Some Colouring Agents in Glasses and Glazes.¹

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THE colouring agents of glasses and glazes are very many; moreover, several of these agents can impart colour to glasses or glazes in what may be described as different ways. An explanation which would include all our present knowledge of the behaviour of any one of them would occupy a long time. I have chosen two colouring materials, copper and iron, and propose to deal with some of the effects which can be produced by them and their compounds. I should like also to make a few remarks on certain effects which can be produced by radiations such as ultra-violet light, X-rays, and gamma-rays from radioactive materials.

I have chosen copper and iron because, in their various modes of action as colouring agents in glasses and glazes, they illustrate fairly completely the manner in which most of the materials used in this connexion behave. For present purposes I will not draw any definite distinction between glasses and glazes, but will use the terms somewhat indiscriminately.

Copper can be introduced into a glass or glaze so as to produce reds, browns, yellows, greens, blues, purples, and black. In some instances the colours can be well seen by transmitted light; in others the material is too opaque to show the colour except by reflected light. These various effects are produced by compounds of copper or by metallic copper itself. Of the compounds of copper, attention will be especially devoted to the two oxides of copper, cuprous oxide and cupric oxide. Cuprous oxide is the colouring agent in the brilliant scarlet Egyptian glass, specimens of which appear to be correctly attributed to at least as far back as the XVIII. Dynasty and up to Roman Egyptian times. It would appear from the absence of any specimens attributable to more recent times that the knowledge of how to produce this glass successfully was then lost.

Microscopic examination of a specimen of the scarlet Egyptian glass given to me some years ago by Prof. J. N. Collie, and of other specimens given to me more recently by Mr. Horace Beck, showed that the colour was due to small crystals of cuprous oxide. Chemical examination of the glass itself revealed that it was an ordinary lead glass containing about 30 per cent. of lead oxide, and the quantity of cuprous oxide varied from about 8 per cent. to 10 per cent. Based on this information the glass was successfully made after a few trials. During those trials yellow crystals were often observed in parts of the glass, and recently Mr. Horace Beck provided me with an orange yellow bead found at Faversham, in Kent, the colouring matter of which was again identified as cuprous oxide, but mainly in the yellow form. The red form of cuprous oxide is the better-known form, and is produced when copper is heated in a

limited supply of air; it can generally be well seen on the underside of the black scale detached from a piece of metallic copper which has been heated for a short time to a high temperature in air and then kept at a lower temperature for some time.

A ready method of producing the red oxide is to add a solution of copper sulphate to a solution of glucose and then to add caustic potash to the mixture. On heating the clear blue solution so obtained, reduction of cupric oxide by glucose occurs, with consequent precipitation of red cuprous oxide. At the first stage of heating it is generally possible to notice the formation of a yellow precipitate mingled with the red; these colours can be better shown by using Fehling's solution, which is made up from copper sulphate, Rochelle salt, and caustic potash, and is a clear blue solution. If a small quantity of the solution of glucose be poured into a large quantity of boiling Fehling solution the red oxide is formed. If a small quantity of Fehling solution be added to a large volume of boiling solution of glucose, the yellow form is produced, and is permanent in the sense that it may become rather more orange in tint but does not reach the red stage.

Without going into the doubtful composition of this yellow form, in respect of the extent to which it may be considered hydrated, it may be remarked that if it is heated out of contact with air the yellow form persists, and is apparently completely freed from water at a temperature of about 350° C. The difficulty of making any statement about the temperature at which the yellow form can exist in glass will be appreciated if a short description is given of the behaviour of cuprous oxide glass during its preparation.

If the proportion of cuprous oxide introduced into the glass be about 8 per cent., the whole of it dissolves in the glass at the temperature of 1000° C. at which the glass is made. If the glass be quickly chilled from this temperature, no colour, except the almost unavoidable green colour due to oxidation of part of the copper, will be seen; the glass is a nearly colourless transparent one. On re-heating this glass it is possible to produce, according to the temperature to which the glass is raised and the length of time during which it is heated, comparatively large crystals or aggregations of crystals of red cuprous oxide, smaller crystals of the same form, or particles so small as not to be recognised as crystals under the microscope. Along with these are frequently obtained definite crystals of the yellow form, clouds of yellow particles, and, if the re-heating be gentle, the particles of yellow cuprous oxide are so small as to be unrevealable by the microscope, and what is obtained is a clear yellow transparent glass. Here, then, from two forms of one and the same oxide of copper, we have a range of colours associated with the proportions in which

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the two forms are mixed in the glass and with the size of their particles. What is the inner nature of the difference between the red and yellow forms which may account for their difference in colour is yet to be made out.

Much ancient Egyptian glass does not contain lead, but is mainly of the composition of an ordinary window glass—that is to say, its principal ingredients are silica, lime, soda, with varying quantities of potash, magnesia, and alumina. It has not been found possible to make the brilliant scarlet cuprous oxide glass satisfactorily in a glass of this composition. The temperature required for the proper making of such a glass is too high for the persistence of the scarlet colour, and the resulting glass is of a brown or brownish-red colour. A scarlet coloured glass of the common soda-lime type could be made if the composition of the glass were so chosen that its fusing point was as low as that of the lead glass which the Egyptians used. If the Egyptians ever did make such a glass, it would have been so unstable that it could scarcely be supposed any specimens of it would have persisted to the present day.

Ancient brown glass of the soda-lime type just referred to appears to have been very widely distributed. Recently I have been given some beads of this glass which, I am informed, work up through the sand on the coast of Zanzibar. Whatever attribution is given to the various specimens, they all seem to be very similar in composition and to depend for their colour upon the presence in the glass of minute particles of metallic copper. Whether the production of this brown or brownish-red glass preceded that of the scarlet glass is a question which cannot be dealt with here. It is worth while, however, to refer to one property of cuprous oxide. This oxide does not form salts with acids except with the halogen acids: hydrofluoric, hydrochloric, hydrobromic, and hydriodic. With the oxygen-containing acids, if it re-acts with them, metallic copper is produced along with a cupric salt of the acid. With sulphuric acid this change takes place at the ordinary temperature; with a weaker acid, like acetic acid, the action is very slow unless the temperature is raised.

Taking these reactions as analogous to what may occur in a glass, and considering silica as a weak acid, it will be understood that if the temperature of a glass, either the lead glass or the soda-lime glass, be raised high enough, the result will be the production of metallic copper dispersed through a greenish cupric oxide glass. If the percentage of cuprous oxide used were high, about that used for the scarlet glass, there would be sufficient green to make the red of copper look, by reflected light, distinctly brown. With less copper present the colour would get nearer to a red, and it will be easily understood how, by using progressively less and less copper it would be possible to arrive at a glass resembling the well-known red glass which owes its colour to particles of copper so finely comminuted as to render the glass quite transparent to the eye. The transparent red copper glass and the brilliant *sang-de-bœuf*

Chinese glazes are made under conditions which tend to reduce any cupric oxide which may be formed, so that the resulting glass is not rendered dingy by a green tint, due to dissolved cupric oxide, marring the brilliant red due to the dispersed metallic copper. It should be added that for this brilliant glass so little copper is used (it is in the neighbourhood of 0.5 per cent.) that any colour from cupric oxide which would arise from such a change as is mentioned above under the action of silica would be so pale as to have practically no effect on the brilliance of the red due to the dispersed copper.

Here, then, we have again considerable variations in the appearance of the glass dependent upon the size of the particles of the colouring agent dispersed through it, and this is made evident when thin pieces from different portions of glaze from one and the same Chinese *sang-de-bœuf* vase are examined by transmitted light. Under the microscope, for example, some pieces are distinctly red, others are purple, others again are blue, and others look like neutral coloured glass. Closer study shows that in the most brilliant red portions no particles can be seen by the microscope. In some of the less transparent red pieces, particles are revealed either by a cloudiness or as discrete particles. In the purples these particles are larger, and in the blues they are still more marked, while in the neutral colours the particles are generally seen less closely packed but distinctly larger in size.

The colours produced by cupric oxide in glasses and glazes need not be dealt with in detail, as there is much common knowledge about these. One or two points not in common knowledge may, however, be emphasised. In a glass of the same composition, cupric oxide may give a very marked blue colour if the glass is made at a comparatively low temperature (1000° C. to 1100° C.); whereas with the same concentration of copper and the same glass made at a higher temperature, about 1300° C., for example, there is a very marked green shade in the blue. It is worth pointing out that the blue low-temperature glass is green while hot.

It would lead us into too much detail to do more than direct attention to the possible analogies between the action of water in solutions of cupric salts and the action of the oxides of the alkali metals in glasses coloured by cupric oxide. The change from blue to green just mentioned in the case of the low-temperature cupric oxide glass calls to mind the fact that a green solution of cupric chloride, which becomes blue when sufficient water has been added, becomes green again on heating it. A study of the changes of colour which can be produced in aqueous solutions and salts, and of the methods of modifying these colours, has been of great assistance to me in shortening the experimental work necessary to arrive at the compositions of a number of glasses in which it was desired to produce certain colours either with copper or other colouring agents.

As an example of the change of colour effected by adding water to a salt, copper sulphate may be mentioned. This salt, in its anhydrous condition

or with only one molecule of water, is colourless. Crystals containing five molecules of water are the ordinary blue copper sulphate crystals, and the solution of these in water is blue. If we take boric anhydride and an oxide of an alkali metal as analogous to sulphuric acid and water, a very similar story can be told. A small quantity of cupric oxide does not dissolve in fused boric anhydride, but forms a white borate which is dispersed through the fused mass. The addition of an alkali will bring about solution and give a clear blue transparent glassy mass. The most striking example is to take boric anhydride and the alkali lithium oxide in, say, three different proportions, such as one molecule of lithium oxide to one, four, and ten of boric anhydride. With 0.5 per cent. of cupric oxide the first is a fine deep blue; the second is a paler blue; the third is still paler; and if the proportion of alkali oxide be lowered until there is only just sufficient to bring about complete solution of the cupric oxide in the mass, there is but little colour to be seen at all.

With many glasses made at a high temperature, cupric oxide gives an olive-green colour. Without going so far as to say that the dusky shade in the green is invariably due to some reduction of the cupric oxide to the lower oxide of copper, there is evidence of this in certain instances which I have come across. To take one: in making trials for a glass which was intended to be of a green colour with only a slight tinge of olive in it, and of a sufficiently light shade to enable the light of a candle flame to be seen through a 1-inch thickness of the glass, the furnace conditions happened to change on one occasion so that the glass was exposed to a reducing atmosphere. The resulting glass was so black that a bright June sun was invisible through a piece of the glass one-fortieth of an inch thick. Such a state of affairs might be considered to come about by the glass being a mixture of red copper glass with a green cupric oxide glass, through which mixture but little light could be transmitted. Now red glass owing its colour to finely dispersed metallic copper is rendered colourless by fusing it and quickly chilling it. The black glass referred to might therefore be expected to become green if fused and quickly chilled, but it did not change from its intense black colour. This just gives a hint of the possibility of a cuproso-cupric compound being present in the glass analogous to, though not so definite as, ferroso-ferric oxide, the well-known black iron scale.

Again, an analogy with solutions helps a little. If to a colourless solution of cuprous chloride in hydrochloric acid there be added a transparent green solution of cupric chloride, the mixture turns black. Although dusky greens and the black glass just referred to might be accounted for by varying mixtures of red and green glass, the colour of this solution could scarcely be accounted for in the same way. Moreover, in experimenting with red copper glasses, and studying the way in which the red colour can be prevented from developing by sudden chilling and can be produced by subsequent

heating, I have repeatedly noticed that, instead of obtaining a clear colourless glass in bulbs made from the red glass and quickly chilled, the bulb has been sometimes of a dusky hue and sometimes of a definite neutral tint. As no other colouring agent but copper was present in these glasses, I am inclined to attribute the neutral shade to a cuproso-cupric compound which is stable in the glass and is analogous to the compound formed when the cuprous and cupric chloride solutions are mixed, rather than to a physical mixture of red and green glasses.

I must not deal further with cupric oxide glasses except to mention that, unlike cuprous oxide glasses, copper glasses and many other coloured glasses, such as gold glasses, selenium glasses, cadmium sulphide glasses, and opal glasses, cupric oxide glasses cannot be rendered colourless by sudden chilling, nor, indeed, can the tint of these glasses be modified to any noticeable extent in this way. An attempt to explain this difference, which seems to divide colouring agents generally into two classes, would involve a very lengthy account of the various phenomena which have been observed, and would, moreover, be to a considerable extent little more than a re-statement of facts which would involve differentiation between the meanings of such terms as 'solution,' 'chemical combination,' and 'dispersion,' and would lead to much argument. I must content myself with this short and incomplete account of the modes of behaviour of copper and its oxides in glasses and glazes.

Passing on now to iron, there are colours produced by ferric oxide, ferroso-ferric oxide and ferrous oxide, but I do not know of any glass or any material which could be called glassy which owes its colour to metallic iron in a fine state of dispersion. Starting in the first place with ferrous oxide, which gives the well-known green colour to glass of the nature of window glass, I need only point out that this colour is considerably modified by the composition of the glass, and without going into a number of details I will mention the way in which this tint is modified by the presence in the glass of zinc oxide or magnesium oxide. The former intensifies the colour produced by any given amount of ferrous oxide and changes the usual green into almost a blue. A similar change occurs with magnesium oxide, but the intensification of the colour is less marked. Among the alkalis, lithium oxide also tends to give a bluish tint to glasses containing ferrous iron. A notable example of this is seen in an early Chinese glaze which, through the kindness of Mr. G. Eumorfopoulos, I had the opportunity of examining. The thinner parts of this glaze are practically colourless, but the thicker parts have a beautiful blue tint. An examination of the glaze showed that it was for such glazes unusually rich both in lithium oxide and in magnesium, and the colouring material was identified as iron. If the Chinese workers had substituted zinc oxide for the magnesium oxide in their glaze mixture, the colour would have been very much more marked.

(To be continued.)