

[CONTRIBUTION FROM THE METALLURGICAL LABORATORIES OF CAMBRIDGE UNIVERSITY]

## Copper Oxide Films

By H. A. MILEY<sup>1</sup>

## Introduction

The new electrical method described elsewhere<sup>2</sup> has been used for studying the rate of oxidation of copper in air at several temperatures. In this method the time required for the cathodic reduction of the oxide is measured, and this number multiplied by the current strength furnishes the quantity of electricity expended. Each millicoulomb per square cm. represents a film thickness of

$$\frac{M \times 10^8}{2D \times 96,494 \times 10^3} = t \quad (1)$$

where  $M$  is weight of oxide furnishing one gram-atom of oxygen for cathodic reduction (143.14 for cuprous oxide and 79.57 for cupric oxide),  $D$  is density of the oxide (6.00 for cuprous oxide and 6.45 for cupric oxide) and  $t$  is thickness of the oxide in Ångström units per millicoulomb per square cm.; when the above values of  $M$  and  $D$  are substituted in equation (1) the numbers 12.36 for cuprous oxide and 6.39 for cupric oxide are obtained for  $t$ .

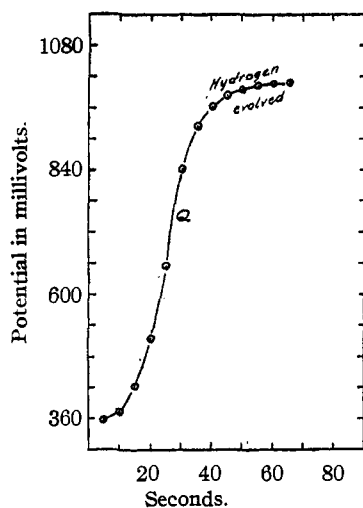


Fig. 1.—The potential-time curve for a thin (invisible) cuprous oxide film.

**Procedure.**—The copper was rolled to a thickness of 0.50 mm., and contained oxygen 0.04 and other impurities 0.01%. It was abraded with French emery No. 1G and finished with No. 1F, cut into strips measuring  $1.75 \times$

5.5 cm., and washed in benzene. Oxidation was carried out for a required time in an electric furnace of high heat capacity, so as to ensure that the desired temperature was attained rapidly; in the furnace, the specimen rested in thermal contact with a nickel frame actually attached to the thermometer, to minimize temperature differences between the thermometer and specimen. After cooling, the whole surface of the specimen—except the experimental area measuring 2 to 2.5 sq. cm.—was covered with paint containing titanium oxide dispersed in half its weight of clear "Brushing Belco" nitrocellulose varnish.

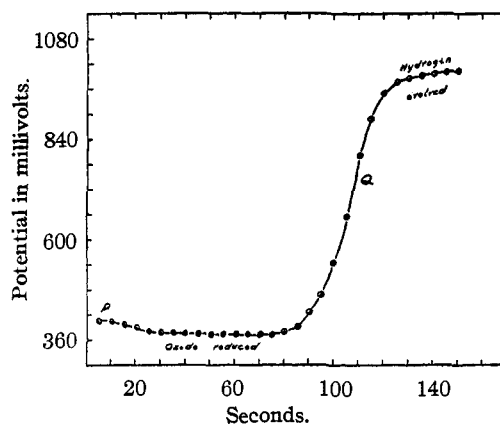


Fig. 2.—The potential-time curve for a cuprous oxide film of intermediate thickness.

For measuring the thickness of the oxide film on the experimental area, the whole was subjected to cathodic reduction in 0.2  $M$  ammonium chloride solution at a constant current of 1 to 0.5 m. a. per sq. cm., provided by applying 110 v. through a resistance of 50,000 to 100,000 ohms (this high voltage and high external resistance prevents small fluctuations of resistance or polarization in the electrolytic cell from affecting the current strength). The end-point marking complete reduction was obtained by noting the movement of the potential drop needed to force this constant current through the cell—oxide-covered copper/ammonium chloride/copper. This potential clearly should rise sharply when the reduction of the oxide is over and the liberation of hydrogen begins. Typical potential-time curves are shown in Figs. 1, 2 and 3. Reduction of oxide to metallic copper is observed over the initial part of the curves and the evolution of hydrogen over the latter part; the inflection point  $Q$  is taken as the instant when the reduction of the homogeneous oxide film is just complete, and is used in calculating the thickness. Values for the thicknesses thus obtained from oxide films which confer interference colors on copper agree well with those obtained optically by Constable;<sup>3</sup> the two sets of values, reproduced from a previous note,<sup>4</sup> are shown below.

(1) Carnegie Research Scholar, Cambridge University, 1936 and 1937.

(2) Miley, *Iron and Steel Inst.* (London), Carnegie Schol. Mem., 25, 197 (1936).

(3) Constable, *Proc. Roy. Soc.* (London), A117, 386 (1928).

(4) Evans and Miley, *Nature*, 139, 283 (1937).

TABLE I  
THICKNESS (MEAN GENERAL INTERCEPTS) OF COPPER  
OXIDE FILMS

Tinted to	Electrical (New), Å.	Optical (Constable), Å.
First Order		
Dark brown	370	380
Red-brown	410	420
Purple	460	450
Violet	485	480
Blue	520	500
Silvery green	800	880
Second Order		
Yellow	940	980
Orange	1170	1200
Red	1240	1260

The peak (P, Fig. 2) is probably due to the fact that reduction occurs preferentially at privileged places, such as the bottom of pores in the film, where metallic copper is in contact with oxide at the commencement of the experiment. An additional potential drop would be needed to force the current through these pores, but this need will disappear as the freshly reduced copper grows outward through the film toward the liquid. This explanation is in accord with Pease and Taylor's belief<sup>5</sup> that the high temperature reduction of copper oxide by hydrogen is autocatalytic—an opinion not shared, however, by Lewis.<sup>6</sup> It is suggested, in the present work, by the fact that the peak (P) is absent for thin films, which are known to be very porous.<sup>7</sup> However, the validity of the results set forth below will *not* be affected if this interpretation of the peak is subsequently shown to be wrong.

Where copper is covered with a double film, showing an underlayer of red cuprous oxide and an outer layer of black cupric oxide, two arrestments are obtained (Fig. 3) and the thickness of the two layers can be obtained separately, by observing the times represented by *R* and *Q*.

It will be noted that the cathodic reduction of copper oxide differs from that of iron oxide<sup>2</sup> in that it leaves a residue of metallic copper, whereas the reduction product on iron (ferrous oxide) is dissolved by ammonium chloride; this explains

(5) Pease and Taylor, *THIS JOURNAL*, **43**, 2176 (1921); **44**, 1637 (1922).

(6) Lewis, *J. Chem. Soc.*, 820 (1932); more references to work on the reduction of copper oxide by gases are given in this paper.

(7) Evans, *Nature*, **118**, 51 (1926).

the differences in the shape of the curves, and the fact that on iron incomplete cathodic reduction converts late colors to early colors, while on copper the corresponding change is less easily observed, since the local reduction of metallic copper at privileged points destroys the uniformity of the surviving oxide.

In this paper the word "thickness" is taken to mean the average of the intercepts made by the film on a large number of parallel lines drawn perpendicular to the *general* plane of the surface. This is  $\sigma$  times the thickness as defined by some authors, where  $\sigma$  is the specific surface.

## Results

Figures 4 and 5 show the relation between the film thickness ( $y$ ) and the time of heating ( $t$ ). The general form of the curves resembles that

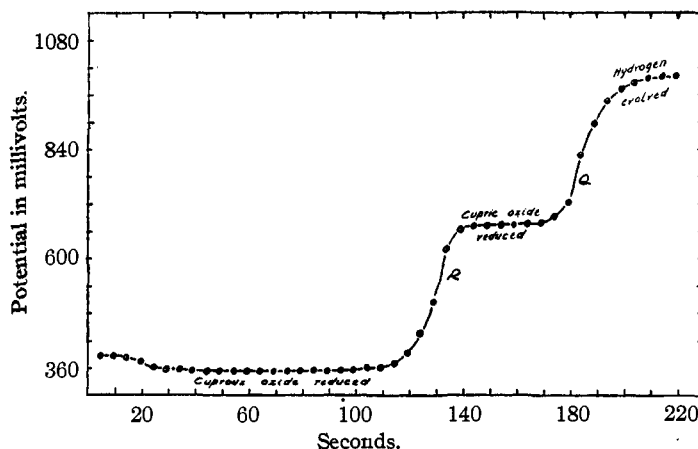


Fig. 3.—The potential-time curve for a duplex copper (cuprous-cupric) oxide film.

previously obtained<sup>4</sup> at 18° (in purified air) and at 62° (in a furnace). The rate of oxidation is fast at first, but falls off; the parabolic law  $dy/dt = k/y$ , or  $y^2 = kt + A$ , found by Pilling and Bedworth<sup>8</sup> to be obeyed in the range 800 to 1000°, was only found valid for short intervals (Figs. 6 and 7). This is indicated by the short straight initial portions of the curves which express the relation between the squares of the film thickness ( $y^2$ ) and the time of heating ( $t$ ). This limited validity of the law is in general agreement with the results of Dunn<sup>9</sup> from 180 to 240°; however, Dunn used different methods of measurement, and the results are not expected to be identical. It should be noted that  $A$  is not zero.

(8) Pilling and Bedworth, *J. Inst. Metals*, **29**, 529 (1923).

(9) Dunn, *Proc. Roy. Soc. (London)*, **A111**, 210 (1926).

Winterbottom<sup>10</sup> has recently used a polarimetric method to study the early growth of oxide films on copper and has obtained results in general agreement with those published elsewhere<sup>4</sup> and repeated in the broken curves of Fig. 4.

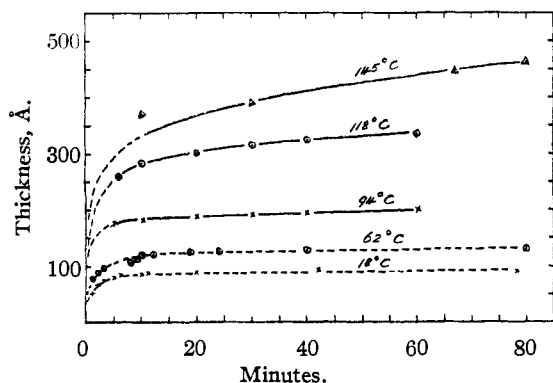


Fig. 4.—Oxidation of copper in an electric furnace after standard abrasion (broken curves for 18 and 62° repeated from the data given elsewhere<sup>4</sup>).

#### Composition of the Films

It is well known that, when copper is heated, two layers of oxide are formed which can sometimes be detached from one another; the outer layer is black and presumably cupric oxide, the inner layer red and presumably cuprous oxide.

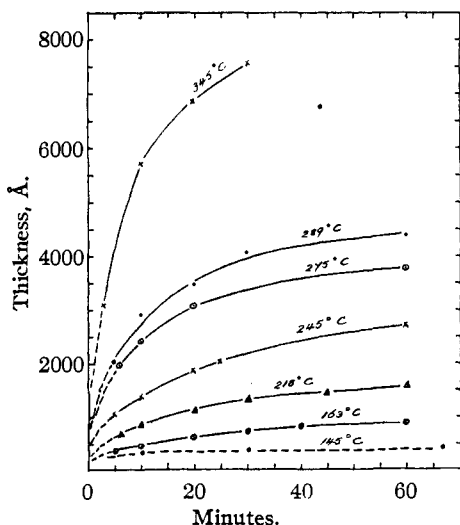


Fig. 5.—Oxidation of copper in an electric furnace after standard abrasion (broken curve for 145° repeated from the data of Fig. 4).

Electron diffraction patterns obtained by Darbyshire<sup>11</sup> for oxide films anodically stripped from tinted copper which had been heated in a

(10) Winterbottom, *Nature*, **140**, 364 (1937).

(11) Darbyshire, *Trans. Faraday Soc.*, **27**, 675 (1931).

bunsen flame, and by Preston and Bircumshaw<sup>12</sup> for the oxide films produced on copper in air at ordinary temperatures and at 100° revealed only cuprous oxide in the films; Hinshelwood<sup>13</sup> and Constable<sup>14</sup> considered the oxide in tinted films, formed at 200 to 300°, to be cupric oxide, while

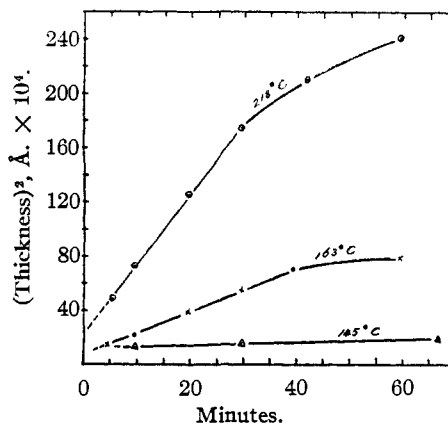


Fig. 6.—Relation between (thickness)<sup>2</sup> and time for copper oxide films.

the work of some others has been based on the assumption that such films consist entirely of cuprous oxide. In studying the catalytic union of hydrogen and oxygen on copper Tedeschi<sup>15</sup> postulated the oxide formed at 260° to be cupric oxide, while Van Cleave and Rideal<sup>16</sup> found cuprous oxide to be the one formed except when a

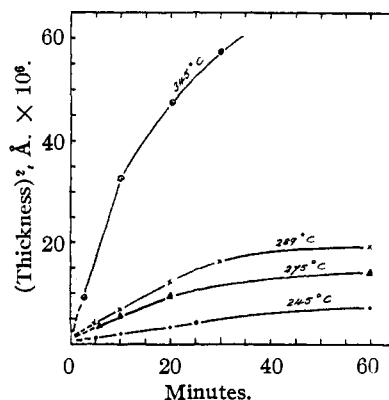


Fig. 7.—Relation between (thickness)<sup>2</sup> and time for copper oxide films.

mixture of the two oxides was obtained under certain conditions. The electron diffraction experiments of Thomson<sup>17</sup> showed that cuprous

(12) Preston and Bircumshaw, *Phil. Mag.*, **20**, 706 (1935).

(13) Hinshelwood, *Proc. Roy. Soc. (London)*, **A102**, 318 (1923).

(14) Constable, *ibid.*, **A115**, 570 (1927).

(15) Tedeschi, *Gazz. chim. Ital.*, **66**, 57 (1936).

(16) Van Cleave and Rideal, *Trans. Faraday Soc.*, **33**, 635 (1937).

(17) Thomson, *Proc. Roy. Soc. (London)*, **A128**, 654 (1930).

oxide was formed when polished copper blocks were heated gently in an electric furnace or exposed to air at ordinary temperatures, but an oxide of unknown structure was obtained by heating the blocks on red hot brass until they were tinted and allowed to cool in air. By electron diffraction studies and chemical tests Murison<sup>18</sup> showed this oxide of unknown structure to be a mixture of cuprous and cupric oxides. When the specimens were heated in air from 300 to 500° the cuprous oxide and the cuprous-cupric oxide patterns were equally probable. If air or oxygen were blown through the furnace tube while the specimen was being heated, the cuprous-cupric oxide pattern invariably was obtained. A cupric oxide pattern was never obtained from the surface films; it was obtained only after heating cuprous oxide powder at temperatures over 600°.

The electrical method has made it possible to measure the respective amounts of the oxides formed on copper under different conditions.<sup>19</sup> The results obtained show that: (1) the oxide films responsible for the early interference colors—and also the still thinner, invisible films—are sometimes entirely and often largely cuprous oxide; (2) sometimes a considerable amount of cupric oxide also is formed on heated copper and its amount increases with film thickness. When copper is heated to tints beyond the middle of the second order, under strongly oxidizing condi-

(18) Murison, *Phil. Mag.*, **17**, 96 (1934).

(19) The cuprous oxide reduces at a lower potential value than cupric oxide (Fig. 3).

tions, cupric oxide appears as a separate sooty layer outside the color film, obscuring the later colors.

A film of a given color may contain either no cupric or a considerable amount of this oxide. It thus appears that the cuprous-cupric oxide layer contains either an intimate mixture of the two oxides or even a solid solution possibly with the greater concentration of the cupric oxide toward the outer surface and of the cuprous oxide toward the metal base. Under such conditions light is still reflected mainly from the outer and inner surfaces of the cuprous-cupric oxide film, and normal interference effects are observed until a separate layer of cupric oxide is formed over it.

The author gladly acknowledges his indebtedness to Dr. U. R. Evans for much advice and information, and most valuable suggestions.

#### Summary

The thicknesses of oxide films produced on heated copper have been estimated by measuring the number of millicoulombs needed for their cathodic reduction. The relations between film thickness and time of heating indicate that the parabolic law  $y^2 = kt + A$  is only valid for short periods and that  $A$  is not zero for abraded surfaces. The color film on tinted copper may contain cupric as well as cuprous oxide—apparently in intimate admixture—but under strongly oxidizing conditions, a separate sooty film (presumably cupric oxide) obscures the later colors.

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## The Electron Diffraction Investigation of Nitrosyl Chloride and Nitrosyl Bromide

BY J. A. A. KETELAAR AND K. J. PALMER

An investigation of the molecular structure of nitrosyl chloride and bromide seemed to be of interest especially with regard to the conclusions which Klinkenberg<sup>1</sup> has drawn from the determination of the crystal structures of some complex compounds formed by nitrosyl chloride and nitrosyl fluoride. He found that the nitrosyl group in many compounds is present in the state of the univalent ON<sup>+</sup> ion. In this respect there may be specially mentioned the case of the compound 2ONCl·SnCl<sub>4</sub>, which is isomorphous with

(NH<sub>4</sub>)<sub>2</sub>SnCl<sub>6</sub> and so really has the constitution (ON)<sub>2</sub>SnCl<sub>6</sub>.<sup>2</sup> In the same way he found the compounds (ON)ClO<sub>4</sub> and (ON)BF<sub>4</sub> to be isomorphous with the corresponding ammonium compounds.

Electron diffraction photographs were prepared in the usual way<sup>3</sup> with a film distance of about 11 cm., the electron wave length being 0.0613 Å. Some ten to fifteen photographs were taken of each compound and several of the best were inter-

(1) L. J. Klinkenberg, *Rec. trav. chim.*, **56**, 749 (1937).

(2) In course of publication.

(3) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).