

INFLUENCE OF POTASSIUM IODATE ON CHROMIUM DEPOSITION

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Chromium plating finds not only decorative but also functional applications. Generally chromium deposits are obtained from electrolytes with an approximate ratio of 100:1 of chromic acid to sulphuric acid. The Self Regulating High Speed (SRHS) chromium plating electrolytes, which are often employed for hard chromium plating though of higher efficiency have the disadvantages of cathodic etching and higher corrosivity. These are mainly due to the presence of a fluorine compound as a bath constituent. In this paper we report the results of experiments carried out with nonetching electrolytes but containing sulphate and potassium iodate. Different concentrations of chromic acid, sulphate and potassium iodate were used and current efficiency, rate of build-up, throwing power, deposit nature and microhardness were evaluated.

Keywords: Chromium plating, low concentration, KIO_3 and HENE

INTRODUCTION

EXPERIMENTAL

Electrodeposited chromium is extensively used for decorative and functional applications. The functional applications of chromium coatings are based on their high hardness, high resistance to wear, low coefficient of friction, nonwettability etc. Both decorative and functional coatings are conventionally produced from electrolytes containing chromic acid and a small quantity of sulphuric acid, usually present to the extent of 1% of the former. Though good quality deposits with sufficiently high hardness, may be obtained from this electrolyte, its major disadvantage is its low cathode efficiency (of about 12-15%). The search for high efficiency electrolytes led to the development of fluorine compound containing electrolytes and self regulating high speed chrome plating baths. These solutions can be operated with a cathode efficiency of about 20%. However, their most considerable characteristic is their tendency to etch portions of the cathode surface which are in contact with them but not directly exposed to the current and over which a low current density exists as long as plating goes on, leading to what is known as 'cathode etching'. In view of the increasing interest in nonetching high speed electrolytes, it was considered useful to investigate the influence of iodate as a catalyst along with sulphate in chrome plating solutions.

Surface preparation

The sequence of pretreatment used in preparation for Hull Cell experiments or plating one was the usual.

Hull cell experiments

Polished and cleaned mild steel cathodes of 100 x 75 x 0.25 mm size were employed and a cell current of 7.0 A was passed for a duration of 5 minutes. The current density at the desired point was calculated by using the formula $C = (5.1-5.24 \log L) C$ being the cell current and L the distance in cm of the point from the nearer end of the cathode.

Current efficiency

The electrodeposition assembly for carrying out current efficiency experiments consisted of two lead-tin anodes of 93% lead content, of 7.5 x 2.5 cm size like the experimental mild steel specimens made cathodic. A direct current supply with a very low a.c. ripple was used. An instrument enabling measurement of the circuit current or coulombs of electricity passed was used. The cathode efficiency was calculated gravimetrically by weighing the specimens before and after plating. The cathode efficiency experiments were conducted at different current densities ranging 15.5-93.0 A/dm².

TABLE I: Effect of concentration of chromic acid and sulphate on deposition characteristics at 323 K

No.	Concentration of each ingredient g/l		Current density A/dm ²	Current efficiency (%)	Rate of build up $\mu\text{m/h}$	Nature of deposit
1.	CrO ₃	75.0	7.75	5.4	1.9	Semibright at the edges with blue coloured oxide film over the middle portion
			15.50	16.4	11.7	Uniform bright
			23.25	15.6	16.8	Uniform bright, but stain at the edges
			33.00	18.7	26.7	" " "
			40.75	16.5	29.4	" " "
2.	CrO ₃	100.00	7.75	10.3	3.7	Bright at the edges and milky over the middle portion
			15.50	15.6	11.2	Fully bright deposits
			23.25	17.5	18.8	" " "
			33.00	18.8	26.9	Bright over the middle portion and stain at the edges
			40.75	18.5	33.0	" " "
3.	CrO ₃	125.0	7.75	10.7	3.8	Uniform semibright
			15.50	17.0	12.2	Uniform bright deposit
			23.25	19.9	21.3	" " "
			33.00	19.6	28.1	" " "
			40.75	19.6	35.0	Uniform bright but stain at the edges

Rate of build-up

The deposit build-up rate corresponding to each experiment was calculated by using the following formula

$$\text{Rate of buildup} \left(\frac{\mu\text{m}}{\text{h}} \right) = \frac{m \times 10000 \times 60}{d \times A \times t}$$

where *m* is the mass of chromium deposited and '*d*' its density. *A*, the area plated and *t*, the duration of deposition (in minutes) respectively.

Throwing power

The throwing power for each solution was determined at 15.5 A/dm² by using a Haring - Blum cell. The above value was calculated by using the following formula :

$$\text{Throwing power (\%)} = \frac{P - M}{(P + M) - 2} \times 100$$

'*P*' being the ratio distances for the farther and nearer cathodes from the anode and *M*, the metal ratio for the nearer and farther cathodes.

Microhardness

A Soviet make Microhardness tester of PMT-3 model was used. A diamond pyramid intendor was pressed on to the deposit under a load of 50 g for 15 seconds and the indentation diagonal measured after the load was removed. The Vicker's microhardness of the deposit was determined in each case making use of the formula

$$\text{Hardness} \left(\frac{\text{kg}}{\text{mm}^2} \right) = \frac{1854 \times P}{d^2}$$

P is being load applied in grams, and *d* the diagonal of the indentation obtained in micrometers.

Crack density

The crack density of deposited chromium was also estimated for some specimens by suitably calculating the number of cracks per linear centimeter from the average number of cracks along the two cross wires on microscopic examination.

Cathodic etching

In order to evaluate the cathodic etching, a cell with a lead - tin (93 : 7) anode, mild steel cathode of the same size as of the anode and the electrolyte under study was used. The cathode surface was electrolytically cleaned and weighed and after immersing all the electrodes with current switched on, electrolysis was carried out with a cathodic current density of 0.39 A/dm². The electrode was then washed, dried and reweighed. Weight loss if any was taken as due to cathodic etching.

RESULTS AND DISCUSSION

The results of the Hull - Cell experiments carried out are given in Figs. 1 to 6.

Fig. 1 illustrates the nature of the deposit patterns for different chromic acid concentrations at 324 K and for 7 A

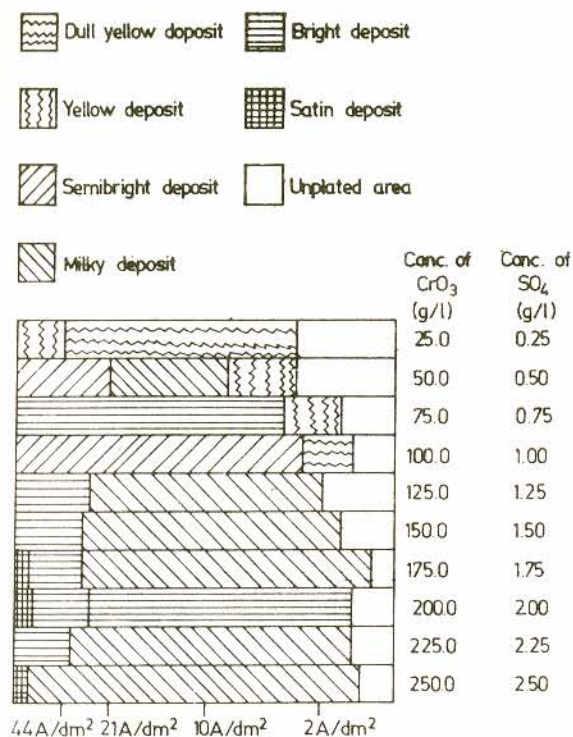


Fig. 1: Hull cell pattern for various composition of chromium plating baths

cell current. It is observed that when the chromic acid concentration is very low at 25 g/l with 0.25 g/l sulphate, the electrolyte produces only yellow coloured oxide films. With an increase in concentration of chromic acid to 50 g/l and with 0.5 g/l sulphate, the bath produces semibright and milky

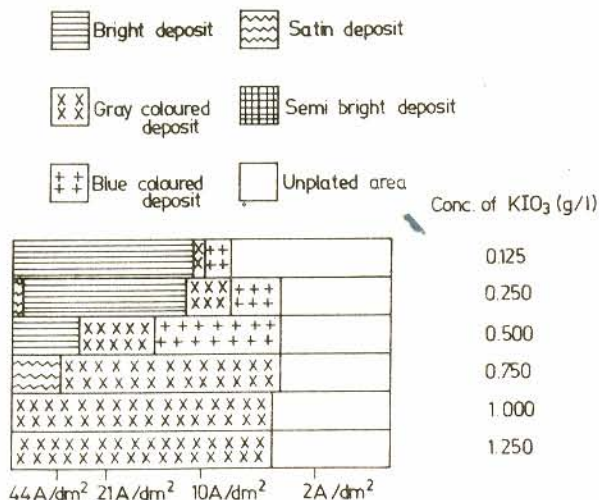


Fig. 2: Hull cell pattern for various concentration of KIO_3
Bath composition: $CrO_3 = 125$ g/l; $SO_4^{2-} = 1.25$ g/l

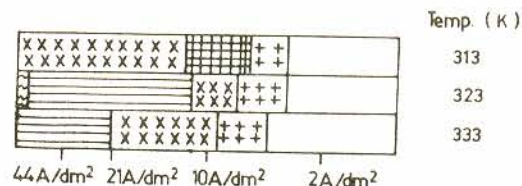


Fig. 3: Effect of temperature on the hull-cell pattern
Bath composition: $CrO_3 = 125$ g/l; $SO_4^{2-} = 1.25$ g/l; $KIO_3 = 0.25$ g/l

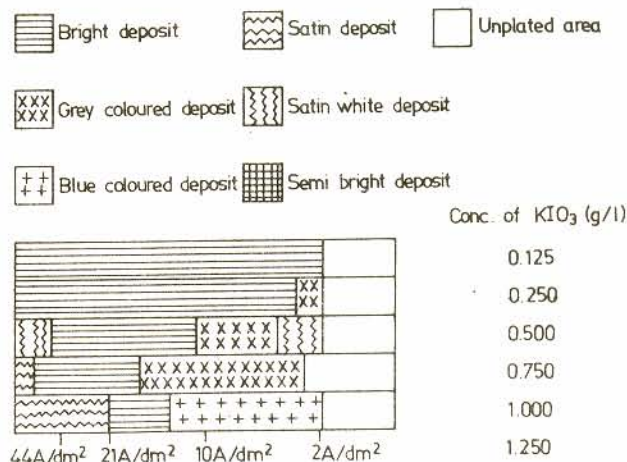


Fig. 4: Hull cell pattern for various concentration of KIO_3
Bath composition: $CrO_3 = 250$ g/l; $SO_4^{2-} = 2.5$ g/l

chromium deposits at the high and medium current densities respectively. A further increase in chromic acid and sulphate concentrations respectively to 75 g/l and 0.75 g/l results in more or less the same type of patterns as for lower concentrations. Concentrations of 100 g/l of chromic acid and 1 g/l sulphate result in semibright more or less over the entire surface of the Hull-cell plate except over the low current density area where yellow coloured chromium oxide is noticeable. At the high current density end both bright chromium and milky chromium are observed for a solution with 125 g/l chromic acid and 1.25 g/l sulphate. Any further

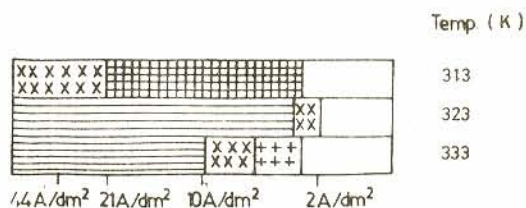


Fig. 5: Effect of temperature on the hull-cell pattern
Bath composition: $CrO_3 = 250$ g/l; $SO_4^{2-} = 2.50$ g/l; $KIO_3 = 0.25$ g/l

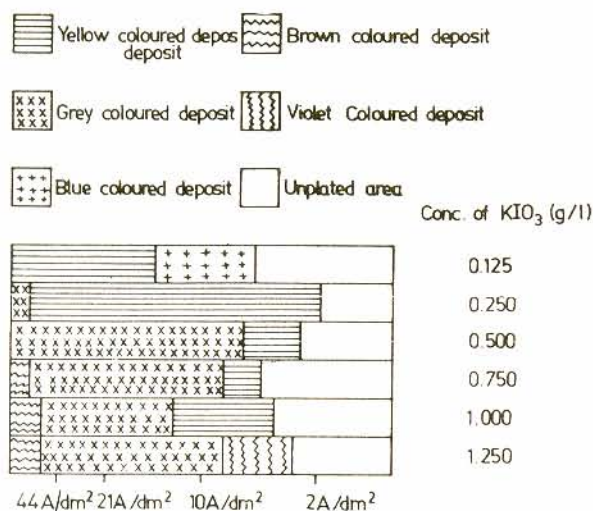


Fig. 6: Hull cell pattern for various concentration of KIO_3

Bath composition: $\text{CrO}_3 = 125 \text{ g/l}$; $\text{SO}_4^{2-} = \text{—}$

rise in chromic acid concentration up to 250 g/l along with a corresponding increase in sulphate concentration at 100 : 1 ratio does not produce any change in the pattern. One can conclude therefore that good chromium deposits are obtainable under the constraints referred to.

Fig. 2 illustrates how the pattern of chromium is affected when potassium iodate is introduced into the chrome plating electrolyte with 125 g/l chromic acid and 1.25 g/l sulphate. The current density range corresponding to chromium layer with acceptable appearance gets reduced when KIO_3 is present to at 0.125 g/l or 0.25 g/l concentration, the bright chromium being confined to high enough current densities. With an increase in concentration of KIO_3 , only grey coloured and blue coloured films are obtained. It is therefore possible that a chrome bath with 125 g/l chromic acid, 1.25 g/l sulphate and 0.25 g/l of KIO_3 may prove useful for plating.

Fig. 3 points to the effects of temperature on $\text{CrO}_3\text{-H}_2\text{SO}_4\text{-KIO}_3$ electrolyte. It can be informed that operation at 323 K is more suitable than 313 K or 333 K.

Fig. 4 illustrates how KIO_3 in conventional chrome bath at 323 K influences its deposition characteristics. The suitability of 0.25 g/l KIO_3 concentration for obtaining good quality chromium electrodeposits is thus confirmed. One can find from Fig. 5 the effects of temperature change on the deposition characteristics of the electrolyte composed chromic acid (250 g/l), sulphate (2.5 g/l) and KIO_3 (0.25 g/l). A temperature of 323 K appears to be beneficial for production of good chrome deposits.

Fig. 6 includes the Hull Cell patterns obtained when an electrolyte containing 125 g/l chromic acid along with different concentrations of KIO_3 but with no sulphate at 323 K. It is observed that only coloured layers are obtainable.

Data on cathode current efficiency, build-up rate, nature of deposit details are given in Table I. It can be seen that the cathode current efficiency and the rate of build-up as is normally the case in chromium plating, increase with increasing concentration of chromic acid the cathode efficiency. It may also be seen that the cathode efficiency increases with increase in current density as usual in chrome plating process. Thus it may be seen that a cathode efficiency of about 10-19% could be obtained from a chrome bath containing chromic acid 125 g/l and sulphate 1.25 g/l at 323 K when operated at current densities namely 7.75 - 40.75 A/dm². From the results it may be seen that the rate of build-up increase with increase in current density.

Table II gives the results of cathode efficiency experiments with different chrome plating electrolytes containing KIO_3 . It may be seen that for the chrome bath containing chromic acid 125 g/l, sulphate 1.25 g/l and KIO_3 0.25 g/l, the cathode efficiency increases with an increase in current density and reaches a maximum of about 25.9%, when operated at 93 A/dm² (6 asi). A rise in concentration of chromic acid to 200 g/l or 250 g/l along with sulphate and KIO_3 causes the cathode efficiency to increase with an increase in current density. But the dilute chromium plating bath containing 125 g/l chromic acid along with sulphate and KIO_3 has a greater cathode efficiency than solutions based on chromic acid concentrations, i.e., 200 g/l and 250 g/l. In all the cases studied the rate of build-up increases with an increase in current density.

Throwing power

The results of throwing power experiments carried out at 15.50 A/dm² and at 323 K with electrolytes containing 125 g/l and 250 g/l chromic acid along with sulphate but in the absence and presence of KIO_3 are given in Table III. The results show that all chrome plating electrolytes examined including the conventional one have, only negative throwing power. An increase in chromic acid concentration however makes the throwing power more negative or lesser. The bath containing KIO_3 appears to have somewhat better throwing power than the electrolytes without KIO_3 .

Influence of current density variation

Table II points to the microcracked nature of deposits produced from the bath containing KIO_3 . The extent of microcracking however decreases with an increase in current density. It is significant that the less concentration chromium

TABLE II: Effect of change of bath composition on deposition characteristics at 323 K

Bath ingredients g/l	Current density A/dm ²	Current efficiency (%)	Rate of build up μm/h	Vicker's		Crack density Cracks/cm	Nature of deposit
				Micro-hardness Kg/mm ²			
CrO ₃	125.00	15.5	11.5	7.7	905	1200	Uniform bright
SO ₄ ²⁻	1.25	31.0	19.6	26.1	965	1012	" "
KIO ₃	0.25	46.5	21.4	42.8	851	960	" "
		62.0	22.5	54.0	965	630	" "
		77.5	23.4	70.2	997	570	Uniform bright but satin at the edges
		93.0	25.9	103.6	1030	585	" "
CrO ₃	250.00	15.5	13.0	8.6	677	720	Uniform bright
SO ₄ ²⁻	2.50	31.0	16.4	22.1	715	660	Bright at the centre but stain at the edges
KIO ₃	0.25	46.5	18.1	36.2	802	480	" "
		62.0	20.8	49.9	851	375	" "
		77.5	20.8	62.3	905	360	Uniform semibright
		93.0	21.0	84.0	905	360	" "
CrO ₃	250.00	15.5	12.6	8.4	851	960	Semibright at the edges with blue coloured film over the middle portion
SO ₄ ²⁻	2.50	31.0	16.6	22.1	715	900	Uniform bright
KIO ₃	0.50	46.5	19.3	38.6	905	900	" "
		62.0	19.7	47.3	851	660	Uniform semibright
		77.5	20.0	59.9	851	435	" "
		93.0	19.9	79.6	851	585	" "

TABLE III: Percent throwing power values for different plating compositions at 323 K and 15.5 A/dm²

Bath	Ingredients g/l	Throwing power (%)
CrO ₃	125.00	-12.24
SO ₄ ²⁻	1.25	
CrO ₃	125.00	-8.6
SO ₄ ²⁻	1.25	
KIO ₃	0.25	
CrO ₃	250.00	-15.35
SO ₄ ²⁻	2.50	
CrO ₃	250.00	-10.64
SO ₄ ²⁻	2.50	
KIO ₃	0.25	

inhibits a greater crack density than the concentrated bath.

Cathode etching

It was found from experiments on cathodic etching with KIO₃ containing electrolytes showed no loss of substrate steel unlike in the case of electrolytes of which KIO₃ was not a constituent.

CONCLUSION

The results of experiments carried out indicate that efficiencies higher than the conventional chrome bath and microcracked chromium with no cathodic etching can be obtained from the composition with operating parameters as below:

Chromic acid	125.00 g/l
Sulphate	1.25 g/l
KIO ₃	0.25 g/l
Temperature	323 K
Current density	7.75 - 93.0 A/dm ²