Semi-bright |

Substrate, brass panels; sodium silicofluoride, 2-3 g/L; sulfuric acid, 1-2 ml/L; temperature, 30-35°C; plating duration, 2-3 minutes; running voltage, 3.75-4.0V; current density 8-10 A/dm$^2$.

In second run sodium silicofluoride 1-8 g/L, $CrO_3$ 300-350 g/L, $H_2SO_4$ 1-2 ml/L were used at temperature 30-35°C, plating duration 2-3 minutes, running voltage 3.75-4.25V and current density 8-10 A/dm$^2$. Influence of sodium silicofluoride concentration on throwing power is shown in table 2. Best results in terms of throwing power were obtained at sodium silicofluoride concentration 2-3 g/L. Sodium silicofluoride concentrations higher than 3 g/L led to poor throwing power. The appearance of the plates was good with sodium silicofluoride 2-3 g/L, as shown in column 5 of table 2.

Table 2: Influence of sodium silicofluoride concentration on throwing power

| Plates No | $Na_2SiF_6$ (g/L) | Throwing power (cm) | Quality |
|---|---|---|---|
| 9 | 1 | 4.5 | Dull |
| 10 | 2 | 6.0 | Greyish white |
| 11 | 3 | 5.6 | Greyish white |
| 12 | 4 | 4.9 | Slightly smoky |
| 13 | 5 | 4.5 | Slightly smoky |
| 14 | 6 | 4.2 | Slightly smoky |
| 15 | 7 | 3.9 | Slightly smoky |
| 16 | 8 | 3.7 | Slightly smoky |

Substrate, brass panels; chromic acid, 300-350 g/L; sulfuric acid, 1-2 ml/L; temperature, 30-35°C; plating duration, 2-3 minutes; running voltage, 3.75-4.25V; current density 8-10 A/dm$^2$.

In third set of experiments, V-0663 concentrations, 1-13 g/L, $CrO_3$ 300-350 g/L, $H_2SO_4$ 1-2 ml/L were used at temperature 30-35°C, plating duration 2-3 minutes, running vsoltage 3.75-4.20V and current density 8-10 A/dm$^2$. Influence of V-0663 concentration on throwing power is shown in table 3. Best results in terms of throwing power were obtained at V-0663 concentration 6-8 g/L. Also appearance of the plates was good. Sodium silicofluoride gave similar results in terms of appearance. No marked difference was noticeable in the plates.

Table 3: Influence of V-0663 concentration on throwing power

| Plates No | V-0663 (ml/L) | Throwing power (cm) | Quality |
|---|---|---|---|
| 17 | 1 | 1.2 | Smoky |
| 18 | 2 | 1.9 | Dull |
| 19 | 3 | 2.8 | Smoky |
| 20 | 4 | 3.7 | Slightly smoky |
| 21 | 5 | 4.5 | Slightly smoky |
| 22 | 6 | 5.6 | Slightly smoky |
| 23 | 7 | 6.3 | Greyish white |
| 24 | 8 | 5.6 | Semi-bright |
| 25 | 9 | 5.0 | Greyish white |
| 26 | 10 | 4.7 | Greyish white |
| 27 | 11 | 4.3 | Slightly smoky |
| 28 | 12 | 3.7 | Slightly smoky |
| 29 | 13 | 3.2 | Slightly smoky |

Substrate, brass panels; chromic acid, 300-350 g/L; sulfuric acid, 1-2 ml/L; temperature, 30-35°C; plating duration, 2-3 minutes; running voltage, 3.75-4.20V; current density, 8-10 A/dm$^2$.

In fourth run, temperature effect on throwing power was studied. Plating was carried out using, $CrO_3$ 300-350 g/L, $H_2SO_4$ 1-2 ml/L, $Na_2SiF_6$ 2-3 g/L, plating duration 2-3 minutes, running voltage 3.75-4.10V at current density 8-10 A/dm$^2$. Temperature effect on throwing power is shown in table 4. Within the temperature range 25-35°C, throwing power was consistently good for bright chrome plating, however, the brightness of the plates was good within temperatures 35-45°C as shown in column 5 of table 4.

Table 4: Influence of temperature on throwing power

| Plates No | Temp. (°C) | Throwing power (cm) | Quality |
|---|---|---|---|
| 30 | 15 | 2.8 | Smoky* |
| 31 | 20 | 4.4 | Smoky |
| 32 | 25 | 4.7 | Slightly smoky |
| 33 | 30 | 5.3 | Slightly smoky |
| 34 | 35 | 5.7 | Greyish white |
| 35 | 40 | 4.5 | Semi-bright |
| 36 | 45 | 3.8 | Semi-bright |
| 37 | 50 | 3.3 | Slightly smoky |

*High current density area charred

Substrate, brass panels; chromic acid, 300-350 g/L; sodium silicofluoride, 2-3 g/L; sulfuric acid, 1-2 ml/L; plating duration, 2-3 minutes; running voltage, 3.75-4.10V; current density, 8-10 A/dm$^2$.

Experiments were carried out at various current densities using, $CrO_3$ 300-350 g/L, $H_2SO_4$ 1-2

ml/L, $Na_2SiF_6$ 2-3 g/L, at temperature 30-35°C, plating duration 2-3 minutes and running voltage 3.75-4.55V. Influence of current density on throwing power is shown in table 5. Throwing power increased with increase in current density, as shown in 3rd column of table 5 [11]. Brightness of the plates also increased with increase in current density.

Table 5: Influence of current density on throwing power

| Plates No | Current density $A/dm^2$ | Throwing power (cm) | Quality |
|---|---|---|---|
| 38 | 6 | 4.2 | Dull |
| 39 | 8 | 5.6 | Slightly smoky |
| 40 | 10 | 6.5 | Slightly smoky |
| 41 | 11 | 6.7 | Greyish white |
| 42 | 13 | 7.0 | Semi-bright |
| 43 | 15 | 7.3 | Slightly smoky |

Substrate, brass panels; chromic acid, 300-350 g/L; sodium silicofluoride, 2-3 g/L; sulfuric acid, 1-2 ml/L; temperature, 30-35°C; plating duration, 2-3 minutes; running voltage, 3.75-4.55V.

*Physical tests*

Thickness of chromium coating, on mild steel panel was measured by microscopic observation of the cross-section normal to the coating [12]. Thickness of the chrome coatings on nickel coated mild steel panel was found 0.5 μm. Adhesion of the nickel plus chrome coatings on mild steel panel was tested by bend test [13]. No peeling was observed. Adhesion of the chrome coating was good. The throwing power of bath was good. Chromium was deposited on nickel coated mild steel panels: nickel was first deposited from Watts nickel bath to nickel thickness 15~25 μm; adhesion and brightness of the obtained chrome deposit on nickel coated mild steel panels were good [14].

## Experimental

*Chemicals*

Chromium trioxide, $CrO_3$, OXYCHEM, USA; sulfuric acid, $H_2SO_4$, BDH, England; nickel sulfate , $NiSO_4.6H_2O$, Inco, Canada; nickel chloride, $NiCl_2.6H_2O$, Inco, Canada; boric acid, $H_3BO_3$, US Borax Inc., USA; V-0663, patented chemical, Dr. Hesse and Cie, Germany. Other chemicals, $Na_2SiF_6$, NaOH, $Na_2CO_3$, $Na_3PO_4$, $Na_2SiO_3$, $C_2H_5OH$ were of laboratory grade or better and were used as received.

*a- Hull cell Experiments*

Preparation of electrolyte: To prepare baths technical grade $CrO_3$, containing 0.15% sulfate, maximum, was added in a beaker containing distilled water and its density was measured with the help of hydrometer. The density of the solution was adjusted such that the concentration of $CrO_3$ was 300-350 g/L [15]. Finally, concentrated sulfuric acid, 1-2 ml/L, was added.

*Cathode*

Rectangular brass panels, locally purchased, of 2.5x4.0625 $in^2$ dimension of 20 gauge sheet were used for plating purposes. These sheets were mechanically buffed to a high finish. Subsequently washed and degreased with ethanol before plating.

*Anode*

Insoluble 6% Sn-Pb alloy, Dr. Hesse and Cie, Germany, was employed as anode. The area of anode was 2.5x2.5$in^2$.

Chrome plating on brass panels: The nature of deposits over a wide current density range was ascertained from Hull cell experiments carried out on brass panels using constant current electrolysis. Indigenously prepared D.C. power supply was used. Plating duration was 2 to 3 minutes.

*b- Nickel and Chrome Plating on Mild Steel Panels*

Cathode: Mild steel panels, containing 0.5-1% carbon and 0.45-0.5% manganese, which were used for plating purpose, had a surface area of 1x2 $in^2$ and thickness 1mm. It was locally purchased.

*Anodes*

Pure nickel metals, Inco, Canada, having area 1.5x6.0 $in^2$, were employed as anodes for nickel plating in a container. Insoluble 6% Sn-Pb alloys, Dr. Hesse and Cie, Germany, were employed as anodes on both sides of central cathode. The area of each anode was 1.75x6.0 $in^2$.

Two mild steel panels were nickel plated from Watts nickel bath; $NiSO_4.6H_2O$ 300 g/L, $NiCl_2.6H_2O$ 68 g/L, $H_3BO_3$ 40 g/L at temperature 55-60°C, pH 4.2-4.5 and current 1 ampere to nickel thickness 15~25 μm and running voltage 1.50-1.75V in a glass container then immediately chrome electroplated from the bath obtained from the best results of Hull cell experiments ($CrO_3$ 300-350 g/L, $Na_2SiF_6$ 2-3 g/L, $H_2SO_4$ 1-2 ml/L) at temperature 30-35°C and current density 8-10 $A/dm^2$, running voltage 3.75-4.1V and plating duration 2-3 minutes.

**Conclusions**

For chromium plating from a chromic acid bath, sodium silicofluoride and sulfuric acid, were used as additives.Hull cell experimeents were carried out to observe the effect of chromic acid concentration, sodium silicofluoride concentration, temperature and current density. Results showed that: **a-** improved throwing power was achieved with enhanced concentrations of $CrO_3$, **b-** best results in terms of throwing power were obtained at sodium silicofluoride concentration 2-3 g/L, **c-** in the temperature range 25-35°C, throwing power was consistently good for bright chrome plating, **d-** throwing power increased with increase in current density. Adhesion and brightness of the obtained chrome deposit on nickel coated mild steel panels were good.

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