

ELECTRODEPOSITION OF BLACK CHROMIUM FROM SELF REGULATING ELECTROLYTES

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ABSTRACT

A strong need is felt by a practical plater for a black chrome bath which can be operated around the ambient temperature (30°C) and at normally employed current densities and preferably not associated with any necessity of controlling the catalyst concentration. In the work now reported, experiments were carried out on the solubility of calcium fluoride at 30°C in chromic acid solutions with a concentration range of 200–425 g/l. Barium hydroxide was introduced in adequate quantities to desulphate chromic acid and also to counteract any drag-in of sulphate. Hull-cell experiments were carried out at 23° and 31°C in order to assess approximately the current density range over which black chromium deposition was possible. This was followed by experiments in plating to study the effects of different parameters like chromic acid concentration, current density, temperature and duration of deposition on the nature of finish and deposition.

Key words: Electrodeposition, black chromium, self regulating electrolytes

INTRODUCTION

Application of black finish to components where a non-reflecting surface is desired for functional or decorative use is widely practised in the metal finishing industry [1]. Amongst the various finishes, black chromium occupies a unique place. For flat plate solar collectors, black chromium has been established itself as the best plated finish [2–14] due to its high absorption and low emission of solar energy as well as its durability especially when applied over a nickel undercoat.

Most of the black chromium baths employ chromic acid as the electrolyte with fluoride/fluosilicate as a catalyst and are operated preferably at a temperature of 20°C and at higher current densities than normally employed for decorative/hard chromium plating [15, 16]. A large bath volume with suitable cooling arrangements is therefore required and this assumes significance in tropical countries like India. In addition, the catalyst concentration should be controlled to close limits in order to produce quality deposits. But as the catalyst contents are low, further problems in regard to control are encountered in production practice. A fluosilicate based bath requiring a reasonably low optimum c.d. of 23.5 A. dm⁻², and an operating temperature of 20°C was reported [17] and the bath needs control of its low (0.5 g/l) catalyst concentration. A mixed catalyst bath was operated [18] at low c.d.s. of 10–25 A.dm⁻² and low temperature, viz. 20–22°C and with no mention whether the bath needs control of its catalyst content or not. A bath containing acetate and modifiers and operating at a low c.d. of 21.6 A.dm⁻² and a temperature of 24°C was reported [6, 7], without any indication of control to be effected on the catalyst(s).

Thus there is a need for a black chrome bath which can be operated around the ambient temperature (30°C) at normally used c.d.s. without control of the catalyst content. Earlier work by the authors [19] on the use of calcium fluoride as a catalyst in chromium bath prompted a study of the possibility of black chromium deposition from such chromic acid – based electrolytes. This paper reports the results of these studies.

EXPERIMENTAL

Solubility determination

Self regulation demands that the catalyst calcium fluoride be present in

excess of its solubility in the chromium bath. Therefore, solubility determination was carried out in chromic acid solutions of different concentrations, using one litre solution of chromic acid and calcium fluoride (National Fluorine Corporation grade) at 30°C by gravimetry. Concentrations of chromic acid studied were: 150, 200, 250, 325 and 425 g/l.

Hull cell studies

Mild steel panels were nickel plated from a Watts solution at 40°C and 3.2 A.dm⁻² for 10 minutes, buffed to brightness, taken through the conventional cleaning procedure and chromium plated by passing a current of 15 A in the modified Hull Cell for 10 minutes at the temperatures of 23°C and 31°C, to ascertain the c.d. range over which black chrome deposition was possible. Each bath contained adequate barium hydroxide to desulphate the chromic acid and also to take care of possible drag-in of sulphate.

Rate of build up of black chrome

A precise determination of cathode efficiency of black chrome deposition was not possible due to variation in the oxide content of the deposits and due to non-availability of deposit density values. Hence deposition rate was found in terms of mg/cm², minute for three of the baths A, B and C. The duration of experiment was 30 minutes at low c.d.s. of 15–30 A dm⁻². Nickel plated steel was used as the substrate.

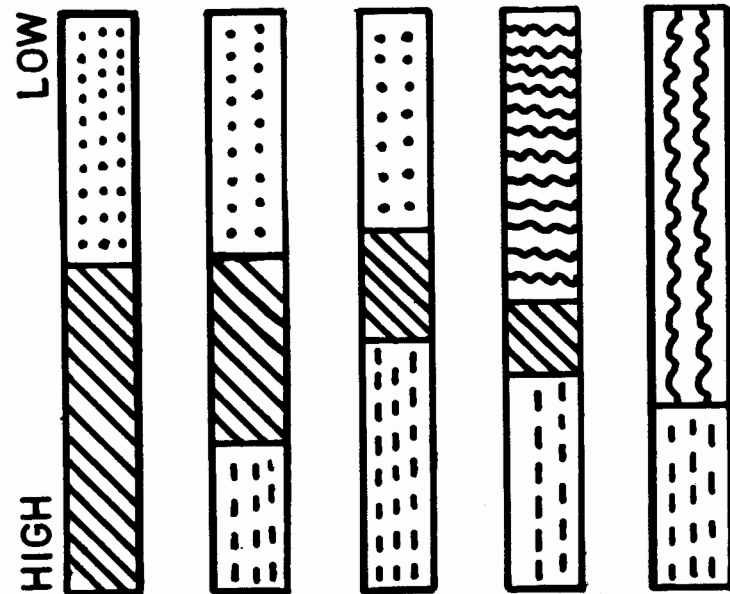
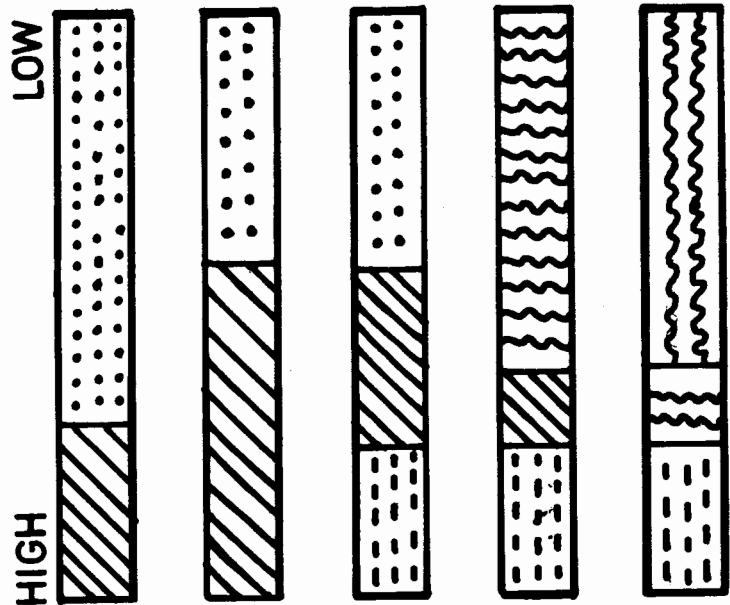
Studies on thickness build-up

Black chrome coatings are known to build up to a certain thickness and then the build up tapers off. Hence it was considered necessary to study the bath behaviour in this regard. Typically these studies were made in bath 'A' at 31°C and c.d.s. of 31.0 and 46.5 A.dm⁻² for durations in the range of 5–30 minutes.

RESULTS AND DISCUSSION

Solubility of calcium fluoride in chrome acid

The data in Table I show that the solubility of calcium fluoride in chromic



BATH
A

B

C

D

E

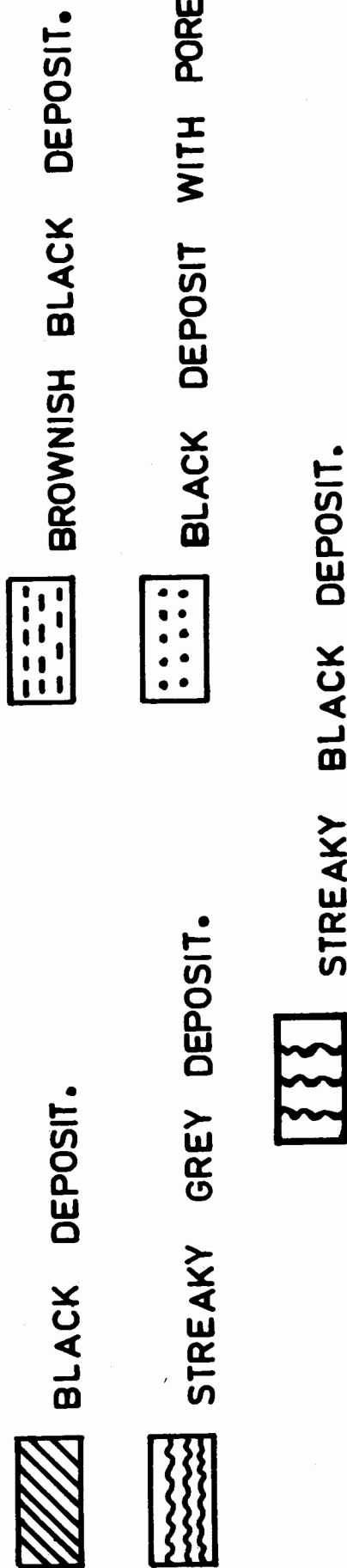


FIG.1 HULLCELL PATTERNS CHROMICACID CALCIUM FLUORIDE BATH.

acid in the range of 150-425 g/l is 0.83-2.43 g/l giving a chromic acid to catalyst ratio of 180:1. Therefore, an adequate amount (5 g/l) of calcium fluoride was used in all the baths studied to provide self regulation in regard to fluoride ion concentration. The compositions of the baths are presented in Table II.

Table I: Solubility of calcium fluoride in chromic acid solution at 31°C

Concentration of CrO ₃ (g/t)	Solubility of CaF ₂ (g/t)	Ratio of CaO ₃ /CaF ₂
150	0.83	180:1
200	1.15	174:1
250	1.34	187:1
325	1.79	181:1
425	2.43	175:1
		Mean 179:1

Table II: Bath formulations studied

Bath	Ingredients in g/l		
	CrO ₃	Ba(OH) ₂	CaF ₂
A	150	8	5
B	200	8	5
C	250	9	5
D	325	10	5
E	425	10	5

Influence of parameters on nature of finish

The observations in regard to Hull cell patterns (Fig 1) are summarised in Table III. Some important inferences are as follows:

Table III: Hull cell data for different baths

Cell current: 15 A Duration: 10 mins

Bath	Current density range in A.dm ⁻²					
	Black deposit		Brownish black deposit		Black deposit with pores	
	23°C	31°C	23°C	31°C	23°C	31°C
A	76.0-17.0*	76.0-37.2	-	-	17.0-4.5	37.2-4.5
B	44.6-17.0	76.0-17.0	76.0-44.6	-	17.0-4.5	17.0-4.5
C	25.6-13.6	44.6-17.0	76.0-25.6	76.0-44.6	13.6-4.5	17.0-4.5
D	30.7-21.0	54.5-37.2	76.0-30.7	76.0-54.5	-	-
E	-	-	76.0-37.2	76.0-44.6	-	-

* The c.d. values are calculated for the distances ranging from 0.6 to 8.3 cm from the high c.d. and of the Hull cell panel.

(i) Black chromium deposition a priori is possible over the entire c.d. range studied. (ii) Satisfactory black chrome deposition is possible with all the baths except 425 g/l composition at the bath temperatures at 23°C and 31°C, amongst them, bath 'A', 'B' and 'C' are capable of giving black chrome at low enough c.ds. (iii) With an increase in chromic acid content of the bath, the range of c.d. over which black chrome deposition occurs is narrowed down, at the bath temperature of 23°C. (iv) With a rise in chromic acid content, in the range of 150-250 g/l, the c.d. range over which black chrome plating takes place, tends to get shifted to low c.d. values. The c.d. range is very narrow at a chromic acid concentration of 325 g/l and is nil at 425 g/l. (v) The widest c.d. range of 17.0-76.0 A.dm⁻² for black chrome is noticed at

31°C in 200 g/l bath while the 150 g/l bath behaves similarly at 23°C. This coupled with (iv) above means that if black chrome deposition is being carried out at 23°C at a c.d. close to the upper limit, one should be careful in keeping the chromic acid content nearly constant, as otherwise the nature of the deposit is likely to change in appearance from black to brownish black. (vi) A rise in bath temperature tends to widen the c.d. range for black chrome plating, in the case of baths B and C. (vii) A brownish black deposit is seen at high c.ds. in baths with 250-425 g/l chromic acid at both the temperatures, while such deposition is noticed at 23°C only with 200 g/l bath and no such deposition when chromic acid concentration is 150 g/l. (viii) At low enough c.ds. (usually below 17.0 A.dm⁻² and at both the temperatures, black deposits are possible with 150-250 g/l solutions, although they appear to be porous.

Deposition rate of black chrome

Concentration of chromic acid appears to have no specific influence on the rate of build-up of black chromium (Table IV). The rate of build up, however, increases with c.d., but not necessarily proportionately, the behaviour is specific to each bath at each of the temperatures studied (Fig. 2).

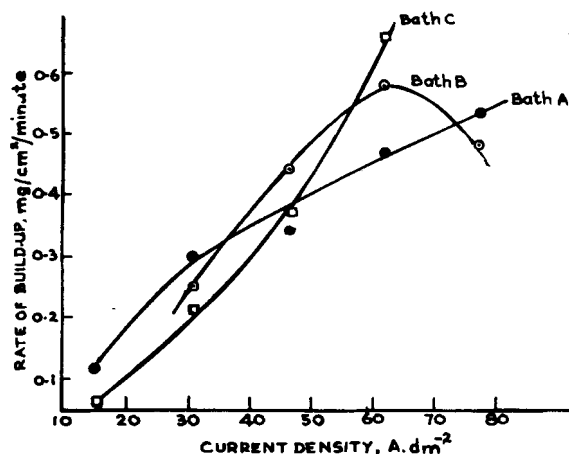


Fig. 2 Variation of deposit mass with current density at 31°C

Table IV: Variation of deposit mass with current density for different baths

Bath	Temp. °C	Deposit mass in mg/cm ² /minute at c.d. (A.dm ⁻²)					
		15.5	23.3	31.0	46.5	62.0	77.6
A	23	-	-	0.26	0.31	0.35	0.31
	31	0.11	-	0.30	0.34	0.47	0.53
B	23	0.09	-	0.28	0.38	-	-
	31	-	-	0.25	0.44	0.58	0.48
C	23	0.07	0.13	0.24	-	-	-
	31	0.06	-	0.21	0.37	0.66	-
Duration in minutes		30	30	30	20	15	10

The deposition rate with time (Fig. 3) in 150 g/l bath at 31°C shows that the maximum build up is reached in about 20 minutes at 31.0 A.dm⁻²; and 10 minutes at 46.5 A.dm⁻²; further electrolysis does not result in any substantial deposition of black chromium.

CONCLUSIONS

(i) At 31°C, (the ambient temperature in tropics like India) a bath containing chromic acid (200 g/l) barium hydroxide (8 g/l), and calcium fluoride (5 g/l)

is suitable for black chromium deposition over a wide range of c. ds. This is an advantage in practice in that even if a complicated shape is plated and the c.d. on high points is large by virtue of geometry, still one can ensure black chrome deposition over these areas. An additional benefit is that an increase in CrO_3 concentration to 250 g/l does not affect the production of black chrome in the low c.d. range of 17.0-45.0 A. dm^{-2} . Similarly, a fall in chromic acid content to 150 g/l permits black chrome deposition, but over a narrower c.d. range but at rather high c. ds. The bath can be used at 23°C also at low c. ds. of 13.0-25.0 A. dm^{-2} . The bath is also self regulating thereby eliminating the necessity for control of the catalytic concentration. (ii) At 23°C, (the ambient temperature elsewhere in the globe,) the bath with 150 g/l chromic acid, 8 g/l barium hydroxide, and 5 g/l calcium fluoride permits operation over as wide a c.d. range for black chrome as with the other bath. In this bath also, a rise in chromic acid upto 200 g/l does not affect black chrome deposition in the low c.d. region of 17.0-45.0 A. dm^{-2} , a still further rise in chromic acid concentration narrows down the c.d. range for black chrome considerably. This bath can be used at 31°C as well, but one should use rather high c.ds. (37.0 A. dm^{-2}) to obtain black chrome deposits.

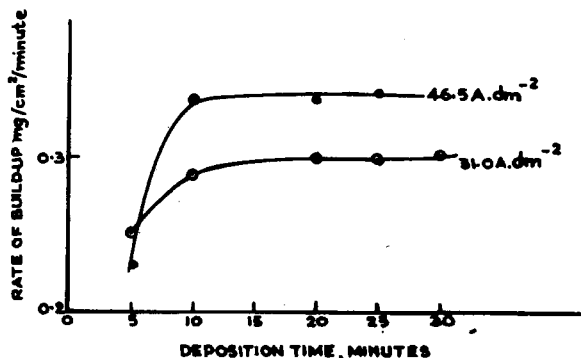


Fig. 3: Influence of deposition time on mass of deposit in bath -A' at 31°C

REFERENCES

1. A K Graham, *46th Annual Tech Proc Amer Electropl Soc*, (1969), p 61
2. Anon., *Prod Finish (Cincinnati)*, **40** (4) (1977) 80
3. Anon., *Prod Finish (Cincinnati)*, **41** (4) (1977) X 68
4. M Zahn, *Plating*, **66** (12) (1979) 22
5. P G Hamphroys, *Prod Finish (Cincinnati)*, **45** (11) (1981) 48
6. A C Benning, *Plating Surf Finish*, **68** (2) (1981) 49
7. A C Benning, *Second coatings for Solar Collectors Symposium*, American Electroplaters' Society, St Louis, October 1979, 65
8. J R Williams, *Proc AES- Coatings for Solar Collectors Symp*, November (1976)
9. J Hajdu and T Sullivan, *Plating Surf Finish*, **69** (9) (1982) 29
10. K J Cathro, *Metal Finish*, **76** (10) (1978) 57
11. F A Schneiders, *Plating Surf Finish*, **68** (12) (1981) 30
12. J Balachandra, *J Electrochem Soc India*, **29** (2) (1980) 79
13. G S S Prasad, S Mohan and K I Vasu, *J Electrochem Soc India*, **29** (1980) 85
14. J F Longland, *Finish Indi*, **2** (11) (1978) 33
15. B A Shenoi and S Gowri, *Metal Finish J*, **19** (5) (1973) 139
16. N Vasudevan, V K William Grips and Indira Rajagopalan, *Surf Technol*, **14** (1981) 119
17. L Sivasamy, S Gowri and B A Shenoi, *Metal Finish*, **72** (3) (1974) 48
18. M Selvam, K N Srinivasan, N V Shanmugam, S John and B A Shenoi, *Proc National Solar Energy Convention*, Annamalai Univ, Annamalai Nagar, Dec. (1980) 246
19. R M Krishnan and N V Parthasaradhy, *Metal Finish*, **69** (9) (1971) 59