

Studies on Copper Red Glaze.

By

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INTRODUCTION.

The beautiful red glaze coloration found among old Chinese porcelains has received world-wide appreciation and has long been a center of interest in art pottery. On account of the delicacy and difficulty of the art of producing it, it is said that the art has many times been lost.

L. A. Salvétat¹⁾ was the first Western ceramist who tried to reproduce it on a scientific basis. Th. Deck²⁾, A. Buenzuli³⁾, Ch. Lauth⁴⁾, Dutailly⁵⁾, H. Seger⁶⁾, Heubach⁷⁾, L. Franchet⁸⁾, etc. are the other investigators whose names are found in the literature. As to the conditions favourable for the development of the red color, the nature of the firing atmosphere has been a matter of much discussion. Salvétat preferred a reducing atmosphere, while Seger and others were of the opinion that alternate reducing and oxidising atmospheres are necessary. Recent workers seem to have come to pay attention not only to the nature of the atmosphere, but also to the firing conditions, as the most important factors which affect the coloration.

The authors tried to gain more knowledge of the subject through more scientific experiments with regard to the factors which have a decisive influence on the development of the copper red color.

EXPERIMENTAL PART.

DESCRIPTION OF THE APPARATUS.

An electric furnace of a simple type with silicon carbide resisters with an automatic temperature regulator of the potentiometer type was

used for the thermal treatments of high accuracy. Temperature was measured by means of a platinum-rhodioplatinum thermocouple, whose accuracy may be safely taken as $\pm 10^{\circ}\text{C}$.

INFLUENCE OF THE NATURE OF THE ATMOSPHERE UPON THE COLORATION.

The simple cases of the $\text{Na}_2\text{O}-\text{SiO}_2$ system given below were tentatively taken as the composition of the glaze, and the amount of copper as 2% of fritted glaze. The frits were heat treated in various atmospheres of pure gas, 1) hydrogen, 2) carbon monoxide, 3) carbon dioxide, 4) nitrogen and 5) oxygen, which are the essential constituents of the ordinary kiln atmosphere and considered to exert a decisive influence on the glaze coloration, the temperatures chosen being 600° , 700° , 800° , 900° and 1000° C. and the heating duration, 60 minutes in each case.

Glaze Composition

Na_2O . 1 SiO_2

Na_2O . 2 SiO_2

Na_2O . 3 SiO_2

Na_2O . 4 SiO_2

The result judged from the standpoint of the possibility of red color development was as follows:

- 1) Purely reducing gases such as hydrogen and carbon monoxide are unfavourable; the former turns the surface of the glaze a metallic copper color and the latter, black.
- 2) Oxygen turns it blue, as well known.
- 3) Carbon dioxide and nitrogen, in both dry as well as wet conditions, were found promising for the development of the red color when the glaze was treated at around 700° or 800°C . for 60 minutes.

SELECTION OF COLOR INTENSIFIERS.

In view of the fact that most of the Oriental porcelain glazes are of the type poor both in silica and alumina, but rich in lime, and also taking

Seeger's formula for the red glaze again into consideration, the authors prepared glazes of the following compositions, adding to each 1% of CuO in the form of the carbonate and also 1% of color intensifiers, such as arsenious oxide, barium oxide, ferric oxide, lead oxide, tin oxide and zinc oxide, which are found as popular intensifiers in the literature and the effectiveness of which are considered to be worth a trial.

Composition						
Series	Na ₂ O	K ₂ O	CaO	Al ₂ O ₃	SiO ₂	B ₂ O ₃
A	0.500	—	0.500	—	2.000	0.500
B	0.375	0.075	0.550	0.125	2.500	0.375
C	0.250	0.150	0.600	0.250	3.000	0.250
D	0.125	0.225	0.650	0.375	3.500	0.125
E	—	0.300	0.700	0.500	4.000	—

The glazes made into frits were heat-treated in atmospheres of nitrogen and carbon dioxide, at systematically selected temperatures for 60 minutes, and the results with respect to red color development studied.

Series A and B both showed no signs of producing red coloration. But with Series C, when lead, iron, tin and zinc oxide was added, beautiful ruby colors developed when the glazes were treated at around 700° and 800°C. Tin oxide was found to be the most effective intensifier for producing an intense red color. Glazes of the D and E Series are rather rich in silica and alumina; they showed signs of a red color, but generally of a brownish tinge, and so were considered to be doubtful as effective compositions. Further experiments showed that the tone of the red color produced by the addition of arsenious, barium, zinc or lead oxide was not so good as expected for the composition of the glaze C, so the effects of only two intensifiers ferric and tin oxides, were studied with respect to the amount of them necessary to be added, and also the proper reheating treatments for developing the best colors.

Glaze composition C
 Amount of coloring oxide . . . 1% of frit.

Glaze No.	Amount of intensifier in % of frit.	
CSn-1	SnO ₂	1
CSn-2	"	2
CSn-3	"	3
CSn-4	"	4
CSn-5	"	5
CFe-1	Fe ₂ O ₃	1
CFe-2	"	2
CFe-3	"	3
CFe-4	"	4
CFe-5	"	5

These were melted in an oil-fired laboratory kiln and made into frits, and then reheated in neutral atmospheres at systematically selected temperatures for 1 hour and the results were carefully observed. The best ruby color was obtained 1) by the addition of 2—4% of either tin or ferric oxide for 1% of cupric oxide (glaze numbers CSn-2, -3, -4 and CFe-2, -3, -4), 2) through reheating in neutral atmospheres of nitrogen or carbon dioxide gas, 3) at around 700°C., 4) for one hour, for glaze of this composition.

RELATION BETWEEN STATE OF COPPER AND COLOR

In order to avoid any uncertainty in the conditions under which the glaze was prepared, the glaze prepared by oil firing was melted this time in an electric furnace under exact temperature control at 1200°C; in a current of nitrogen and carefully fritted. The colorless frit developed a red coloration through reheating at 700° and 800°C. in an atmosphere of nitrogen simply. This phenomenon proves that the simple fact of reheating practically colorless copper-containing glaze in a neutral atmosphere itself is effective and sufficient for producing red coloration.

In order to get a better idea as to the state in which copper is effective in red glazes, the authors tested three cases, adding varying proportions of a reducing agent to copper: 1) a batch containing cane sugar

in the proportion of 18% of cupric oxide, which amount is calculated to reduce cupric oxide to metallic copper; 2) a batch containing 9% of the amount of the oxide, calculated to reduce cupric oxide to cuprous oxide; and lastly 3) a batch containing less than 9% of cane sugar. These three glazes containing varying amounts of carbon were carefully melted in an electric furnace in a neutral atmosphere and then made into frits from the molten state by water granulation. All of these before reheating invariably showed a slightly greenish color.

Through reheating at 700° C. for one hour, the first frit turned entirely grey without showing any sign of red coloration, the second, deep red and the third also turned red, the coloration, however, not being so good as that of the second.

The above experiments show that the coloration of a red copper glaze seems to be not due to the presence of either CuO or metallic copper, but seems to be favoured by the presence of Cu₂O or lower oxides of copper in the glaze.

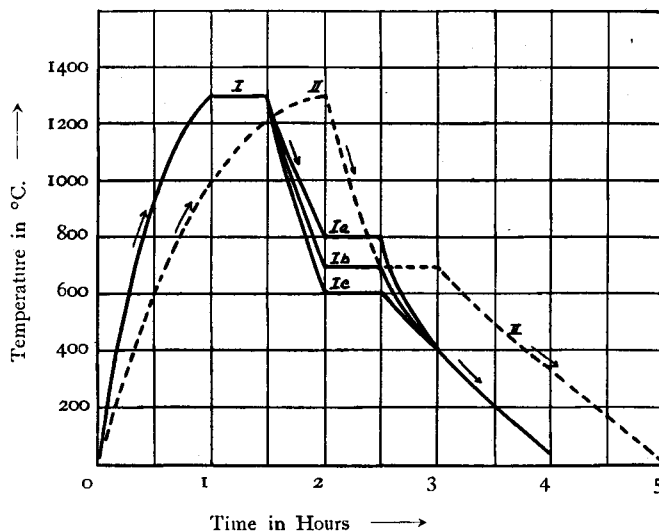
EFFECT OF REHEATING DURATION UPON COLORATION.

The frits which were found to develop excellent colors through proper temperature treatments in the foregoing experiments, were again tested for the color by systematically changing the duration of reheating from 1 to 8 hours, the temperature chosen being 700°C. When the duration of reheating remained within 3 hours, frits containing from 2% to 4% of SnO₂, showed beautiful red colors, but those reheated longer than 3 hours lost transparency and turned somewhat brownish. Through these experiments we learn 1) that the duration of reheating has an influence on the coloration of red copper glazes, and 2) that the duration of reheating depends greatly upon the percentage of tin oxide added.

APPLICATION OF THE COLOR DEVELOPING PRINCIPLES TO GLAZED WARES.

In order to ascertain if the foregoing observations about frits are

Fig. 1.



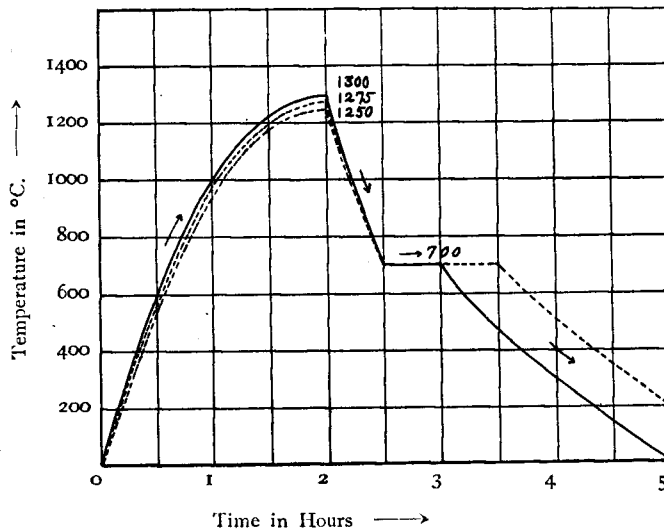
true also in the case of the glazed wares, frits CSn-1, -2, -3, -4 and -5 were wet ground, the slurries coated on a biscuited Seger porcelain body, composed of Katoh kaolin 25, felspar 30 and flint 45, and heat-treated in a porcelain pipe electrically heated from the outside by glowing silicon-carbide resistors, carbon dioxide gas being passed all the time. The thermal treatment was as shown by curve I in Fig. 1. The temperature was raised at a quick rate up to 1300°C. when the glaze was supposed to have assumed homogeneous and complete fusion, and that temperature was maintained for 30 minutes; then it was made to fall to 800° (Ia) 700° (Ib) and 600° (Ic), which temperatures were maintained for 30 minutes and then allowed to fall naturally to the room temperature. The specimens showed a red color at a certain depth in the glaze, but on and near the surface layer of the glaze, no sign of red color was found, which may be supposed to be due to absence of copper caused by volatilisation during the high temperature treatment. Only specimen CSn-4, heat-treated as shown in curve I-Ib showed fair ruby coloration. Next, in order to avoid possible volatilisation of copper, the heating was regulated as in curve II, i. e. as soon as 1300°C. was reached, without being kept at that tem-

perature any longer the glaze was quickly cooled down until it reached 700°C. and kept at this temperature for 30 minutes and then cooled naturally. The result showed much improvement; a fine red color was observed even on and near the surface of the glaze and found to be almost perfect from the standpoint of the red coloration and the whole specimens were blood red showing no green spots. In the course of the treatment, as soon as the temperature was lowered to 700°C. a sample was quickly withdrawn from the furnace, and upon investigation it was found that the color was green, with only a few tiny red spots.

TIME TEMPERATURE RELATION FOR PROPER HEAT TREATMENT.

The object of heating frits to temperatures above 1000°C. is to ensure complete fusion of the glaze on the body. In order to elucidate the effect of this heating upon the condition of the glaze, the following three cases were tried: a) 0°—1300°—700°—0°C. b) 0°—1275°—700°—0°C. c) 0°—1250°—700°—0°C. In each case, the temperature of 700°C. was maintained for 30 minutes. Case a) gave the best result from the

Fig. 2.



standpoint of color tone, in cases b) and c) the color was dark, probably due to incomplete fusion of tin oxide.

When the frit was treated at 700°C. for 1 hour instead of 30 minutes, it lacked transparency and showed an opaque red tone, which may be supposed to be due to devitrification of the frit. Hence too long heating around the color developing temperature range is considered unfavourable. (Fig. 2.)

CONTENT OF COLOR INTENSIFIER FOR BRIGHTER RED COLOR.

In the foregoing experiments the amount of copper oxide was always taken as 1% of the frit and the resulting red color was of a deep dark tinge. So further experiments were made to find the content of copper necessary to produce a brighter red, by reducing the percentage of CuO to 0.1—0.5% of the frit and keeping SnO₂ always as 3%. Frits were thus prepared as follows :

Glaze Composition C.		
Frit No.	SnO ₂ %	CuO %
X-1	3	0.1
X-2	„	0.2
X-3	„	0.3
X-4	„	0.4
X-5	„	0.5

The best result was obtained in the case of X-3, i. e. the frit containing 3% SnO₂ and 0.3% CuO.

The most suitable content of tin oxide was then sought for and the result was found most favourable when the content of SnO₂ was equal to or less than 3 times the percentage of CuO. For the base composition C, the following contents of oxides of copper and tin answered well.

Frit No.	SnO ₂ %	CuO %
Y-1	1.5	0.5
Y-2	1.0	0.3

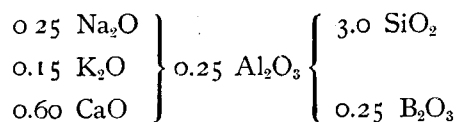
EFFECT OF STEAM UPON COLOR.

A strong current of aqueous vapour was passed over the test pieces, and no color was found. This may be supposed to be due to the absence of copper through its being volatilised and carried off with the steam. Wet nitrogen gas, however, saturated with steam at about 50°C. gave an excellent fresh red colour. The effect of water vapour upon coloration is thus significant.

SUMMARY.

In the foregoing experiments with regard to the red copper glaze, the influence of the nature of the firing atmosphere and the time temperature relation upon good coloration was chiefly studied in connection with copper-containing frits whose composition was rather narrowly limited as to the variety of constituents and their proportions. The important facts ascertained through this scientific research may be summarised as follows:—

1) **Base composition.** Glazes rich in alkalies, and having a comparatively low melting temperature are unsuitable for producing a copper ruby color. On the whole, borosilicate glazes rich in lime and containing 0.25 mols of alumina, and 3.0 mols of silica are considered suitable for the base composition; thus,



2) **Coloring agent.** Within the limits of the experiments, for the glaze composition above cited, 0.3—0.5 % of CuO with an amount of a reducing agent which will at least convert CuO into Cu₂O, produces an excellent red color. The copper content seems to be intimately connected with the percentage of intensifier used if fine results are to be obtained.

3) **Intensifiers.** From careful experiments it can be concluded that of various color intensifiers ferric and tin oxides give the best results. These two intensifiers, however, seem to give characteristic tones different from each other; iron oxide gives a darker shade, while tin oxide gives a fresh

brighter tone. Any agreeable red colour may be obtained at will by using both of these together and by changing the proportion of the two. It is considered that a close relation exists between the content of copper and of the intensifier. So far as the experimental results are concerned, the content of tin oxide should be limited to less than 3 times that of cupric oxide in the case of the glaze above mentioned, otherwise turbidity appears.

4) **Firing atmosphere.** The nature of the atmosphere should receive close attention. Neither an oxidising nor a reducing atmosphere gives favourable results. Carbon dioxide, nitrogen and steam, which are considered to be neutral at high temperatures, are proved experimentally to be most suitable and a reducing atmosphere is decidedly unsuitable for developing a red color. In ordinary kiln firing, it is perhaps desirable to have complete combustion of fuel with just the theoretical amount of air; if this is done the hot combustion products containing neither excess oxygen nor reducible constituents, especially when steam is mixed to a certain slight extent therein give fine results. Seger's opinion as regard the best atmosphere, that alternate reducing and oxidising firing is desirable, may be endorsed; this may produce actually the same effect as the purely neutral atmosphere experimented with by the authors.

5) **Color developing temperatures.** The cooling rate has also a most important effect upon coloration, as shown by repeated experiments. The analogy of gold ruby coloration may be applicable in this case. There must be the optimum temperature for each glaze composition, and the temperature should be properly maintained in order to give a good color.

6) **Proper firing schedule.** With glaze of the proper composition, in a neutral atmosphere, a) the firing should be so carried on that the batch composition may fuse to a homogeneous glaze, the temperature being raised to the point where this is accomplished. b) the glaze should next be cooled down to its proper color developing temperature, and c) should be kept at that temperature for a certain time until the color develops to the desired degree, and d) finally it should be naturally cooled.

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