

## CORROSION OF COPPER IN CUTTING FLUIDS

*Mrs. VIJAYALAKSHMI RAMAKRISHNAN, C RAJAGOPAL and Mrs. VENU SUBRAMANIAN*  
 Central Electrochemical Research Institute, Madras Unit, CSIR Complex, Madras - 600 113.

### ABSTRACT

This paper deals with the study of corrosion of copper in a drawing fluid and in certain pretreatment chemicals commonly used in the copper wire making industries by chemical and electrochemical techniques. Some remedial measures for preventing the corrosion of copper are also suggested at the end of the study.

**Key words:** Corrosion of copper, cutting fluid, tarnishing of copper

### INTRODUCTION

In copper wire making industry the copper ingots are first converted into thin sectional rods by hot rolling process. These thin rods are further subjected to various pretreatment operations before they are drawn into wires or strips. The pretreatment operations commonly used by the industry are shown in the diagram (Fig. 1). After pickling and cleaning operations the copper rods are cold drawn using a drawing or cutting fluid to various sizes depending upon the consumer requirement.

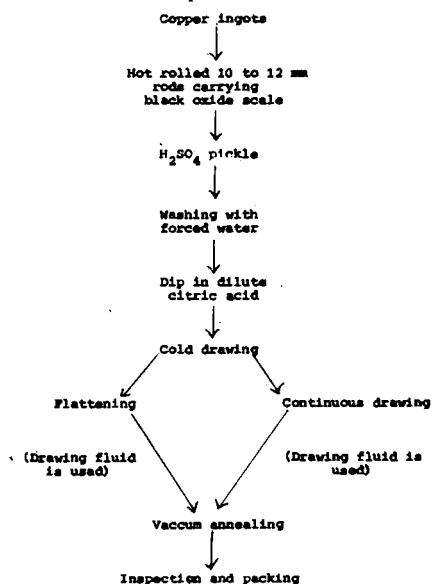


Fig. 1: Operational lay out in copper wire drawing

The drawing fluid performs an important function of lubricating the die, removing the frictional heat and cleaning the copper dust generated during drawing [1]. After the cold drawing, the copper wire is further sent for either flattening or continuous drawing operations. Finally they go for vacuum annealing and then they are air cooled, inspected and packed.

In one of the above operations, the problem of tarnishing of copper has been reported by an industry, which is manufacturing copper wires and strips for electrical applications and hence this investigation has been taken up to find out the exact cause for tarnishing. The corrosive effects of different

pretreatment chemicals and cutting fluids are investigated in this paper by both chemical and electrochemical methods.

### Experimental Procedure

#### Materials and Surface preparation

Copper specimens: a) 5 x 2.5 cm copper strips—cleaned in 10% H<sub>2</sub>SO<sub>4</sub>, polished with carborundum powder (No. 150 grade) degreased with acetone were used.

b) For electrochemical measurements copper rod of 5 cm<sup>2</sup> exposed area (dia 6.3 mm and 24 mm long) with surface prepared as above was used.

#### Systems studied

##### Solutions used

Solution	Composition
i) Tap water	Cl 42 ppm Total alk. 115 ppm Hardness 80 ppm
ii) Hard water	CaSO <sub>4</sub> 500 ppm
iii) Plant coolant water	Collected from industry
iv) Distilled water	---
v) Citric acid	0.2 w/v
vi) H <sub>2</sub> SO <sub>4</sub>	10% w/v

#### Oil-in-water emulsions

A proprietary cutting oil having a pH of around 4.5 was used. The oil in water emulsions were prepared by thoroughly mixing a weighed quantity of (5% w/v) of the oil with water to get a homogeneous emulsion.

#### Temperatures studied

The experiments were carried out both in quiescent and stirred solutions at ambient temperature and a few experiments are also carried out at 85-90° C using a water bath.

#### Cast iron corrosion test

In this test, [2] clean and degreased steel millings were placed on a clean and polished cast iron plate and the emulsion in hard water (3%, 5% and 15% w/v) was poured on to them and stored at 52 ± 5% R.H. at ambient temperature. After 24 hrs, the steel millings were removed and the surface of the plate was examined. The oil was taken to have passed the test if the cast iron surface was free from rust and staining. For comparison purposes, emulsions prepared in distilled water, tap water and plant coolant water were also tried.

**Copper strip corrosion test**

This test [3] was carried out as per the relevant IS Specification and also with emulsions as in the cast iron test. In a measured quantity of the oil at 100°C, a polished and weighed copper strip was immersed for 3 hrs. The degree of tarnish film was compared with reference to the table of classification under clause C1-1 and C7-1 of the specification. The oil was taken to have passed the test if the copper strip showed not more than slight tarnish classification I. The loss in weight suffered by copper during the test was also found out.

**Other corrosion rate tests***Weight loss determination*

The corrosion rates of copper were found out in various systems using weighed coupons. The different durations of exposure were 3 hrs, 1 day and 5 days both at ambient temperature and for 3 hrs at 85-90°C.

*Electrochemical measurements*

i) Instantaneous corrosion rate measurements were made in the different systems using the corrosion meter [4].

ii) Rest potential vs time measurements.

The rest potential of copper was measured in the various systems with time using a digital multimeter. A saturated calomel electrode served as reference and connected to the cell using an agar-saturated KCl bridge.

iii) Anodic and cathodic polarization measurements were carried out using an IC controlled Galvanostat. A platinum spiral served as the counter electrode.

**Humidity test**

The treated copper specimens were kept in a desiccator wherein a 100% R.H. is maintained at ambient temperature. The different treatments given are (1) dipping in oil-water emulsion (2) dipping and wiping and (3) dipping and degreasing with solvent. A clean copper without any treatment was a control run. At the end of 24 hrs, the specimens were visually examined for tarnishing referring to the Table I. (I.S. Specification slightly modified for experimental convenience).

Table I: Tarnishing grade modified from I.S.

Classification	Designation	Description
I A	Slight tarnish	As bright as freshly polished strip
I B	Slight tarnish	Bright orange film/patches
II A	Moderate tarnish	Red film
II B	Moderate tarnish	Multicoloured with green pink yellow interference patches
III A	Dark tarnish	Brassy yellow or golden yellow film
III B	Dark tarnish	Multicoloured with green, grey or pink interferences
IV	Corrosion	Black or grey or brown film

**Results and discussion**

Table II gives the pH and electrical conductivity of different waters and emulsions. The pH is near neutral in the emulsion as well as in water. So the corrosion of copper will be similar to neutral solutions. Electrical conductivity is slightly more in emulsions than in corresponding waters. It is well known that the water miscible cutting fluids are complex materials containing an oil, emulsifiers, wetting agents and sometimes blended with sulphur, chlorine, etc. [5]. It is quite likely that increase in conductivity is due to these substances present in the emulsion.

Table III shows the corrosion rates of copper in 10% sulphuric acid and 0.2% organic acid, as they are used to remove the black oxide scale on hot-rolled copper rods.

Table II: pH and electrical conductivity of different waters and emulsions

System	pH (Electro-metric)	Electrical conductivity (mhos/cm) x 10 <sup>3</sup>
Distilled water	5.2	0.061
Emulsion in distilled water	6.6	1.258
Tap water	6.8	3.700
Emulsion in tap water	6.6	1.628
Hard water	6.1	0.614
Emulsion in hard water	6.4	2.479
Plant coolant water	6.5	2.220
Emulsion in plant coolant water	6.7	2.664

Table III: Corrosion rate measurements in acid solutions

No.	Concentration of acids used	Corrosion rate in mdd	
		1 day	5 days
1.	10% Sulphuric acid	15.4 ± 1.0	22 ± 11
2.	0.2% Citric acid	8.8 ± 1.2	8 ± 1

It is seen that the corrosion rates are quite high and it is essential that an appropriate inhibitor has to be added to reduce the attack. This will also help in reducing the acid fumes. Since the organic acid dip is not giving any desirable effect on the copper surface, it may be eliminated from the sequence of operations.

The corrosivity of the cutting fluid, both straight or soluble, is tested by cast iron corrosion and the copper strip corrosion tests. The results of cast iron corrosion test are given in Table IV.

Table IV: Cast iron corrosion test with cutting oil emulsions

No.	Water used	Emulsion conc. as per IS: 1115-1973		
		3%	15%	Emulsion conc. in plant, 5%
1.	Hard water 500 ppm of calcium sulphate as per IS: 1115-1973	Stains	Stains	Stains
2.	Plant coolant water	Stain	None	Only slight stain
3.	Tap water	Only slight stain	None	Stain
4.	Distilled water	None	Only slight stain	None

This particular test is carried out mainly to assess the corrosivity of cutting oil on cast iron. It is seen from the Table that the cutting oil is corrosive to cast iron plate, thereby showing the insufficient quantity of additive or the absence of additive. Table V shows the results of copper strip corrosion test, which is to examine the corrosivity of the fluid towards non-ferrous metals. Since the cutting oil is used as an aqueous emulsion (oil in water) for drawing purpose, it is necessary to examine the corrosiveness of the emulsion also. Though the requirement of grade I tarnish film as per IS 1115-1957 is obtained in most of the cases, the weight losses show that the oil and the emulsions are corrosive, the former being more than 200 mdd and the latter

$9 \pm 5$  mdd. The observation of slight tarnish film indicates the absence of active sulphur in the oil [6,7]. It is yet to be understood why high corrosion rates are obtained in the weight loss experiments.

Table V: Copper strip corrosion test with the cutting oil and 5% emulsions

Temp: 85-90°C		Duration: 3 hrs.		
No. System	Wt. loss mdd.	Visual observation of tarnish grade	Remarks	
1. Cutting oil alone	237	I	As per IS: 1115-1957 the cutting oil passed the test	
2. Emulsion in hard water (500 ppm calcium sulphate)	$9.6 \pm 3.2$	I	Satisfactory as emulsion also	
3. Emulsion in plant coolant water	$6.4 \pm 3.2$	I	- do -	
4. Emulsion in tap water	$14.4 \pm 14.4$	II	Unsatisfactory	
5. Emulsion in distilled water	$4.8 \pm 4.8$	I	Satisfactory as emulsion	

In the case of aqueous emulsions the quality of water used for mixing is of utmost importance from corrosion point of view [8]. The salts like chloride and sulphate in the water can cause corrosion of the tools and the copper surface. In addition to this, the water hardness consumes coolant concentrate by way of precipitation. In Table VI the corrosion rates of copper in tap water, hard water, etc. are given.

Table VI: Corrosion rate of copper in different waters by wt. loss method under unstirred condition

Temp - room		Duration: 5 days
No.	Type of water	mdd.
1.	Distilled water	0.8
2.	Hard water (500 ppm calcium sulphate)	$3.5 \pm 0.2$
3.	Plant coolant water	$0.75 \pm 0.05$
4.	Tap water	0.6

It is seen that the corrosion rate is maximum in the hard water and it is around  $0.7 \pm 0.1$  mdd in others including distilled water. So it may be concluded that purer the water used for mixing the coolant, lesser the corrosion problem.

Table VII deals with the corrosion rate of copper in different emulsions for different durations.

Table VII: Corrosion rate of copper in different emulsions by wt. loss under unstirred condition

Temp - room		mdd		
No.	Type of emulsion	mdd		
		3 hrs	1 day	5 days
1.	Emulsion in distilled water	$20.8 \pm 11.2$	$2.4 \pm 0.4$	$0.44 \pm 0.20$
2.	Emulsion in hard water (500 ppm calcium sulphate)	$9.6 \pm 3.2$	0.8	$0.38 \pm 0.02$
3.	Emulsion in plant coolant water	$14.4 \pm 1.6$	$0.8 \pm 0.4$	$0.24 \pm 0.08$
4.	Emulsion in tap water	$11.2 \pm 4.8$	0.8	0.4

It is seen from the Table that the corrosion rate of copper is reduced with respect to time of immersion. It is also observed that the corrosion rate in emulsions is less than that in corresponding water. This may be attributed to the formation of a hydrophobic-oil film on the metal surface and the non-availability of oxygen at the reaction site.

In Table VIII the corrosion rates of copper in emulsions at higher temperatures (85-90°C) are also given as the cutting operation is likely to produce some heat during the process.

Table VIII: Corrosion rate of copper in different emulsions by weight loss under unstirred condition

Temp 85-90°C		Duration 3 hrs.		
No.	Type of emulsion	mdd		
		I Batch	II Batch	III Batch
1.	Emulsion in distilled water	$4.8 \pm 4.8$ (IA)	$17.6 \pm 1.6$ (IB)	9.6 (IIIA)
2.	Emulsion in hard water (500 ppm calcium sulphate)	$9.6 \pm 3.2$ (IA)	$12.8 \pm 3.2$ (IB)	3.2 (IIIA)
3.	Emulsion in plant coolant water	$6.4 \pm 3.2$ (IA)	$11.8 \pm 4.8$ (IB)	Negligible (IIA)
4.	Emulsion in tap water	28.8 (IB)	-	-
5.	Emulsion in distilled water + copper powder	Negligible (IB)	$14.4 \pm 8$ (IIB)	3.2 (IIIB)
6.	Emulsion in hard water + copper powder	Negligible (IB)	$22.4 \pm 9.6$ (IIB)	Negligible (IIIB)
7.	Emulsion in plant coolant water + copper powder	$6.4 \pm 3.2$ (IB)	$1.6 \pm 1.6$ (IIB)	Negligible (IIIB)

Note: Tarnishing grade in brackets

The corrosion rates are also determined in emulsions containing deliberate additions of copper powder because the coolant gets contaminated with some amount of copper during the drawing operation apart from carry over from the pickling tank due to inadequate washing. Visual observations are also presented. It may be seen that the colour of the tarnish film is increasingly intense in the emulsions containing copper powder than in those without copper. It is also observed that the tarnishing film darkens on repeated use, particularly the ones containing copper. But at the same time no conclusions could be drawn from the weight loss experiments as the values are quite irregular and irreproducible.

Coming to the electrochemical measurements with respect to the cathodic polarization, the corrosion behaviour of copper in unstirred condition is almost the same as that of water showing that the process is diffusion controlled. This is further supported by the curves obtained with stirred solutions.

The anodic polarization curves of copper in the different systems under unstirred and stirred conditions show that there is a steep polarization to very high positive potential in the case of distilled water and the peak decreases to less positive potential from sample water, tap water and reaches minimum in hard water (Figs 2 and 3). The pattern under stirred condition is the same, but the peak value obtained is high. Visual observations made of the specimen at the end of polarization experiments indicated localised type of attack by the formation of green spots. The polarization curves confirm that this is a localised type of attack in all the cases.

The instantaneous corrosion rates measured by using the CECRI-CEERI corrosion meter [4] for copper in waters and emulsions are given in Figs. 4 and 5 respectively.

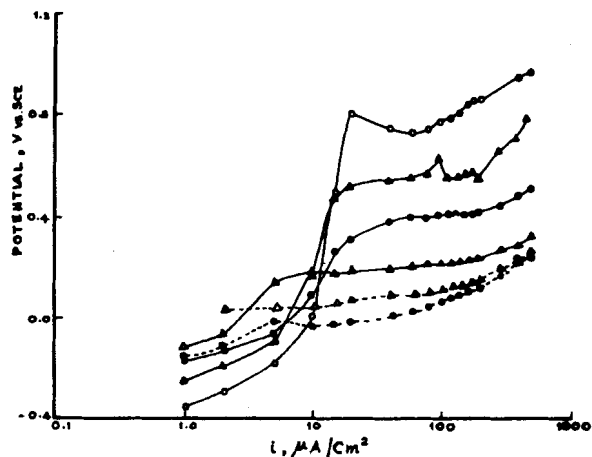


Fig. 2: Anodic polarization of copper in waters and emulsions in unstirred solutions at room temperature

- — ● tap water
- △ — △ hard water
- — ○ emulsion in distilled water
- — ● emulsion in tap water
- △ — △ emulsion in hard water
- ▲ — ▲ emulsion in plant coolant water

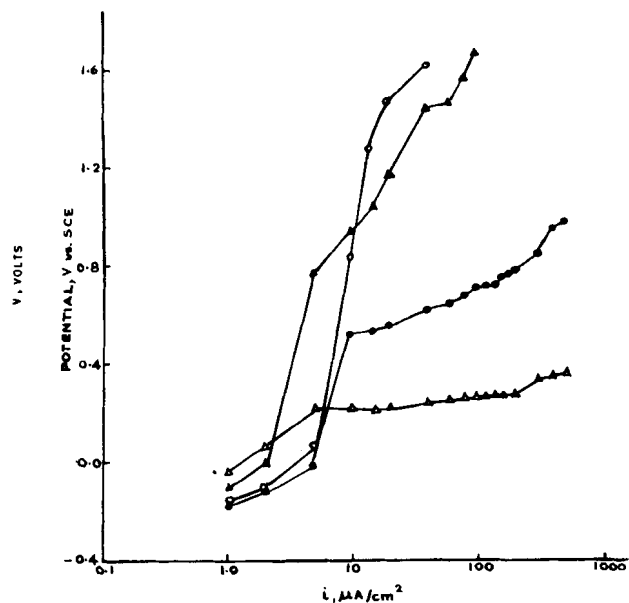


Fig. 3: Anodic polarization of copper in emulsions under stirred condition at room temperature

- — ○ emulsion in distilled water
- — ● emulsion in tap water
- △ — △ emulsion in hard water
- ▲ — ▲ emulsion in plant coolant water

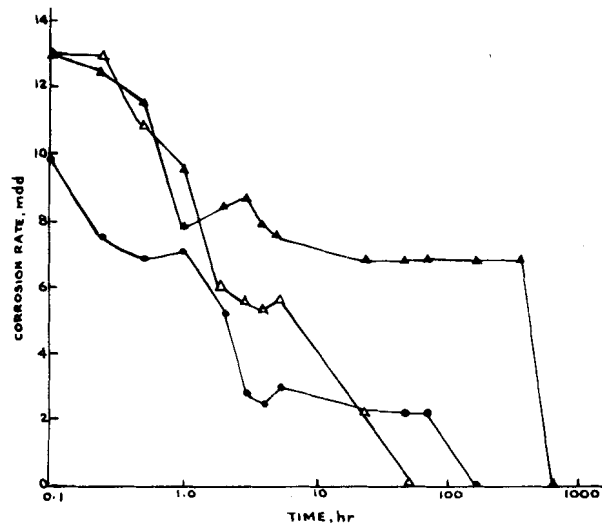


Fig. 4: Corrosion rate of copper vs time using corrosion meter in different waters under unstirred condition at room temperature

- — ● tap water
- △ — △ hard water
- ▲ — ▲ plant coolant water

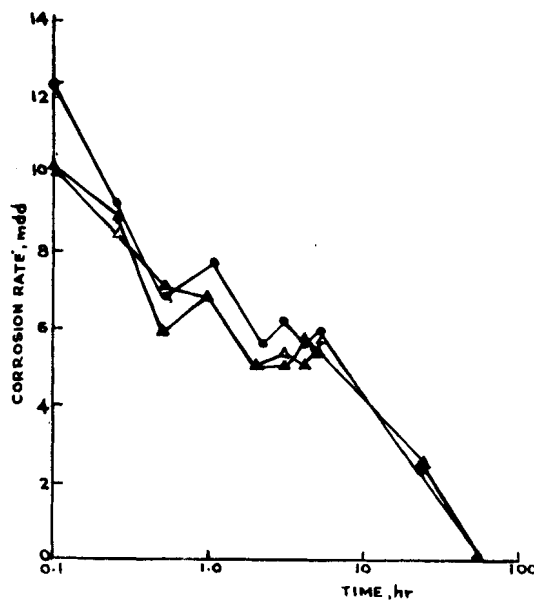


Fig. 5: Corrosion rate of copper vs time using corrosion meter in different emulsions under unstirred condition at room temperature

- — ● emulsion in tap water
- △ — △ emulsion in hard water
- ▲ — ▲ emulsion in plant coolant water

The corrosion rate of copper steadily decreases to a negligible value starting from 10-12 mdd during the course of 100 hrs. This is in agreement with weight loss data obtained after exposure for 5 days at room temperature. The decrease in corrosion rate may be due to some protective film formation.

It is well known that copper suffers only low corrosion rates in natural fresh waters owing to formation of a protective film such as cuprous oxide [9]. The potential of copper is generally displaced towards more positive values. The potential variation vs time of copper in different waters and emulsions is shown in Fig. 6.

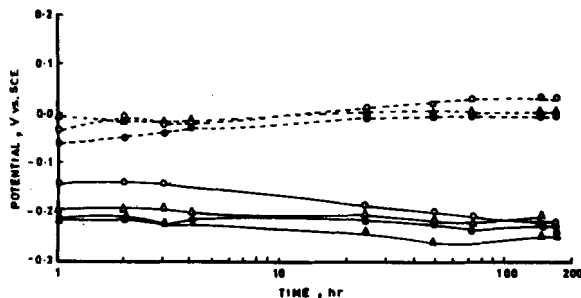
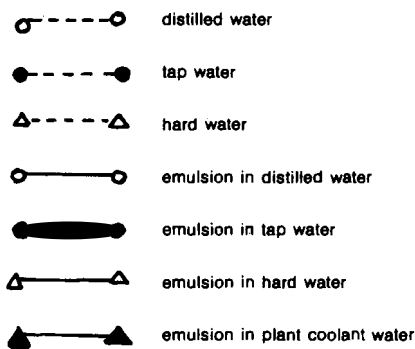


Fig. 6: Potential vs time of copper in different waters and emulsions under unstirred condition at room temperature



It is seen that in the case of emulsions, the potential is more negative than in waters. Although this observation is different from what is reported in literature still the weight loss data confirm that the decrease in corrosion rate in emulsions is due to some film formations.

To find out the effect of condensation of moisture on the metal surface carrying residual fluid on the surface, 100% relative humidity test has been carried out for a period of 24 hrs. The results of the experiment are reported in Table IX.

Table IX: Tarnishing behaviour after 24 hrs. of copper carrying cutting oil emulsion film at 100% RH at room temperature

No. Emulsion	Without wiping	With wiping	Cleaned with solvent
1. Emulsion in distilled water		Light orange film with dark patches here and there (IB)	No change
2. Emulsion in tap water	Green spots		
3. Emulsion in hard water			
4. Emulsion in plant coolant water			

Control expt.: No change

It is seen that uniform orange tarnish film is observed in all the cases where the film is not completely removed. It is also observed that the surface cleaned with solvent and the control specimens are not at all affected.

It has been reported that stains are produced when any reacting fluid comes into contact with the surface [10]. While oxygen in the air is always reacting with copper, the reaction is slow leading to gradual darkening of the surface. However, moisture condensation hastens the process. To avoid this problem residual fluids have to be completely removed off the surface. The final packing of copper wires or strips also should be in tact to avoid any moisture condensation.

#### Conclusions

In this study the main factors responsible for the tarnishing/corrosion of copper have been examined both by electrical and electrochemical methods and the precautionary measures are suggested.

#### Acknowledgement

The authors thank the Scientist-in-Charge, CECRI Unit, CSIR Complex, Madras for his keen interest and encouragement in the work.

#### References

1. R K Springborn (Ed), *Cutting and grinding fluids selection and application*, Am Soc Tool and Manfr Engrs Dearborn, Michigan (1967) p. 43
2. IS: 1115-1973
3. IS: 1115-1957
4. Mrs Venu Subramanian et al, *Trans SAEST*, 19 (1) (1984) 37
5. Ref 1, pp. 31-42
6. H H Uhlig (Ed) *The Corrosion Hand Book*, John Wiley & Sons, Inc (1948) p. 567
7. L L Shreir, (Ed) *Corrosion Vol. 1* Newnes - Butterworths, London, 2nd Ed (1976) p. 2:126
8. Ref 1, pp. 102-105
9. Ref 6, p. 65
10. Howard, J Menden Hall (Ed) *Understanding of copper alloys*, John Wiley & Sons (1977) p. 281