

Studies on Electrodeposition of Copper from Methanesulphonic Acid Bath.

Felicita Florence^{1*}, Nisha¹, Susai Rajendran², K.N. Srinivasan³, S. John³

¹Department of Chemistry, Holy Cross College (Autonomous), Tiruchirappalli-2, Tamilnadu,India.

²Servitte College of Education, Thokamalai,Tamilnadu,India.

³IMF Division, CECRI, Karaikudi, Tamilnadu,India.

*Corres.authors: feli_florence@yahoo.co.in, Phone: 9865431672

Abstract: Methanesulphonic acid is an alternative electrolyte system which could replace Sulphuric acid in practical applications. The present aim of this work is to study the electrodeposition of copper from copper methanesulphonic acid bath with different additives such as PEG and Gelatin to get bright deposits. Deposit characteristics were studied by SEM, XRD and EDAX studies. XRD pattern shows that the copper methanesulphonate bath has strong influence on crystal orientation than the additives. SEM studies reveal that the grains of the deposits obtained from the sulphonate bath are finer when compared to sulphate bath and also the fine grain structure was obtained in the presence of Gelatin as an additive in CMS bath. Thus a formulation consisting of 25g/l of copper as copper methane sulphonic acid, 30 ml/l of Free methane sulphonic acid, 50ppm of chloride ion, 32 ppm of Gelatin and CD 2-4 A/dm² has very fine deposits compared to PEG as an additive. This is the optimum bath conditions to get bright deposits.

Key words: Electro deposition, Copper Methane Sulphonic acid, Additives, Poly Ethylene Glycol, Gelatin.

1. INTRODUCTION

Acid copper baths containing CuSO₄ in high concentration are often used to obtain Cu electrodeposits¹. Certain metal salts, such as those of Cu, Ni and Sn, are soluble in most acid electrolytes (e.g., H₂SO₄, HCl, HBF₄, MeSO₃H, etc.), and solubility considerations are not important in the selection of acid electrolytes for electroplating process involving such metals. MSA has largely replaced fluoroboric acid, the previous industrial standard, as the electrolyte of choice for electrochemical processes involving lead. In general, the low toxicity of MSA, especially when compared to HF complex acids like fluoroboric acid and fluorosilicic acid, makes it a safe electrolyte to handle. The benign nature of MSA, especially when compared to HF complex acids like

fluoroboric acid and fluorosilicic acid, makes it an environmentally advantageous electrolyte². The wide acceptance of Methanesulphonic acid (MSA) as an acid electrolyte for electrochemical processes, especially those involving tin and lead, has resulted from a combination of diverse physical and chemical properties. These properties include high saturation metal salt solubilities, high conductivity, ease of effluent treatment and low relative toxicity. Methanesulphonic acid (MSA) electrolytes have been used at a high current density and at a high copper ion concentration. Traditionally and especially for nanotechnology applications, organic substances are added to the electrolyte in low concentration (in the order of parts per million) to enhance the quality of the deposit by forming smooth and shiny deposits.

Therefore, the chemical composition of the electrolyte bath has been the topic of numerous studies and various organic or inorganic substances have been tested. Many additives used alone or in a mixture have been studied to elucidate their effect on the nucleation mechanism and on the deposit properties. In particular, many investigations show that polyethylene-glycol (PEG) acts in a synergistic way improving the performance of the galvanic baths and the properties of the deposit. The influence of those additives on the Cu electro deposition mechanisms has thus widely been discussed. When PEG is present, a surface layer forms on the copper electrode that constitutes a barrier for charge transfer^[3-5]. The polymer can adsorb in two different ways. One predominates close to the open circuit potential and may well be a copper chloride complex with the polyethylene glycol as a ligand. The other prevails at more negative potentials where copper plating is carried out; this species is likely to be the simple, neutral polymer molecule⁶. The adsorption is potential dependent and that the texture of the deposit is modified and the roughness is significantly decreased to 0.5 μ m. The inhibiting layer forms by reaction between the adsorbate-covered copper electrode and PEG, i.e., neither Cu⁺ nor Cu²⁺ from the electrolyte are required⁷⁻¹³. The Cu electroplating of the sub micrometers scale patterns was studied. The studies have shown the effect of an accelerator during the electro deposition of Cu for wiring in electronic devices was investigated using a 1-D pattern which has a seed layer only at the pattern bottom. And the role of Cl⁻ ions in suppression of Cu electrodeposition by PEG¹⁴⁻¹⁸. A mathematical model has been described for copper deposition in the presence of Cl⁻ and PEG additives¹⁹. The copper surface morphology evolution during electro polishing was studied and the work examining the evolution of the rough Cu surface morphology during the electro polishing process²⁰. The present study reveals the electrodeposition of copper from copper methane sulphonic acids bath with different additives such as gelatin in order to get bright deposits. Deposit characteristics were studied by SEM, XRD and EDAX techniques.

2. EXPERIMENTAL DETAILS:

2.1 SPECIMENS PREPARATION:

The experiments were carried out in triplicate with copper specimens. Surface preparation prior to deposition is an important factor and can be achieved by mechanical and electrochemical methods. The procedure adopted was removal of surface scales using acid dipping, mechanical polishing to get a smooth surface, degreasing with trichloroethylene^{21,22}.

2.2 PREPARATION OF STOCK SOLUTION:

About 100g of copper carbonate was weighed and transferred in 1000 ml clean beaker and treated with minimum quantity of methane sulphonic acid (\approx 120) till effervescence ceases. A minimum quantity of double distilled water was added for easy evolution of carbon dioxide gas. The solution was made up to 500 ml mark with double distilled water. The oils and suspended impurities present in the solution were removed by filtration. The solution was stored in clean closed container. The stock solution was analyzed for the Cu²⁺ ions concentration.

2.2.1 ANALYSIS OF CU²⁺ IONS:

1ml of the stock solution is pipetted out in a clean iodine flask, diluted with double distilled water to 20 ml, 2 ml of ammonia is added to neutralize the mineral acids and the solution turns dark blue. A small quantity of acetic acid is added to neutralize excess ammonia till the solution turns pale blue. To this solution 15 ml of 10% KI is added and shake well on closing the stopper. The solution turns brown in colour. Then the stopper is removed. A little amount of water is added and titrated against 1/10 N of standard thio solution slowly.

When the solution is straw yellow 1ml of 1% starch is added, the solution becomes bluish black in colour. The titration is continued till the solution turns white. It was found that the stock solution contained 57g of Cu in 500ml of stock solution. 1ml of stock solution contains 0.114g of Cu.

2.2.2 PREPARATION OF BATH :

About 250 ml of the copper methane sulphonic solution is taken in 1000 ml beaker. To this solution 5 ml of Methane sulphonic acid and 12.5 ml of sodium chloride solutions are added. This solution is made up to the mark in the beaker. This solution is used for the plating purpose.

2.3 HULL CELL STUDIES:

The Hull cell is a small plating cell used to conduct a single test to determine plating characteristics through out the current density range used for plating production parts. A Hull cell was used to assess and optimize the conditions for the production of good quality deposits. A regulated power supply was used as a direct current source and a calibrated ammeter along with the cell constituted the electrical circuit. Copper samples were used for Hull cell experiments. The temperature was kept at 30°C. Effect of C.D on the current efficiency of the bath was studied.²³ For this 5 x 10 cm copper panels were used. These panels were

mechanically polished degreased by trichloroethylene and covered the back side of the panel with cellophane tape and weighed. Then dipped in 10% sulphuric acid, washed with tap and distilled water and applied various current densities for duration of one hour. After that panels were washed well with tap and distilled water and weighed. From the difference in weight of panels the current efficiency of the bath was calculated using the following formula.

$$\text{Current efficiency} = \frac{\text{Actual weight gain} \times 100}{\text{Theoretical weight as per Faradays law}}$$

The current efficiency of the bath was calculated with addition agents PEG and gelatin.

2.4 X-RAY DIFFRACTION STUDIES:

The X-ray diffraction is widely used to determine the structure and composition of the materials. Diffraction patterns contain information showing various phases of a material and also residual stresses present within the coating material. The X-ray diffraction pattern for the electro deposited copper specimen obtained from MSA bath with and without additives and copper sulphate bath were recorded using XRD instrument. (make- Panalytical, USA) instruments

2.5 SCANNING ELECTRON MICROSCOPIC STUDIES (SEM):

The morphology of the electrodeposits was examined under high magnification to assess the grain size, deposit nature, heterogeneities and pores present in the deposits using a scanning electron microscope. The scanning electron microscope, which makes use of reflected primary electrons and secondary electrons, enable one to obtain information from regions that cannot be examined by others.

Electro deposited copper specimen obtained from MSA bath with and without additives and copper sulphate bath specimens were cut into 1 x 1 square centimeter size and mounted suitably and examined under the microscope. The SEM photographs were taken by using S-3000 model with an acceleration voltage range of 20,000 V and with the magnification range of 1000.

2.6 EDAX ANALYSIS

The elements present in the electrodeposited copper deposits obtained from MSA bath with and without additives and copper sulphate baths were analyzed using X-ray fluorescence spectrophotometer.

TABLE I: EFFECT OF CD ON THE CURRENT EFFICIENCY OF THE CMS BATH

S. No	Current density A/dm ²	Efficiency
1	0.5	98
2	1.0	90
3	1.5	87
4	2.0	86
5	2.5	85

TABLE II: EFFECT OF PEG ON THE CURRENT EFFICIENCY OF THE CMS BATH CURRENT DENSITY: 0.5 A/dm²

S. No.	Different concentration of PEG (ppm)	Efficiency
1	12	98
2	24	96
3	48	98
4	72	87
5	96	82

TABLE III : EFFECT OF GELATIN ON THE CURRENT EFFICIENCY OF THE CMS BATH CURRENT DENSITY: 0.5 A/dm²

S. No.	Different concentration of Gelatin (ppm)	Efficiency
1	2	76.7
2	4	88
3	8	89
4	16	90
5	32	97

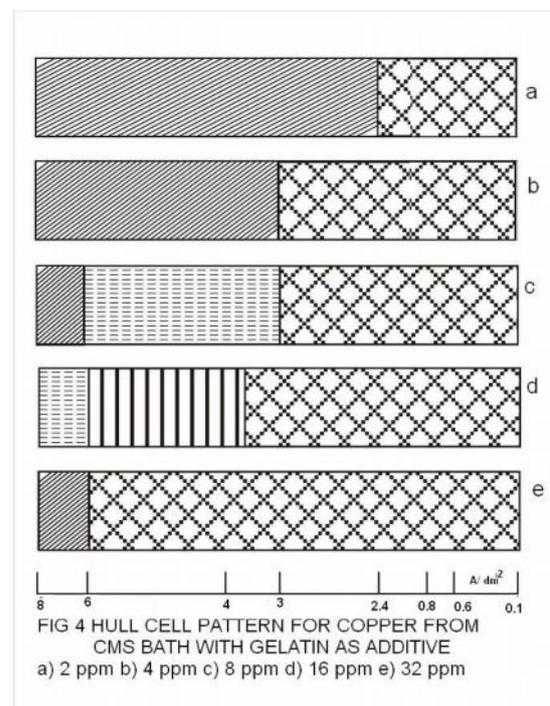
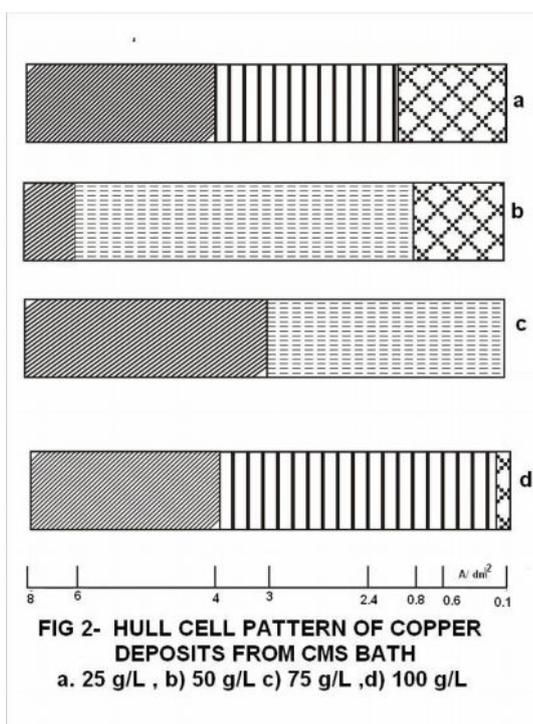
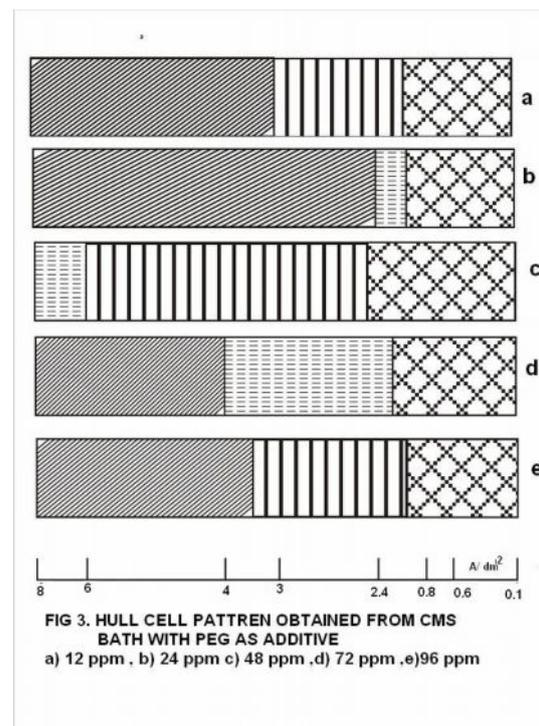
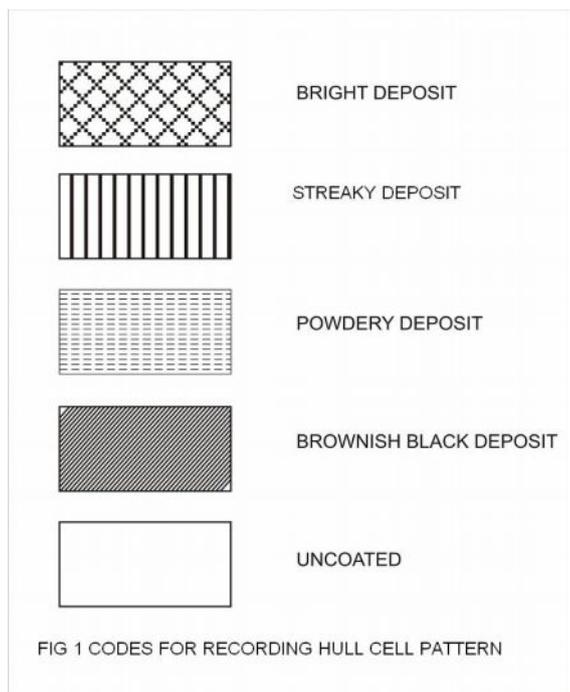
3.RESULTS AND DICUSSIONS

3.1 HULL CELL STUDIES

Fig. 1 shows the code for Hull cell pattern obtained on the 2 A Hull cell. Fig 2 shows the hull cell pattern obtained with different concentration of copper methane sulphonate bath (CMS) with 12ppm PEG in the bath. It is seen from the figure that there is no change in the bright deposition range if vary the concentrations of copper methane sulphonate from 25 to 50 g/l. however with 50 g/l of copper methanesulphonate there is a formation of powdery deposits beyond 0.8 A/dm². Further increase of copper methanesulphonate concentration in the bath up to 100 g/l there is no bright deposit at all obtained on the Hull cell panel. Hence for further studies 25 g/l of copper methanesulphonate bath is used.²³

TABLE IV. ELEMENTAL ANALYSIS OF COPPER DEPOSITS OBTAINED FROM VARIOUS BATHS

Condition	Carbon %	Oxygen %	Copper %
Copper methane sulphonate bath	1.44	---	98.45
Copper sulfate bath	7.28	----	94.31
CMS with Gelatin	2.16	---	97.84
CMS with PEG	26.51	5.43	68.06



3.1.1 EFFECT OF PEG ON THE DEPOSIT CHARACTERISTICS:

Fig 3 shows the Hull cell patterns obtained on the copper panels from copper methanesulphonate bath (25g/l). It is seen from the figure that without PEG in the bath there is a bright region up to 0.24 A/dm². Addition of PEG in the bath shifted the brownish black deposit range to higher current densities. without affecting the brightness range. Hence 48 ppm of PEG is the optimum concentration in the bath to get bright deposits without any black brown characteristics.

3.1.2 EFFECT OF GELATIN IN THE CHARACTERISTICS OF THE COPPER:

Addition of gelatin from a concentration of 2ppm to 32ppm was studied and the deposit characteristics obtained on Hull cell panels were shown in Fig 4. it is seen from the figure that increase in the concentration of gelatin increases the brightness region of deposit. At

a concentration of 32 ppm up to 6 A/dm² there is a bright deposit obtained.

3.1.3 EFFECT OF CURRENT DENSITY ON EFFICIENCY

Table 1 shows the effect of current density on the current efficiency of the bath with PEG as additive. It is seen from the table that the current efficiency decreases with increase in current density. From the Hull cell studies it was found that beyond 0.08 a/dm² the deposits are streaky and powdery. Hence there is a decrease in the current efficiency with increase in current density. Table II shows the effect of PEG concentration on the current efficiency of the bath at 0.05 A/dm². It is seen from the table that the current efficiency is almost constant up to 48ppm and then slightly decreases. This fully agrees with Hull cell results. It is obvious from the table that higher concentration of gelatin increased the bath efficiency of the bath which is in agreement with the Hull cell studies.

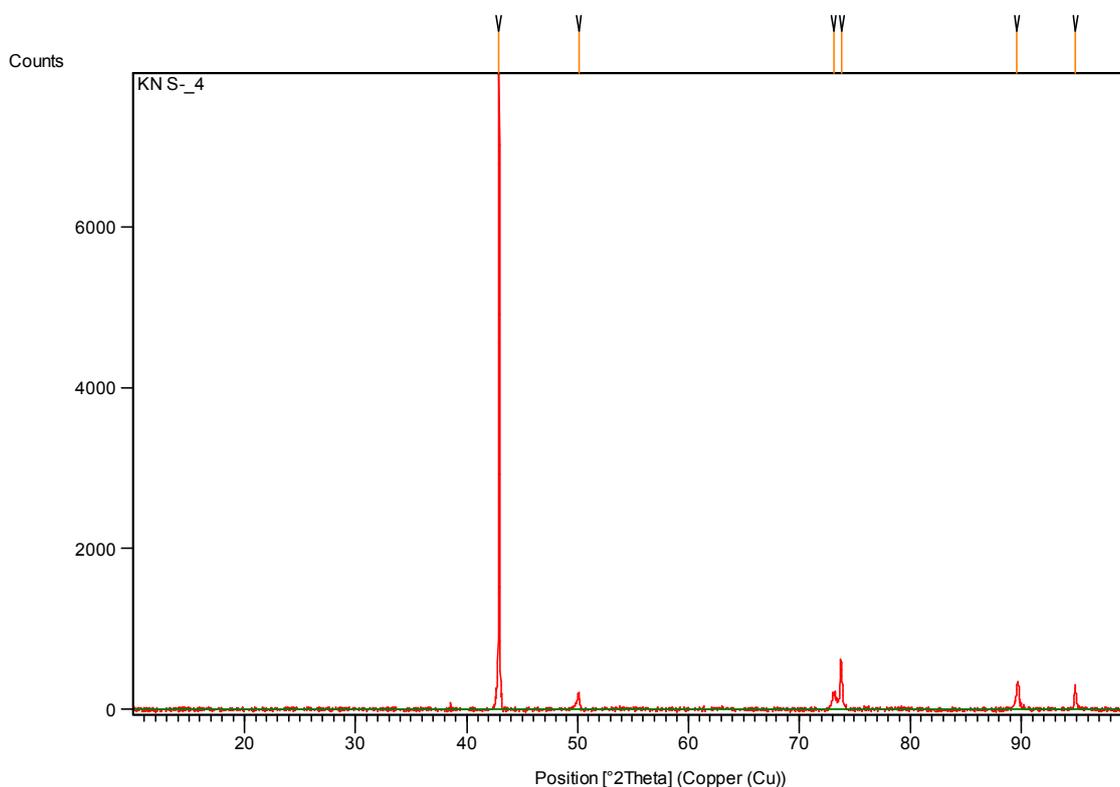


FIG 5. XRD PATTERN FOR COPPER DEPOSITS OBTAINED FROM COPPER METHANE SULPHONATE BATH

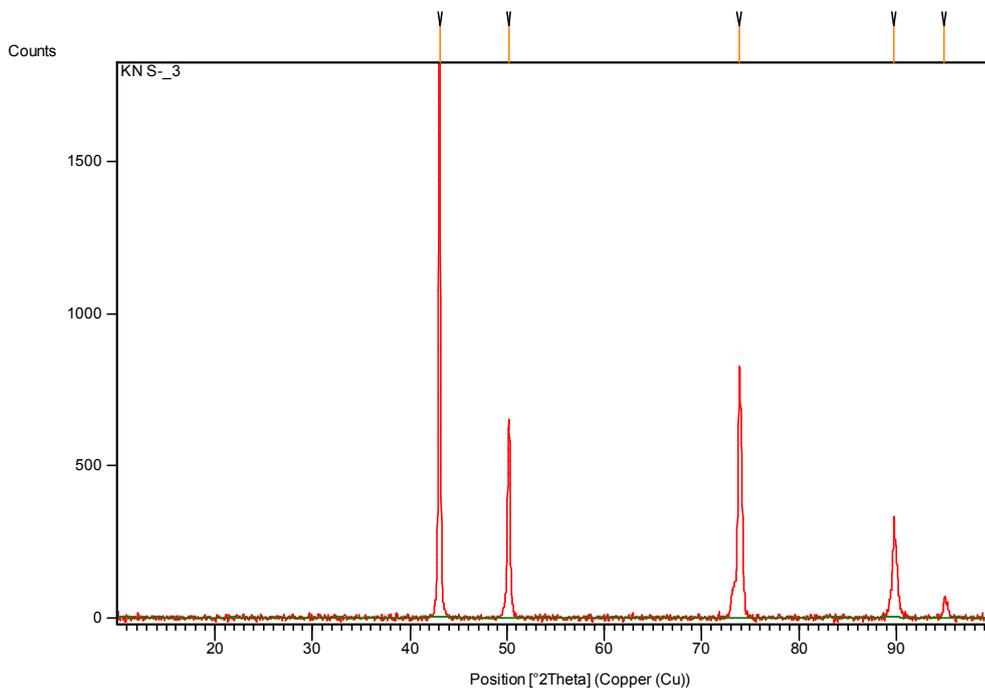


FIG 6. XRD PATTERN FOR COPPER DEPOSITS OBTAINED FROM COPPER METHANE SULPHONATE BATH WITH PEG

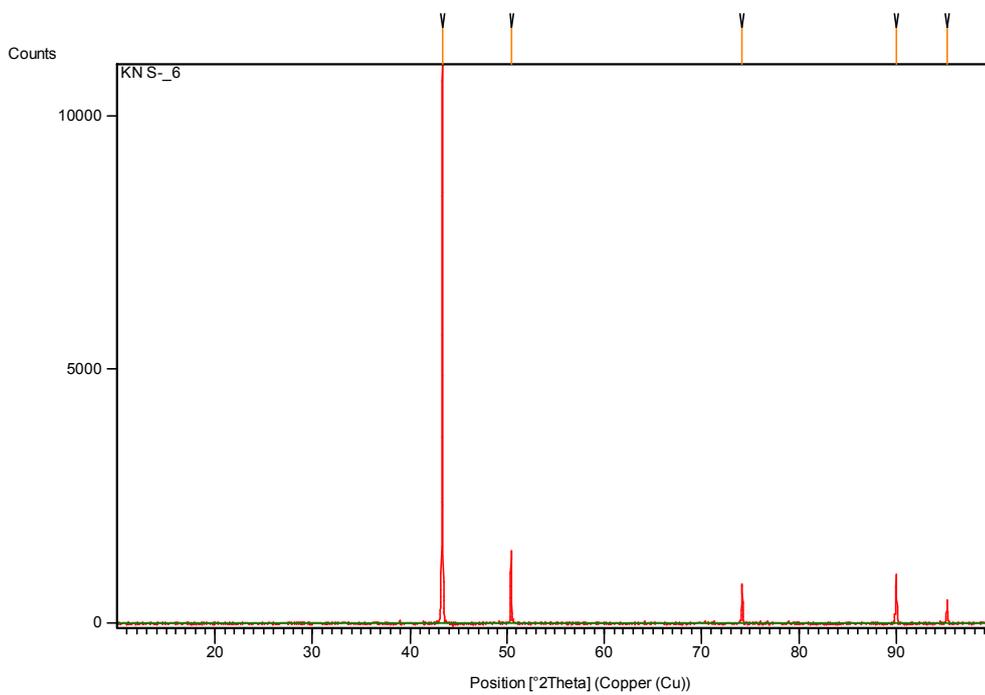


FIG 7. XRD PATTERN FOR COPPER DEPOSITS OBTAINED FROM COPPER METHANE SULPHONATE BATH WITH GELATIN

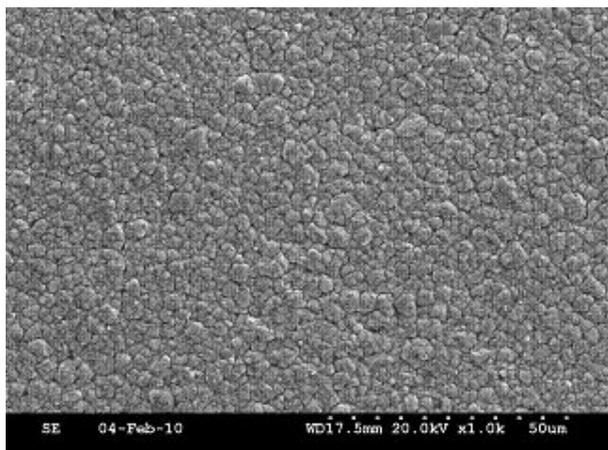


FIG 8. SEM PHOTOMICROGRAPG OF COPPER DEPOSITS OBTAINED FROM CMS BATH

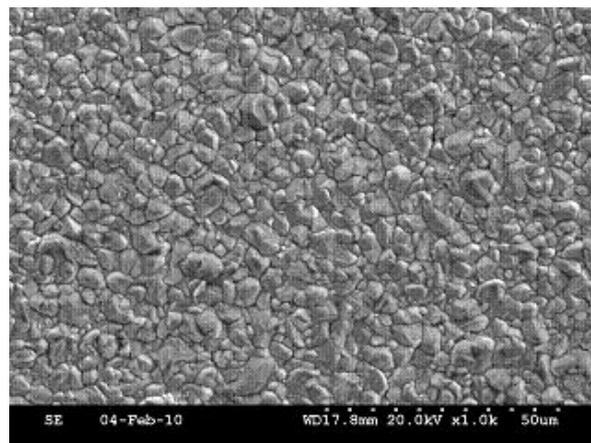


FIG 10. SEM PHOTOMICROGRAPG OF COPPER DEPOSITS OBTAINED FROM CMS BATH WITH GELATIN



FIG 9. SEM PHOTOMICROGRAPG OF COPPER DEPOSITS OBTAINED FROM CMS BATH WITH PEG

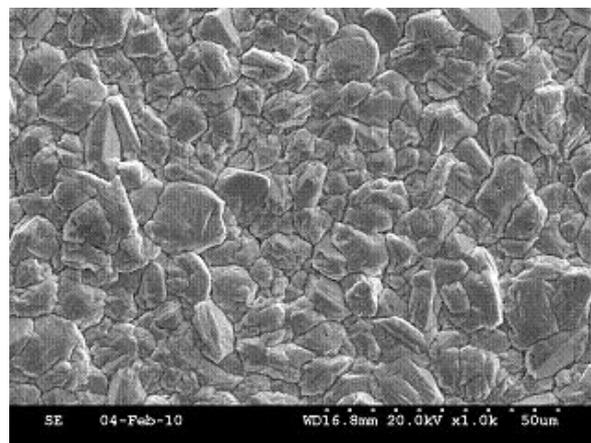


FIG 11. SEM PHOTOMICROGRAPG OF COPPER DEPOSITS OBTAINED FROM COPPER SULPHATE BATH

3.2 X-RAY DIFFRACTION (XRD) AND EDAX STUDIES:

The XRD patterns of the copper film for plain bath and additives for copper methane sulphonate bath are shown in **Figures 5 to 7**. The XRD patterns are much similar to that of JCPDS standard copper metal. From the XRD patterns it is observed that the preferred orientation is (200) plane irrespective of additives added. This may be regarded as the copper methane sulphonate bath has strong influence on crystal orientation than the additives. The copper oxide phase was also observed in the deposit pattern. In the case of deposits with PEG as additive multiple peaks

corresponds to carbon and oxygen were also appeared. Thus the film contains oxygen in addition to copper metal. This was confirmed by the EDAX Test also. The oxygen contents present in the deposits obtained from methane sulphonate bath is less when compared to that of sulfate bath.

3.3 SEM STUDIES

It is seen from the above SEM photomicrographs that the grains of the deposits obtained from the sulphonate bath are finer when compared to the sulphate bath. Also the fine grain structure was obtained in the presence of gelatin as an additive in CMS bath.

4. CONCLUSIONS

An eco friendly and biodegradable copper electrodeposited bath has been developed in the present study and optimized the bath composition. Among the additives studied gelatin produces bright deposits over the entire hull cell range. The deposits obtained are also finer when compared to PEG as an additive. When compared to conventional copper sulfate bath the deposits obtained from copper

methanesulphonate bath are finer and contained less oxygen. . Following is the optimum bath conditions to get bright deposits.

Copper as copper methane sulphonate	- 25 gm/L
Free methane sulphononic acid	-30 ml/L
Chloride ion	-50 ppm
Gelatin	-32 ppm
CD	-2-4 A/dm ²

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