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# The electrobrightening of copper in orthophosphoric acid

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The electrobrightening of copper in orthophosphoric acid was studied at several electrolyte concentrations, temperatures and current densities. Stress-free electrolytic copper plates were used in a rectangular plexi-glass cell, through which a constant current was passed. The results show that there is a critical bath temperature (27° C) at which the surface has a maximum brightness, that an increase in the current density above a limiting value has only a slight effect on surface brightness and that brightness increases with acid concentration.

## 1. Introduction

Electropolishing of metal surfaces comprises two simultaneous processes, brightening and levelling. Brightening occurs first, while levelling requires further dissolution of the metal. The electropolishing of metals and alloys has many uses in industry [1], e.g. light reflectors used in motor cars and solar energy conversion equipment. A good surface finish, comparable to that of a highly mechanically polished surface, can be obtained under suitable electrobrightening conditions. In order to learn more about the mechanisms involved in electrobrightening, the anodic dissolution of copper in orthophosphoric acid was studied. This acid was used by several investigators for the electropolishing of copper and other metals [2–6].

In a recent paper [7], a mass transfer anodic film model was proposed for surface brightening in phosphoric acid. According to this model, surface brightness is obtained when the mass transfer rate for the dissolution products is exceeded causing oxide formation at the anode. In the present study the influence of orthophosphoric acid concentration, bath temperature, and current density has been investigated.

## 2. Experimental procedure

All experiments were carried out with the copper as the anode and at constant current in orthophosphoric acid (7–14 mol $dm^{-3}$) and at a constant bath temperature (5–60° C ± 0·5° C). The electrolytic circuit and cell were similar to those described previously [7, 8]. The electrodes were electrolytic polycrystalline copper plates (99·9%), 12 × 2 × 0·1 cm. These plates were mechanically polished with abrasive papers to grade 600 then heat treated for one hour at 600° C followed by water quenching. Before each experiment, the electrodes were mechanically polished on 600 abrasive paper, washed with distilled water, alcohol, and dried with air. Fresh electrolyte was used in each experiment. A constant charge of electricity per unit area was used for electrobrightening. After electrobrightening, the anodes were removed from the cell, washed, dried, and the brightness was determined by measuring the relative surface reflectance using a photoelectric cell to receive the reflected light at different angles of incidence. The reading of the photocell was a direct measure of reflected diffuse light intensity and is considered as an index of brightness [9]. The light was in the wavelength range 400–750 nm.

## 3. Results and discussions

The electrobrightening of copper in orthophosphoric acid was studied under different conditions. The curves in Fig. 1 indicate that the brightness increases with an increase in the concentration of phosphoric acid. The influence of bath temperature on surface brightness is shown in Fig. 2. The data obtained between 5–60° C show that the surface brightness is a

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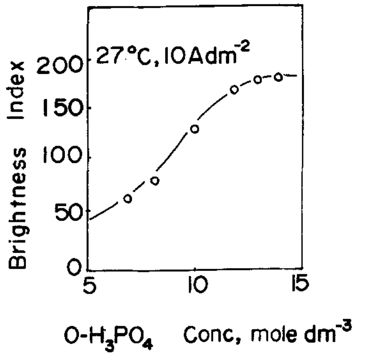

Fig. 1. The effect of orthophosphoric acid concentration on the surface brightness of copper. The intensity of the diffuse reflected light is considered as the brightness index.

maximum at about 27° C. It should be noted that as the bath temperature increases the limiting current increases as indicated in Fig. 3. Increasing the current density above the limiting value only has a slight effect on the surface brightness as shown in Fig. 4.

It was reported that surface brightening sets in when the local concentration of dissolution products at the anode exceeds the saturation concentration. This concentration increases with temperature; higher current density and temperature improve surface brightness [10]. Mass transfer controlled surface brightening is frequently found in electropolishing [11–15]. Mass transfer controlled salt precipitation at the anode governs the transition from etching to brightening.

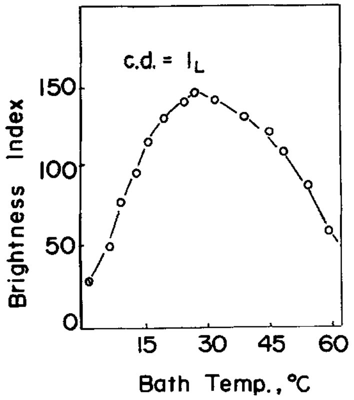

Fig. 2. The influence of bath temperature on surface brightness of copper in 10 mol dm$^{-3}$ orthophosphoric acid.

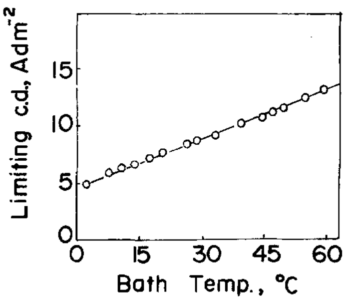

Fig. 3. The effect of bath temperature on limiting current density (c.d.) of copper in 10 mol dm$^{-3}$ orthophosphoric acid.

The anodic oxidation of copper passes through several forms of surface oxides of increasing degree of oxidation [16]. The nature of the process occurring on the copper surface is complex. The copper oxide that appears at a potential near to that of oxygen evolution is identified as CuO [16], but there are phases of intermediate composition between $Cu_2O$ and CuO. This was confirmed by X-ray photoelectron spectroscopy on the surface film of electropolished copper–nickel alloys, composed of $Ni_2O_3$ and $Cu_2O$ and/or CuO [17]. The oxide layer on anodized copper consisted of two phases: cubic $Cu_2O$ and monoclinic CuO, there is no preferred orientation of the crystals, i.e. there is a lack of texture [18].

From the previous literature the change of brightness could be attributed to the surface film character, e.g. its composition and/or thickness. Any factor tending to increase the porosity of the film increases its thickness and in turn affects surface brightness. The increase in brightness with

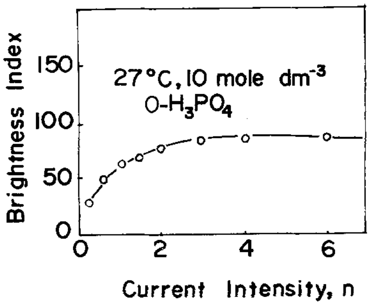

Fig. 4. The effect of current intensity on the brightness of copper: a current intensity value $n$ denotes a current density $nI_L$, where $I_L$ is the experimental limiting current density.

bath temperature is attributed to an increase in film thickness which seems to have its optimum value at about 27° C as shown in Fig. 2. However, potentiodynamic polarization measurements of the electropolishing of copper in orthophosphoric acid suggest that a change in the mechanism occurs at 37° C inasmuch as the activation energy below this temperature is reported to be 24·8 kJ $\text{mol}^{-1}$ and 17·6 kJ $\text{mol}^{-1}$ above.

## 4. Conclusions

Surface reflection gives direct information about certain properties of materials. From the data obtained it can be seen that surface brightness increases with the concentration of orthophosphoric acid, is a maximum at about 27° C and that current intensities in excess of the limiting value have no significant effect on brightness.

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