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HULL CELL STUDIES ON COPPER ELECTRODEPOSITION FROM SULPHAMATE BATH

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Electrodeposited copper serves as a preplate before deposition of nickel, silver or gold. It is also used to prevent case hardening on selected areas of ferrous metal surface. Because of its enhanced electrical conductivity, it is used in electronics and in printed circuit board production. The grain structure of copper deposits from acid sulphate bath is less fine compared to the structure from cyanide baths. To cope up with the stringent pollution control regulations, there is a need to replace cyanide bath by non-toxic ones. There are a lot of plating compositions for copper deposition, based upon cyanide, sulphate, chloride etc. with proven usefulness in the industries. However, above types of baths are either toxic or highly acidic requiring pollution control treatments. Hence it was decided to investigate a bath which will be nontoxic. From view point, sulphamic acid was considered as one of the best alternatives as it is weakly acidic and nonpoisonous.

Keywords: Electrodeposition, copper, sulphamic acid and Hull Cell.

INTRODUCTION

Cyanide copper plating is used extensively in metal plating industry for large number of application. Zinc die-casting parts are to be given an undercoat of copper before nickel and chromium deposition. For such purposes cyanide baths are used. Also for zinc based substrate, a cyanide copper coating helps to prevent immersion deposition. For uniform metal distribution over irregularly shaped articles, a strike from cyanide copper bath has been found to be ideal, because of its good throwing power. For better electrical conductivity steel wires are plated mostly from cyanide bath.

Because of high rate of deposition, acid copper baths are extensively used for electroforming, electrorefining, manufacture of copper powder etc. Electroformed copper is produced in several important industries, band instruments, heat exchangers and reflectors. In radar and aircraft applications also copper deposition plays a role. Automobile bumpers are generally plated with copper (28 μm) before nickel plating [1-2]. Stainless steel cooking vessels are copper plated to improve heat application character of outer surfaces to avoid local hot spots. Carburising is done on selective spots using acid copper plating for masking the unwanted areas. To prevent certain components from fretting corrosion, copper plating is carried out. For making sintered compact pigments copper metal powder is produced by electrodeposition method.

Copper plating finds special applications like stop-off for nitriding [3] and selective carburizing [4-5] as a drawing lubricant for stainless steel and steel [5-6] for electroforming and printed circuit plating [7-8] and for minimising hydrogen embrittlement [9].

Pyrophosphate baths are generally good for copper plating on zinc, aluminium, steel parts and plastics. Various other copper baths based upon cyanide containing Rochelle salt are reported in literature.

From the view point of the non availability of a satisfactory acid based electrolyte for copper deposition, it was desired to carry out investigation to evolve a new formula based upon sulphamic acid, EDTA etc. about which not many

references are available in literature. Even though there are some literature citations about sulphamate as well as EDTA based baths, sufficient data regarding the bath composition, operation conditions and other technical details are not available. Hence the present studies have been carried out in Hull cell for identifying a standard composition for copper deposition from sulphamic acid based electrolytes and EDTA based solution so as to obtain desirable nature of deposit. The results are compared with conventional acid and cyanide baths.

EXPERIMENTAL

Hull Cell

Preliminary studies towards the investigation on the sulphamic acid based copper baths were carried out with a Hull cell (made of PVC) of the following dimensions as shown in Scheme 1.

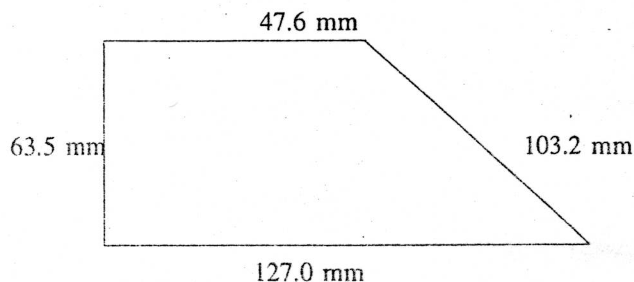
Anode

The anode used was pure electrolytic copper of size 6 cm x 8 cm. The other side of the anode, which is not exposed to the solution was masked from plating by lacquering. The anode was removed from the bath when not in use to avoid chemical dissolution in the solution.

The cathodes used for the Hull cell studies were made of brass or mild steel of size 6.25 x 10 cm. The cathodes were perfectly mirror polished on one side before plating and perfectly degreased with trichloroethylene to remove the greasy polishing materials and then they are masked with red lacquer on the back side.

Power source

A good ripple free D C rectifier (10-12 V) was used with a calibrated ammeter (0-5 Ä range) for the experiments.



Dimensions of Hull Cell
Numbers refer to internal dimensions
Volume of 267 ml of solution is used
Scheme 1

Chemicals used

All the chemicals used for the investigation were of L R grade.

Electrolyte preparation

The electrolytes used for the investigations were prepared to the volume of 250 ml and each type of composition was separately prepared by making use of distilled water in the usual standard method of preparation of electrolytes.

The Hull cell experiments were carried out in the usual manner after the pre-treatment as follows:

* The cathode were mirror polished mechanically.
* They were degreased with trichloroethylene to remove grease, oil, etc.

They were then electrocleaned in appropriate alkaline cleaning composition as follows:

For mild steel

Na_2CO_3	—	25 gl^{-1}
NaOH	—	30 gl^{-1}
Temperature	—	353 K
The other electrode	—	steel or stainless steel
Current density	—	1.5 Adm^{-2}
Cathodically	—	2 minutes
Anodically	—	1/2-1 minute

For brass cathodes

Na_2CO_3	—	20 gl^{-1}
NaOH	—	7 gl^{-1}
Trisodium orthophosphate	—	9 gl^{-1}
Temperature	—	353 K
Duration	—	2 minutes
The other electrode	—	steel or stainless steel
Current density	—	4.5 Adm^{-2}
Cathodically	—	3 minutes
Anodically	—	1/2-1 minute

* Swilled in tap water and rinsed in distilled water.
* Dipped in 5-6% H_2SO_4 at room temperature for 15 seconds.
* Swilled and rinsed.
* Subjected for Hull cell experiment in copper plating solutions of the following composition.

Copper (as hydroxycarbonate)	—	0.125-1 *M* (8- 64 gl^{-1})

Sulphamic acid — 2-4 *M*

*p*H — 9

The current density was calculated using the formula

$$C.D. (Adm^{-2}) = C[5.1 - 5.24 \log L] \quad (1)$$

where C = cell current and L = The distance in cm of the point of interest from nearer end of the cathode (to anode).

RESULTS AND DISCUSSION

Fig. 1 contains the legends for the various patterns of deposits obtained under different conditions. Figs. 2 and 3 contain the results of Hull cell studies carried out with the different concentrations of copper and sulphamic acid under different conditions.

Fig. 2 shows the patterns of deposit obtained with 2 *M* sulphamic acid and with varying concentrations of copper from 0.125 *M* to 1 *M* Fig. 3 shows the patterns of deposit obtained with solution containing 4 *M* sulphamic acid and varying concentrations of copper from 0.125 *M* to 1 *M*

Effect of concentrations of copper 2 *M* sulphamic acid

From Fig. 2, it may be observed that bright copper deposit range increases with increasing concentration of copper as well as with increasing temperature. Among the studies carried out with various compositions, bright copper deposit range is maximum in the case of 0.75 *M* Cu spanning from 0.8 to 5.1 Adm^{-2} for the temperature of 323 K. However, still a wide pattern range is indicated in the case of solutions containing 0.25 *M* Cu in presence of 2 *M* sulphamic acid at 323 K for the wide span of 1.5-3.1 Adm^{-2}. At the lower concentrations of 0.125 *M* Cu in presence of 2 *M* sulphamic acid, the bright current density range is very much limited. 0.6-1.4 Adm^{-2} and that too at 303 K which is shifted to 1-5.1 Adm^{-2} at 323 K. In all the other compositions, there are indications for obtaining bright deposit at higher current density range but they are limited.

Effect of concentration of 4 *M* sulphamic acid

From Fig. 3, it may be observed that bright copper deposit is obtained in all the concentrations of copper from 0.125 *M* to 1 *M* in presence of 4 *M* sulphamic acid, but with different current density ranges for different concentrations of copper and for different temperatures.

The bright range is shown at lower current density levels only (0.1 - 1.5 Adm^{-2}) in the case of 0.125 concentration of copper at all the three temperatures, viz. 303, 313, 323 K respectively, in the presence of 4 *M* sulphamic acid. This is in contrast to the effects observed in the case of concentrations of copper but in 2 *M* concentration of sulphamic acid where the bright deposit range is indicated

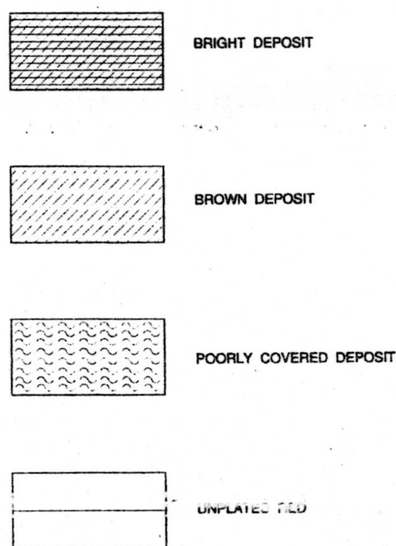


Fig. 1: Legend used for Hull Cell studies

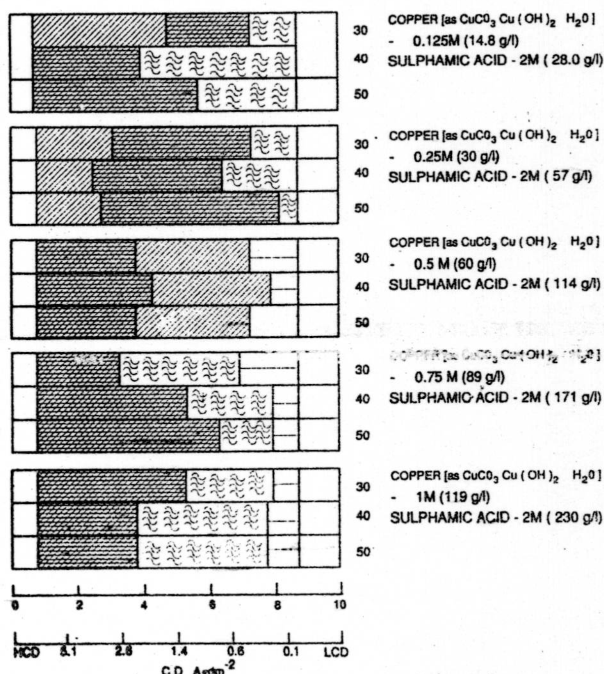


Fig. 2: Result of Hull Cell studies
Effect of concentration of copper in solution containing 2 M of sulphamic acid

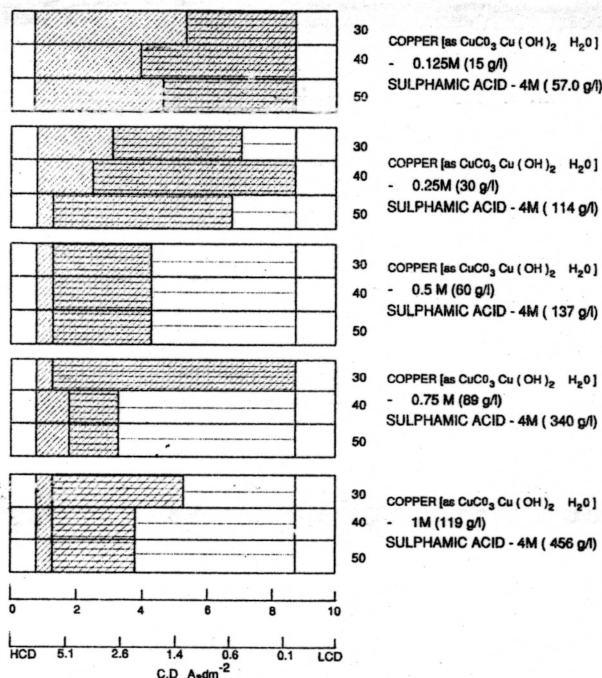


Fig. 3: Result of Hull Cell studies
Effect of concentration of copper in solution containing 4 M of sulphamic acid

at the higher level namely 0.8 to 5.1 Adm^{-2} at higher temperature namely 313 K and 323 K (Fig. 2).

The effect of concentration of both copper and sulphamic acid is observed to be very similar when at 0.25 *M* for copper and 2 or 4 *M* sulphamic acid (Figs. 2 and 3). In both the cases the bright range for copper deposit spans from 0.25 - 4.0 Adm^{-2} with an exception at the temperature of 313 K. At 313 K the bright deposit current density spans widely from 0.1-4 Adm^{-2} for 4 *M* sulphamic acid whereas the bright range is from 1.0- 4.0 Adm^{-2} for 2 *M* sulphamic acid.

At 0.5 *M* copper the bright copper ranges almost from 2 - 5.1 Adm^{-2} in 2 *M* sulphamic acid for all the three temperatures of 303, 313, 323 K and also the same observation for 0.5 *M* copper and 4 *M* sulphamic acid at all the three temperatures of 303, 313 and 323 K and also the same observation for 0.5 *M* copper and 4 *M* sulphamic acid at all three temperatures.

There is a large difference in the cases of 0.75 *M* copper in 2 *M* and 4 *M* sulphamic acid concentration. The bright deposit range in 2 *M* sulphamic acid steadily increases from 2.6 Adm^{-2} to 5.1 Adm^{-2} at 303 K to 1.4-5.1 Adm^{-2} at 313 K and further spans widely from 1 - 5.1 Adm^{-2} at 323 K, whereas in presence of 4 *M* sulphamic acid, except at 303 K the bright density range is much reduced and that is from 2.6-5.1 Adm^{-2} at 313 and 323 K respectively. At 303 K the bright range spans widely from 0.1 - 5.1 Adm^{-2} which is in contrast to that one in the case of 2 *M* sulphamic acid (2.6-5.1 Adm^{-2}).

In 1 *M* concentration of copper for 2 *M* and 4 *M* sulphamic acid concentrations, the patterns remain the same (Figs. 2 and 3) for all the three temperatures 303, 313 and 323 K.

Effect of temperature

From the results indicated in the Hull cell Figs. 2 and 3, it is clear that at temperatures 303, 313 and 323 K the bright current density range shifts from lower to the higher range thereby providing the effect of temperature on the nature of deposition in general. Higher the temperature, higher the bright current density range (common to both the cases of 2 *M* and 4 *M* sulphamic acid).

CONCLUSION

In the light of the above investigations carried out with Hull cell and various concentrations of copper and sulphamic acid at different temperatures, it may be concluded that the wide bright copper deposit range can be obtained under the following conditions:

Copper (as hydroxy carbonate)	—	0.125-1 *M*
Sulphanic acid	—	2 *M* and 4M
*p*H	—	9-10
Temperature	—	303, 313 and 323 K
Current density	—	1.5-5.1 Adm^{-2}

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