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Electronic property of photosensitive film formed during corrosion of copper in aqueous and non-aqueous solutions of bromine

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A photosensitive film was observed on copper plates during corrosion in aqueous and non-aqueous bromine solutions. Sunlight, when incident on the photosensitive film formed, left an image of the markings on the Pyrex glass container through which light was incident on the plate. Photoelectric measurements of the semi-conducting properties of the reaction product of the copper and the bromine solutions have been correlated with image formation. A change in polarity was noted during film formation, the mechanism of which is discussed.

1. Introduction

Bromine water in the absence of light has earlier been found to be mildly corrosive towards copper [1]. Sunlight plays a significant role in the corrosion of metals in aqueous and non-aqueous solutions [2, 3]. Hence in the present study, the influence of sunlight on pretreated copper, immersed in bromine solution, has been examined.

A photosensitive film was found to be formed, which gives an image of the markings on the glass container through which sunlight is incident on the film. There is a change in polarity of the photocurrent during photosensitive film formation.

2. Experimental

Electrolytic copper was washed, dried and polished according to Champion [4]. A mirror-like finish was obtained, which was de-greased by immersion in carbon tetrachloride. When immersed in 0·1 M aqueous bromine a reddish brown film formed on the copper surfaces. The two sides of the plate were connected to a sensitive ballistic galvanometer by sprung copper strip contacts and one surface was exposed to sunlight through the glass container. The change of the photocurrent generated with time was examined. The sensitivity of the galvanometer was 270 K Ω^{-1} V^{-1}, and the intensity of the incident sunlight was 22 500 lm. Copper plates moistened with the solutions gave similar results.

3. Mechanism

The copper reacts with bromine to form a thin, adherent reddish brown film of CuBr as one of the products according to the following reactions:

$$Br_2 \xrightarrow{h\nu} \underset{\text{(excited)}}{Br_2^*} \longrightarrow Br^\bullet + Br^\bullet$$

$$Cu + Br^\bullet \longrightarrow CuBr \text{ (film product)} + e$$

The formation of CuBr was confirmed by standard chemical tests.

Korovin and Ulanovskii [2] have reported the formation of CuCl during the corrosion of copper in sea water in sunlight.

The film formed is photosensitive, giving a photoprint of the markings on the glass con-

tainer (Fig. 1). The exposed part of the plate has a different colour from the rest, as detailed in Table 1.

Table 1.

Treatment	*Observation of colour of*	
	Unexposed areas	*Exposed areas*
Bromine water	Reddish brown	Bluish black
Bromine in acetic acid	Reddish	Bluish black
Bromine in Chloroform	Brown	Purple black

The photocurrent was measured during exposure and current versus time graphs plotted (Fig. 2a, 2b and 2c) showing a change in polarity during exposure. In all the three graphs there is an increase of photocurrent in one direction from *A* to *B*. The photocurrent is formed during this interval of time, i.e. during growth of current from *A* to *B* (7 s in aqueous bromine, 15 s for bromine in acetic acid and 8 s for bromine in chloroform). The mechanism of the growth of photocurrent from *A* to *B* appears to be photo-solution or photo-adsorption of solvent by the CuBr film formed. The change in polarity from *B* to *C* is probably due to the

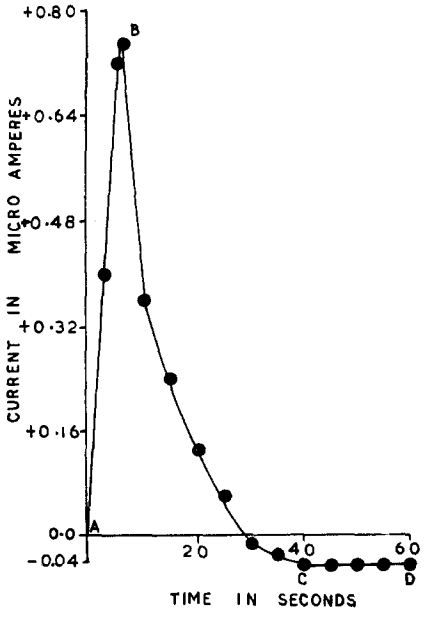

Fig. 2a. Change in polarity during photosensitive film formation on copper in aqueous bromine solution.

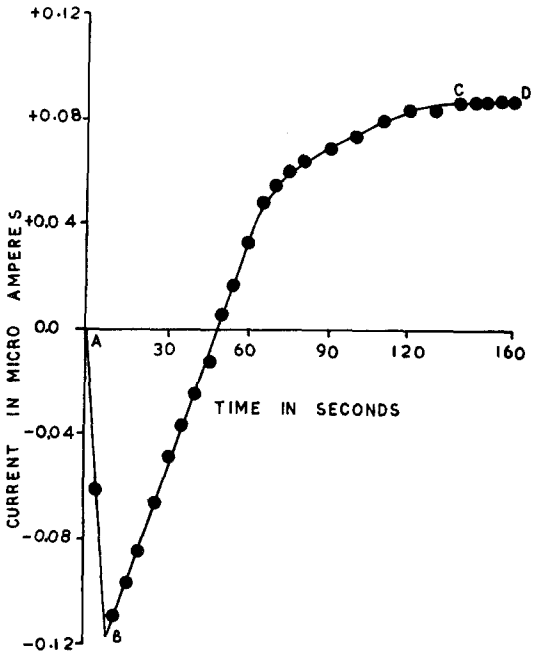

Fig. 2b. Change in polarity during photosensitive film formation on copper in bromine solution in acetic acid.

decomposition of solvated complex in the presence of dissolved oxygen, to form Cu_2O and HBr.

$$CuBr + solvent \xrightarrow{h\nu} CuBr\ (solvated\ complex)$$
$$(H_2O, CH_3COOH, CHCl_3)$$

$$CuBr + O_2 \xrightarrow{h\nu} Cu_2O + HBr + other\ products$$
$$(solvated\ complex)$$

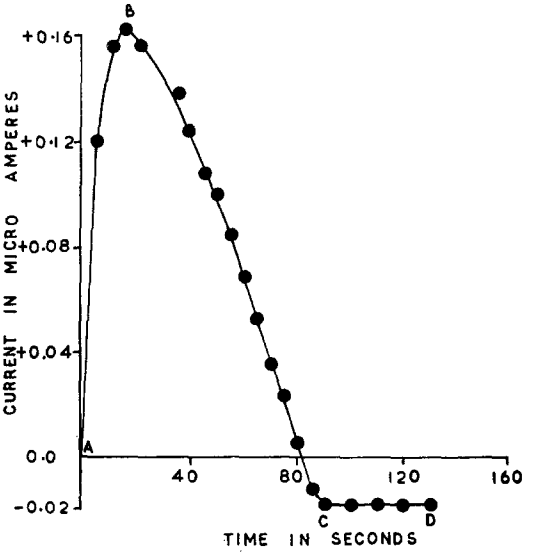

Fig. 2c. Change in polarity during photosensitive film formation on copper in bromine solution in chloroform.

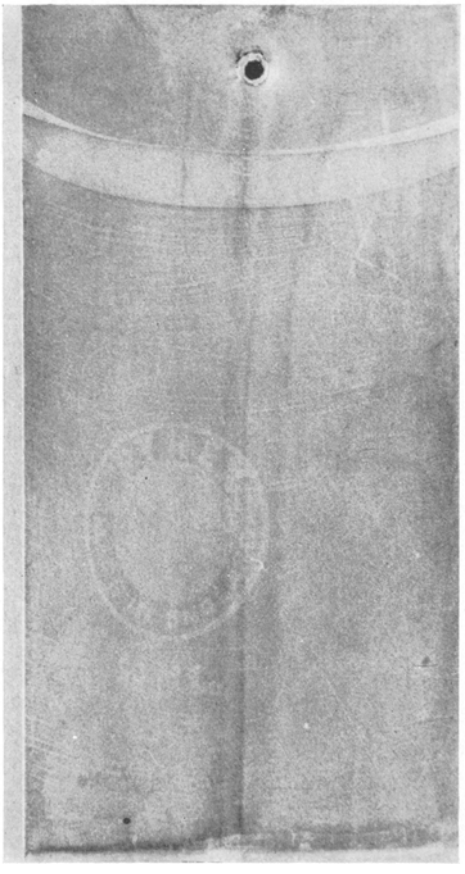

Fig. 1. A photo image of a pyrex glass container obtained when sunlight is incident on the treated plate.

The formation of Cu_2O on copper immersed in chloride ions containing electrolytes under the influence of light has been reported by Bonora and co-workers [5].

The current levels off between *C* and *D* to become constant within 2 min in reasonable agreement with a figure of 1 min reported in the literature [6]. The reason for this behaviour is not understood. A possible explanation might be that both CuBr and Cu_2O layers may be present, CuBr being an n-type semi-conductor while Cu_2O is p-type hence forming a junction of the two types.

Conclusions

The photosensitivity of CuBr film has been confirmed. A visible image is developed in the period during which the photocurrent rises to a maximum and falls with time. It is suggested that image formation is due to photo-solvation or photo-adsorption of the solvent together with further reaction with dissolved oxygen. The observations imply that there is a considerable increase in the corrosion of copper and brass in solutions of halogens exposed to sunlight. Further work is in progress.

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