CCCI.—*The Formation of Protective Oxide Films on Copper and Brass by Exposure to Air at Various Temperatures.*

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IN the course of an investigation dealing *inter alia* with the tarnishing of copper, it was observed by the present author in 1923 that a simple heat-treatment (even as short as one hour) of the freshly-cleaned metal at 97° produced a considerable degree of immunity from tarnishing on subsequent exposure to ordinary room conditions. Thus, whereas unheated specimens passed through a characteristic progression of interference colours, specimens so heated underwent no change of colour, and even after prolonged exposure suffered only a slight general darkening. It was then concluded that the protection was due to the formation of a thin film of oxide. Experiments have since been conducted to obtain information respecting films produced at both lower and higher temperatures, and the inquiry has also been extended by the inclusion of 60 : 40 brass.

EXPERIMENTAL.

The specimens were cut from sheets of high-grade electrolytic copper and 60 : 40 brass respectively, each in the annealed condition. Their dimensions were 10·0 cm. by 5·0 cm., by 1·25 mm. thick, giving an available area for oxidation of one sq. dm., except that three holes ($\frac{1}{8}$ inch diam.) were drilled in each specimen for the purpose of horizontal suspension. Sufficient material was removed by abrasion to ensure uniformity, and the final surface was prepared by means of fine emery paper ("Hubert, No. 1 "). Each specimen was cleaned thoroughly by rubbing with pure cotton wool, and allowed to stand in an evacuated desiccator for weighing and heat treatment on the following day. The method of weighing was essentially the Gaussian method of exchange, with certain important refinements due to Conrady (*Proc. Roy. Soc.*, 1922, *A*, **101**, 211). The heat-treatment was conducted in an electric muffle, the specimen being freely suspended. In the main series of experiments, the time of heating was uniformly 70 minutes from the time of introducing the specimen, or approximately 1 hour at the desired temperature, which varied between 50° and 250° for copper, and between 200° and 425°, for brass. Each specimen was allowed to cool in a vacuum after heating and was re-weighed the following day.

Discussion of Results. (1) *Copper.*

Immediate Effects of Heat-treatment.—The weight-increments obtained are in Table I, together with the corresponding " temper colours." The upper temperature-limit employed (250°) was determined by the appearance of the dull grey scale indicating the end of the interference colour range. Within this range both " first-order " and " second-order " colours were observed. It should be borne in mind that these results are regulated not only by the temperature, but also by the time of heating.*

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* Within the interference colour range it is reasonable to expect a parabolic relationship between thickness of film and time of exposure at any given

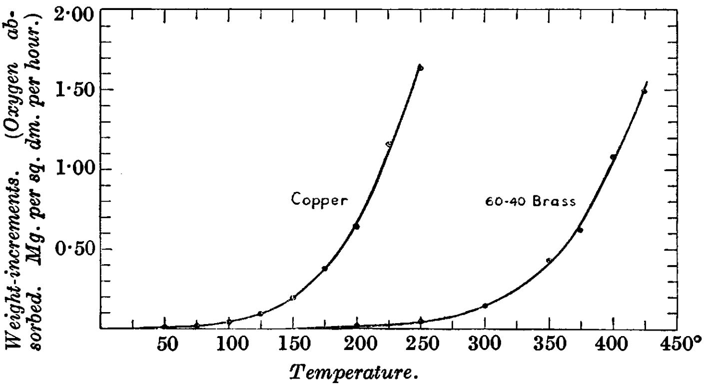
TABLE I.

Copper : Immediate effects of heat-treatment for one hour.

Temp. of heating.	Weight-increment (mg. per sq. dm.).	Change of colour.
50°	0·005	No change.
75	0·02	Merest shade darker.
100	0·04	Slightly darker but still essentially an ordinary copper colour.
125	0·095	Orange.
150	0·195	Bluish-purple.
175	0·38	Greenish-yellow.
200	0·64	Light red with tint of brown.
225	1·16	Bluish- or brownish-grey
250	1·63	Slate-grey.

In Fig. 1 weight-increments are plotted against temperature.

FIG. 1.



Weight-increments resulting from oxidation during heat-treatment.

It is of interest to compare the present results with previous quantitative work upon the oxidation of copper. So far as the author is aware, the only comparable gravimetric data are those due to Pilling and Bedworth (*J. Inst. Metals*, 1923, **29**, 529), who employed, however, considerably higher temperatures (400° to 1100°). These authors found the following empirical exponential relationship between temperature and rate of oxidation :

$$K = AT^n$$

where K = rate constant (square of weight-increment per unit area per unit time); T = absolute temperature; and A and n are constants.

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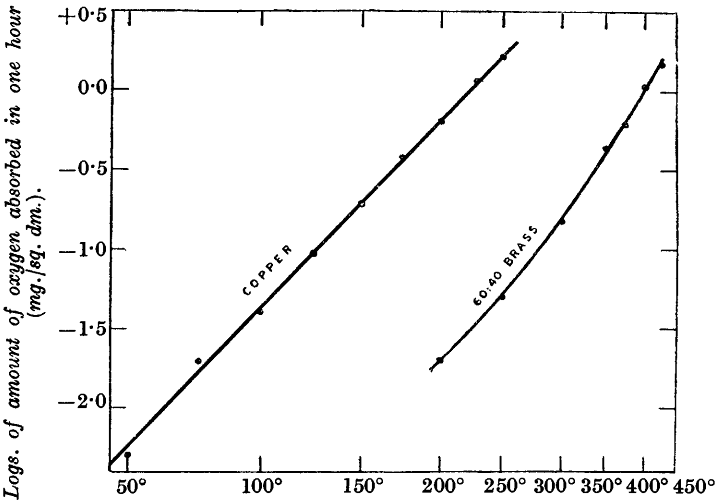
temperature. In previous work by the author (*Trans. Faraday Soc.*, 1924, **19**, 839) this relationship was found to hold for the tarnishing of copper at room temperature, and in the present experiments it has been confirmed by a series of weighings with specimens heated at 150°.

Oxide films within the interference colour range have been studied by Tammann and Köster (*Z. anorg. Chem.*, 1922, **123**, 196), who calculated from optical principles the thickness of the films giving rise to the observed colours. Their figures, however, have been criticised by Evans (*Proc. Roy. Soc.*, 1925, *A*, **107**, 234) and by Dunn (*ibid.*, 1926, *A*, **111**, 211, 217) as being based upon faulty premises. The latter author, moreover, gives a mathematical analysis of the effect of temperature upon rate of oxidation, based on the quantum theory, and deduces the equation

$$d \log W/dT = - Q/RT^2$$

which, it will be noted, is identical in form with the van 't Hoff isochore. Here W is a *linear* function of weight-increment (compare K in previous equation), T is absolute temperature as before, and Q and R are constants. Dunn shows that this expression is in good agreement with Pilling and Bedworth's results for the high-temperature oxidation of copper, and also with his own results for certain of the zinc-copper alloys at similar temperatures.

Fig. 2.



Reciprocals of absolute temperature. (Figures represent degrees C.)
Influence of temperature on rate of direct oxidation.

The present results for the low-temperature oxidation of copper are approximately in agreement with Pilling and Bedworth's equation, *i.e.*, there is but little deviation from the straight line when $\log K$ is plotted against $\log T$. With Dunn's equation, however, the agreement appears to be perfect, as shown by the straight line in Fig. 2, where logarithms of weight-increment are plotted against the reciprocals of absolute temperature.

It is evident that this curve may be employed with a reasonable degree of confidence for extrapolation to atmospheric temperatures. Clearly the value of K so obtained will represent the extent of direct attack by atmospheric oxygen, and any departure from this value as observed experimentally will point to the existence of some other contributory factor under the particular conditions concerned.

Subsequent Effects of Heat-treatment.—After heat-treatment the specimens were freely suspended (together with specimens unheated but otherwise identical) in a room the atmosphere of which had previously received thorough investigation with reference to its tarnishing capacity. In its effects this atmosphere may be taken as typical of winter-time town air containing the usual traces of sulphur compounds, but free from excessive local pollution. Throughout the tests the temperature varied between the limits of 17·0° and 22·2°, and was some 14° above the dew-point during the whole time.

The visible results were particularly striking. Thus after 20 days' exposure * the appearance of a typical series of specimens may be described as follows :

1. Unheated specimen.	Tarnished a reddish-purple colour.
2. Heated at 50° (similarly for 55°).	Reddish-purple (exactly as 1).
3. Heated at 75°.	No change since heat-treatment, *i.e., practically unaltered copper.*
4. Heated at 100°.	No change since heat-treatment, *i.e.,* slightly darker than 3, as result of heat-treatment, but otherwise unaltered.
5–10. Heated at 125—250°.	No change since heat-treatment, *i.e.,* colour as described in Table I.

The remarkable result thus emerges that an hour's heating in air at a temperature as low as 75°—a treatment practically without any visible effect upon the metal—is sufficient entirely to inhibit the development of interference colours on subsequent exposure to tarnishing conditions. The conclusion is inevitable that the protection is brought about by a film of oxide, either so thin as to be almost invisible (as by heating at 75°), or, while still transparent, sufficiently thick to refract light (as by heating at temperatures above 100°).

The very sudden break in behaviour between specimens heated at 55° and 75° is significant, and seems to suggest that a minimum thickness is essential if the film is to afford any protection. Interest attaches to the thickness of the films produced at these temperatures, and an estimate is therefore attempted from the available data.

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* After more prolonged exposure the *visual* comparison is not so striking, since unprotected specimens assume a neutral or steely tint, and, although after this stage second-order interference colours slowly develop, the deep purple of the first order is not repeated.

Assuming the first product of interaction of copper and oxygen to be cuprous oxide (*d* 6·0, assumed; Landolt-Börnstein gives 5·75—6·09) the following relationships obtain for the film produced at 55°.

Weight of oxygen absorbed (from Fig. 2) = 0·007 mg. per sq. dm.
Weight of equivalent Cu_2O = 0·063 mg. per sq. dm.
Volume „ „ „ = $1·05 \times 10^{-5}$ c.c. per sq. dm.
Hence, thickness of Cu_2O film = $1·05 \times 10^{-7}$ cm.
= 10·5 Ångström units.

It may possibly be significant that this figure is very nearly of the same order of magnitude as that usually accepted for the lattice dimensions of cuprous oxide, *i.e.*, 4·26 Å. (see Braggs' "*X*-Rays and Crystal Structure"). Moreover, on account of the emeried nature of the surface, the *actual* area exposed to oxidation must be considerably greater than—very possibly double—the nominal area of one square decimetre which has been assumed in the calculation. Clearly, if it had been possible to employ a value more nearly approaching that of the true area, the figure obtained for the thickness of the film would have approximated even more closely to that quoted for the lattice parameter. *The suggestion emerges, therefore, that the minimum thickness of film necessary for protection may be such that the unit lattice of the oxide is completed for the whole of the surface.*

TABLE II.

Copper : Weight-increments subsequent to heat-treatment.

Period of exposure, and increase in weight (mg. per sq. dm.).

Temp. of heating.	Series A.			Series B.	Series C.
	6 Days.	34 Days.	100 Days.	152 Days.	206 Days.
—	0·29	0·91	1·28	1·68	2·60
50°	0·21	0·76	1·12		
75	0·00	0·30	0·42		
100	0·00	0·17	0·31	0·40	0·43
125	0·00	0·11	0·28	0·39	
150	0·00	0·15	0·24	0·34	
175				0·32	
200	0·00	0·12	0·22	0·34	
225				0·32	
250	0·00	0·19	0·26	0·33	

Weight-increments of the specimens the visible changes of which are discussed above are in Table II (Series A) and are plotted in Fig. 3. Gravimetric data for other (less complete) series after longer exposure are also included in Table II. Although protected specimens slowly increase in weight, they do not appear to undergo any further colour-change. Actually the gravimetric method does not give a satisfactory response to visible changes, and the measurement of loss of reflectivity (*Trans. Faraday Soc.*, 1924, **19**, 851) is in this respect much to be preferred.

The results recorded above were obtained with specimens that had been polished with fine emery paper. Tests conducted upon a limited number of specimens brightly polished with mechanically driven " mops " yielded results which, although quite convincing gravimetrically (the figures comparing favourably with those given in Table II), were not so satisfactory from the point of view of the suppression of visible changes. In these tests, however, no other temperature than 100° was employed for the heat-treatment, and further work seems to be necessary in the case of copper polished in this way.

The Formation of Protective Oxide Films at the Ordinary Temperature.

Cleaned copper specimens exposed to room atmosphere during August–September (a period of optimum freedom from pollution) suffered no visible alteration beyond a slight general darkening. Increase in weight was determined periodically, and its relation to time shown to be parabolic. At the end of a month's exposure the mean weight-increment was 0·2 mg. per sq. dm.,* corresponding with the film produced by an hour's heating at 150°. That the agreement in physical properties was not complete is obvious from the absence of interference colours on the specimens exposed at normal temperatures. Nevertheless, it is of interest to note that once again protection was afforded, for, on subsequent exposure of such specimens to tarnishing conditions, no appreciable change was observed, whereas freshly-cleaned specimens passed through the usual progression of colours. The protection conferred by previous exposure to a relatively pure atmosphere is demonstrated by the following facts. Specimens cleaned in the ordinary way and exposed for a month to the tarnishing atmosphere increased in weight by 0·8 mg. per sq. dm. During the same time pre-exposed specimens increased by 0·06 mg. per sq. dm.; moreover, during their *whole period of exposure* they had increased by only 0·3 mg. per sq. dm.—without, of course, the accompaniment of any colour changes.

Discussion of Results. (2) 60 : 40 *Brass.*

Immediate Effects of Heat-treatment.—Weight-increments and colour-changes are recorded in Table III. As would be expected, the development of colours was not nearly so pronounced as in the case of copper. Thus, from a deepening of the original yellow

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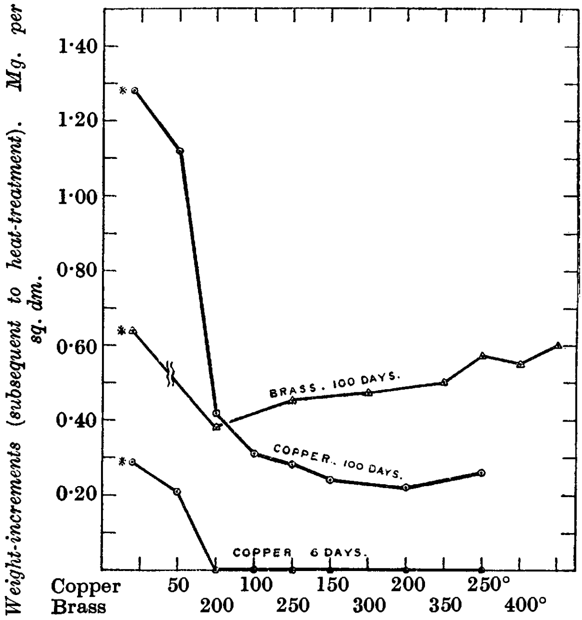
* This corresponds to a rate-constant considerably greater than that obtained by extrapolating to room temperature the straight line of Fig. 2, which demands for 1 month's exposure a weight-increment of only 0·03 mg. per sq. dm.

the metal passed directly to a neutral or " steely " stage, and attempts to obtain an intervening colour were without success. Between the neutral tint and the second-order yellow, however, an imperfect green appeared. A considerably higher temperature was required to produce a visible change than was the case with copper, *i.e.*, 200° as compared with 100°; for equivalent change of appearance the order of weight-increment was then similar to that which had obtained for copper. At the upper limit of temperature employed (425°), specks of white zinc oxide made their appearance over the surface.

FIG. 3.



Temperature of previous heat-treatment. (= not heated).*

Weight-increments resulting from tarnishing subsequent to heat-treatment.

TABLE III.

60 : 40 *Brass :* Immediate effects of heat-treatment for one hour.

Temp. of heating.	Weight-increment (mg. per sq. dm.).	Change of colour.
200°	0·02	Shade darker than unheated specimen. Pale yellow.
250	0·05	Shade darker than preceding specimen.
300	0·15	Considerably darker than preceding specimen. Deep yellow.
350	0·43	Brownish-yellow.
375	0·62	" Slaty " or " steely."
400	1·08	" Steely " with greenish tint.
425	1·49	Yellow.

In Fig. 1 weight-increments are plotted against temperature, and in Fig. 2 logarithms of weight-increments against reciprocals of absolute temperature, as suggested by Dunn (*vide supra*).

It will be seen that the agreement with Dunn's equation is not so complete as in the case of copper, since there is now a slight but definite deviation from the straight line. This is not surprising in view of the more complex nature of the material and the probability of reaction between the initially formed scale and the zinc of the underlying metal. Curiously enough, however, the figures yield a straight line when log K is plotted against log T, in agreement with Pilling and Bedworth's empirical equation. The circumstance is noted, although the explanation, if any, is not obvious.

Subsequent Effects of Heat-treatment.—Available evidence as to the protective effect of oxidation is not so conclusive as that which has been recorded for copper. This is particularly true of the gravimetric results, as will be seen by reference to Fig. 3, where subsequent weight-increments of brass specimens after 100 days' exposure are plotted against the temperature of heat-treatment; corresponding data for copper are included on the same diagram. Although the first heat-treated member of the series (200°) has suffered definitely less attack than the unheated "blank," the reduction is considerably less than that which obtained for copper heated at 75°. Moreover, the weight-increment progressively increases as the temperature of heat-treatment rises (in contradistinction to the behaviour of copper) until, with the specimen heated at 250°, the increase is very little less than that suffered by the unprotected "blank." Nevertheless, the *visible results* were much more satisfactory than these figures would suggest. Thus, after 28 days' exposure untreated specimens had darkened considerably, with development of light brown patches, whilst the specimen heated at 200° had apparently undergone no change. As a result, the treated specimen appeared much lighter than the untreated blank, although when first exposed it was a shade darker owing to the effects of the heat-treatment; the remainder of the specimens appeared to have undergone no further change. After 100 days' exposure untreated specimens had become yellowish-brown generally; there was marked contrast between these and the specimen heated at 200° which was still pale yellow, whilst the remaining specimens had altered but very little in appearance since the first exposure.

It will be seen therefore that although oxide films upon brass are not so efficacious as those upon copper, there is definite evidence that the protection extends to brass, the effects being confined mainly to the suppression of further colour changes.

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