TECHNICAL REPORT

PHOTOCORROSION OF COPPER AND BRASS IN AQUEOUS SOLUTIONS OF COPPER AND FERRIC CHLORIDES

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Corrosion rates of copper and 63/37 brass in etching solutions like $CuCl_2$ and $FeCl_3$ with some additives are increased in the presence of sunlight due to photochemical reactions occurring at the surface of the specimen

Effect of light on the kinetics of corrosion of copper has been reported by Ivan Sekerka and co-workers[1]. They have shown that light energy increases the rate of corrosion in presence of sunlight which has been designated as photocorrosion[2].

In the present work corrosion of copper and 63/37 brass was studied in the following systems in presence and absence of sunlight.

(1) 25 g/l $CuCl_2.2H_2O$ + 50 g/l NH_4Cl + ml/l liq. ammonia.

(2) 25 g/l $CuCl_2.2H_2O$ + 50 g/l NH_4Cl + 50 ml/l NH_4-acetate.

(3) 50 g/l $FeCl_3.6H_2O$ + 100 ml/l conc. HCl.

(4) 50 g/l $FeCl_3.6H_2O$ + 25 g/l $CuSO_4.5H_2O$.

(5) 50 g/l $FeCl_3.6H_2O$ + 25 ml/l conc.HCl + 100 g/l KCl.

All the chemicals used were of BDH quality.

Experimental

The specimens of copper 3 × 6 cm (99.9% Cu) and 63/37 brass (Cu — 63.2%, Zn — 36.6% and Pb — 0.01%) were polished according to the methods suggested by Champion[3]. The weighed specimen plates were immersed in 250 ml. beakers full of the solution. The beakers were placed in troughs containing water, and the troughs in turn were placed in thermostatic water bath. The experiments were carried out in two sets. One set was shielded from sunlight by using a black painted tough with an opaque covering, while another set was placed in a trough transparent to light; also kept in the same thermostatic bath to maintain identical condition of temperature. The specimens were removed after definite time period i.e. 2 hours. Then specimens were cleaned with 5% H_2SO_4, dipped in alcohol-ether mixture, dried and weighed.

The results of corrosion kinetics are expressed in terms of weight loss in mg and mg/dm²/hr, in presence and absence of light.

Results and Discussion

(A) Photocorrosion of copper and 63/37 brass in $CuCl_2$ Solution with additives.

Aqueous solution of $CuCl_2$ finds application as a good etching agent for copper[4,5]. A film of CuCl is formed on the surface of copper, according to the reaction $CuCl_2 + Cu \rightarrow 2CuCl$. 2CuCl is photo-sensitive[6] and produces photocurrent. The presence of Cu_2O was also detected in the film product by X-ray analysis; cuprous oxide is also photosensitive. The formation of Cu_2O may be due to the following reactions:

$$CuCl + n\ H_2O \rightarrow CuCl(H_2O)_n \text{ solvated complex}$$

$$CuCl(H_2O)_n + O_2 \rightarrow Cu_2O + 2HCl + \text{other products (Photo adsorbed)}$$

Addition of NH_4Cl and KCl to $CuCl_2$ solution increases the rate of etching of copper according to Kucherenko et al[7] while Shipley et al[8] have reported the use of aqueous solution containing ammonium chloride adjusted to pH 7.6 for etching of copper.

The results of corrosion kinetics are given in Tables I & II. The rate of corrosion increases with increase in concentration of $CuCl_2$. The rate of corrosion is observed to be higher in presence of sunlight as compared with that in absence of it.

$CuCl_2$ reacts with brass specimen giving a film of CuCl while $ZnCl_2$ formed goes into solution. At first dezincification takes place. Consequently, the surface of the specimen, first becomes red due to the deposition of copper.

TABLE 1 Weight loss data on corrosion of copper and brass (63/37) in aqueous solution containing 25 g/l $CuCl_2$ + 50 g/l NH_4Cl + 50 ml/l liquor ammonia (stock solution). Duration : 2 hours ; Temp : 32 ± 1°C.

Conc.	In absence of light		In presence of light	
% Stock soln.	Loss mg	Loss mg/dm²/hr	Loss mg	Loss mg/dm²/hr
Copper				
10	20.0	27.8	28.0	38.9
20	42.9	59.5	50.4	70.0
40	108.0	150.0	126.0	175.0
50	145.0	201.3	167.0	231.8
100	326.0	452.7	405.0	562.5
Brass				
10	7.0	9.7	15.3	21.2
20	10.4	14.4	21.0	29.1
40	70.0	97.0	109.0	151.0
50	108.0	150 0	139.0	193.0
100	342.0	475.0	404.0	561.0

TABLE 2 Weight loss data on corrosion of copper and brass (63/37) in aqueous solution containing 25 g/l $CuCl_2$ + 50 g/l NH_4Cl + 50 ml/l liq. ammonia + 50 g/l NH_4-acetate (stock sloution). Duration : 2 hours : Temp. 32 ± 1°C.

Conc.	Inabsence of light		In presence of light	
% stock soln.	Loss mg	Loss mg/dm²/hr	Loss mg	Loss mg/dm²/hr
Copper				
10	31.8	44.2	42.0	58.4
20	35.0	48.6	48.3	66.6
40	87.0	120.0	116.0	162.0
50	110.0	152.0	148.0	205.0
100	238.2	330.0	284.0	395.0
Brass				
10	18.5	25.7	23.6	32.7
20	21.7	30.1	34.4	47.8
40	100.0	139.0	138.0	192.0
50	155.0	215.0	172.0	239.0
100	365.0	507.0	413.0	573.0

$$Zn + CuCl_2 \rightarrow ZnCl_2 + Cu$$

$CuCl_2$ further reacts with copper to give CuCl.

$$CuCl_2 + Cu \rightarrow 2\,CuCl$$

The increased rate of corrosion of brass in presence of sunlight is observed, as seen from the results given in Tables I and II. The increased rate of corrosion, is probably due to the photochemical reactions. $CuCl_2$ is photohydrolysed to Cu_2O as discussed in the case of copper.

(B) Photocorrosion of copper and brass in aqueous $FeCl_3$ solution containing additives

$FeCl_3$ is an excellent etching agent for copper[9,10]. Copper reacts with $FeCl_3$ to form a photosensitive film of CuCl according to the reaction,

$$FeCl_3 + Cu \rightarrow CuCl + FeCl_2$$

Again $CuCl_2$ further reacts with copper forming CuCl.

$$CuCl_2 + Cu \rightarrow 2CuCl$$

The formation of the film of CuCl has been proved by x-ray diffraction study[12].

The results of corrosion rate study are given in Tables III, IV and V. The general observation is

TABLE 3 Weight loss data on corrosion of copper and brass (63/37) in aqueous solution containing 50 g/l $FeCl_3.6H_2O$ + 100 ml conc HCl (stock solution). Duration : 2 hours ; Temp : 32 ± 1°C.

Conc.	In absence of light		In presence of light	
% stock soln.	Loss mg	Loss mg/dm²/hr	Loss mg	Loss mg/dm²/hr
Copper				
10	32.3	45.8	42.8	54.4
20	34.0	47.2	46.0	93.8
40	37.0	51.4	53.3	74.0
50	159.0	220.0	210.0	292.0
100	654.0	908.0	715.0	993.0
Brass				
10	25.4	35.2	31.4	43.6
20	55.0	76.4	70.0	97.2
40	156.0	166.6	202.0	281.0
50	178.0	247.6	248.0	344.0
100	478.0	663.0	603.5	837.0

TABLE 4 Weight loss data on corrosion of copper and brass (63/37) containing 50 g/l. $FeCl_3.6H_2O$ + 25 g/l. $CuSO_4.5H_2O$ (stock solution); Duration : 2 hours. Temp. 32 ± 1°C.

Conc.	In absence of light		In presence of light	
% stock soln.	Loss mg	Loss mg/dm²/hr	Loss mg	Loss mg/dm²/hr
Copper				
10	31.3	43.5	89.2	51.4
20	59.8	83.0	68.4	95.0
40	122.9	170.0	142.0	197.0
50	160.2	222.0	178.0	247.0
100	302.0	419.0	386.0	535.0
Brass				
10	32.7	44.0	43.3	60.0
20	74.6	104.0	88.0	122.0
40	172.0	239.0	197.0	273.0
50	334.0	462.0	380.0	527.0
100	585.0	812.0	639.0	887.0

TABLE 5 Weight loss data on corrosion of copper and brass (63/37) in aqueous solution containing 50 g/l. $FeCl_3.6H_2O$ + 25 ml/l. conc. HCl + 100 g/l. KCl (stock solution). Duration : 2 hours; Temp : 32 ± 1°C.

Conc.	In absence of light		In presence of light	
% stock soln.	Loss mg	Loss mg/dm²/hr	Loss mg	Loss mg/dm²/hr
Copper				
10	28.1	39.0	39.0	54.1
20	30.0	16.6	46.0	63.8
40	152.0	210.0	184.0	205.0
50	214.0	297.0	254.0	352.0
100	519.0	720.0	600.0	833.0
Brass				
10	29.1	40.4	36.0	49.9
20	30.5	42.4	39.2	54.4
40	106.0	148.0	121.0	168.0
50	138.0	192.0	165.0	229.0
100	304.0	422.0	340.0	472.0

that the rate of corrosion increases with the concentration of $FeCl_3$, and the rate of corrosion in presence of sunlight is higher than that in absence of light. The increased rate of corrosion is due to Photochemical reactions at the surface of the specimens.

The use of $FeCl_3$ with additives such as KCl, HCl and Cu^{+2} as etchant for copper has been reported by Hanke et al[13].

The addition of $CuSO_4$ to $FeCl_3$, decreases the rate of corrosion of copper in absence of sunlight; while in presence of sunlight, the rate of corrosion is much increased for lower concentrations of the additives. At higher concentrations of additives the rate of corrosion is decreased.

In general, the rate of corrosion of copper in presence of sunlight is greater than in absence of it and semi conducting films formed on copper plate, which consist of CuCl, an 'n' – type and Cu_2O, a p–type semiconductor. The photochemical process is mainly responsible for increase in corrosion in presence of sunlight.

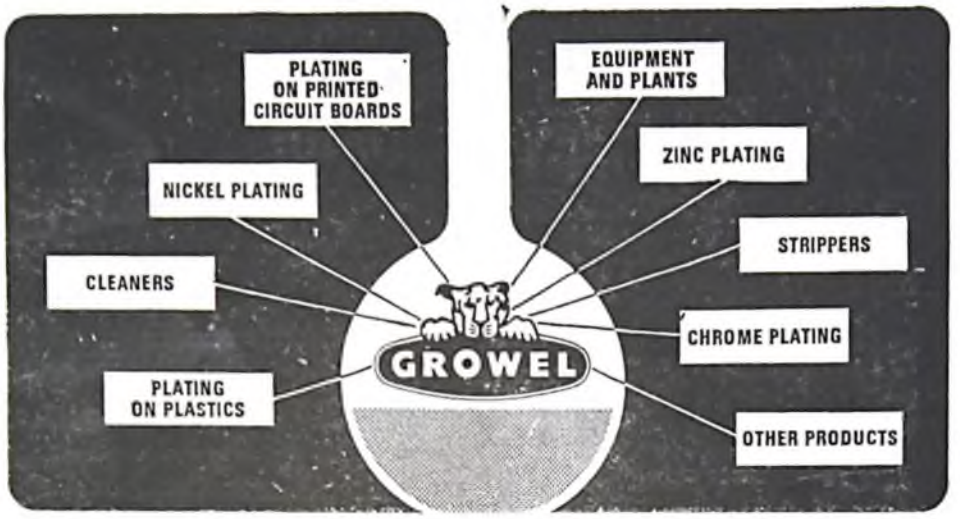
The same trend is observed in the case of brass as was observed in the case of copper.

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