The Platinum Metals in Glass

COLORATION AND OTHER EFFECTS OF METALS IN SOLUTION OR SUSPENSION

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Platinum metals have long been used in the glass industry for crucibles and liners because of their high melting points and their chemical inertness to most molten glasses. Contamination of glass by platinum metals has not been reported except in one or two instances where the glasses had a high content of lead or barium. It is well known that heavy lead glasses are more susceptible to colouring by traces of impurity than other types of glass, and Hampton (1) and his co-workers found that glass of this type, even when made from very pure materials, became coloured when heated in platinum. He was able to produce a colourless specimen only by melting in a thoria crucible. Some optical glass manufacturers have also found a reddish colour in glass having a high lead or barium content after contact with a rhodium-platinum crucible; this coloration was probably due to traces of rhodium in the glass.

Another instance of glass becoming coloured by platinum was reported in 1947 when Rindone, Marboe and Weyl (2) were working on the electrolytic oxidation and reduction of glasses containing various metal ions. Platinum electrodes were used and it was found that platinum ions from the anode tended to pass into solution in the glass. In borate glass the platinum ions were unstable and either reverted to metal, which was precipitated in the glass because of the low solubility of platinum, or, under certain conditions of temperature and viscosity, gave pink colloidal platinum producing a glass analogous to the familiar gold-ruby. Phosphate glasses were known to have a stabilising effect on silver ions in glass solution and they exhibited the same behaviour towards platinum, giving amber-coloured glass, the colour being similar to that of a solution of platinic chloride.

Structure of the Dispersed Metal

During this period work was also being carried out in India on the solution of noble metals in glass. It should be emphasised that in this work the platinum was deliberately introduced in a finely divided state into the glass melt and was not derived from the walls of the container, as it was in the studies of Hampton and of Rindone and his co-workers. The purpose of the investigation was to examine the state of the metal in solution and its effect, if any, on the physical properties of the glass.

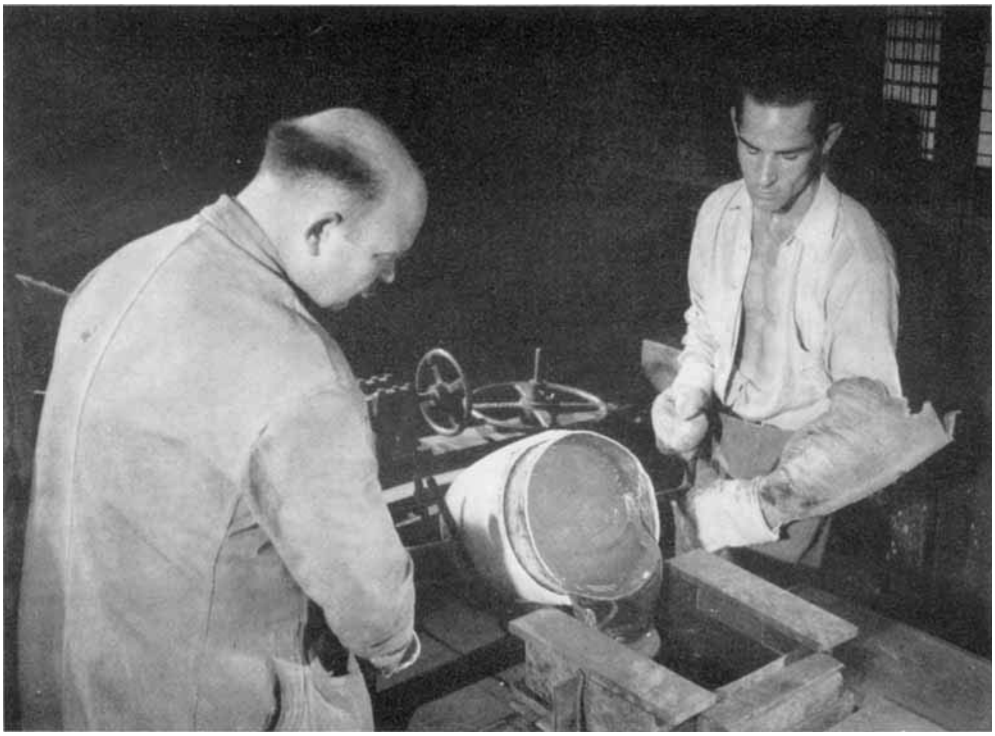
Papers were published by Majumda (3) in 1948 on the magnetic susceptibilities of borax glasses containing gold and platinum, and by Majumda and Mukherji (4) in 1953 on the molar refraction of platinum dispersed in Lindemann glass. X-ray studies were made by Majumda and Banerjee (5) in 1946 and by Banerjee (6) in 1953. The former was a short paper dealing with noble metals dispersed in borax and boric oxide glasses, and included X-ray photographs containing lines due to the metal as well as the normal diffuse bands from the glass. Comparison of these lines with X-ray photographs of the pure metal indicated that the metals have the same lattice spacing when dissolved in the glass as they have in the pure state.

This work was extended in the second paper (6) to a more complete study of colloidal coloured glasses containing gold and platinum. Borate glasses containing these metals were examined, the samples all being prepared under identical conditions, and it was found that the vitreous limit occurred at a metal concentration of 2 to 3 per cent, depending on the type of glass. The platinum dispersed in the glass gave a grey colour which could be intensified by the addition of an oxide of lead, zinc or antimony —which also served to increase the vitreous limit of the glass—although alkali halides, even in very small amounts, suppressed the development of any colour.

The X-ray powder photographs obtained were similar to those described in the previous paper (5). As would be expected, the intensity of the lines caused by the platinum increased as the concentration of platinum in the glass increased, but there was a corresponding decrease in the intensity and sharpness of the bands due to the glass. This was thought to result from the superior absorptive power of the dispersoid, such that at concentrations as low as 2 per cent it could override the low absorption of the glass base. The calculation of lattice constant of the dispersed metal confirmed that it was the same as in the massive state.

The Mechanism of Colour Formation

Glasses coloured by colloidal platinum are examples of " ruby glass ", a term applied to those coloured red by colloidal gold and copper but now extended to cover glasses containing colloidal platinum and silver, even though the colour is different. An understanding of the mechanism of colour formation in these glasses has been a long-standing problem and Banerjee (7), in a paper published in 1954, approached it by a study



Pouring molten optical glass from a 12-litre platinum crucible at the Birmingham works of Chance Brothers Ltd.

of the state of the dispersoid. A colourless glass is usually obtained first, and the colour is developed by heat treatment; it is the nature of the change occurring in this heat treatment that Banerjee attempted to elucidate.

Chemical tests on the colourless specimens showed platinum to be present in the elemental state. The effect of heat treatment is to cause coloration and reference is made to Zsigmondy's theory (8) that this is controlled by the relative rates of two distinct processes. These processes, both of which are temperature dependent, are the formation of colourless, thermodynamically stable nuclei of metal atoms followed by crystallisation of the dispersed phase on these nuclei forming particles large enough to give colour to the glass, which in this instance was grey.

The size of the metal particles in the coloured glasses was determined from the width of the metal lines in X-ray photographs. As the concentration of platinum in the metal increased, the size of the particles increased from about 60 to 243 Å, all in the colloid range. In transparent coloured glass the metal particles are only partly colloidal, but after prolonged heat treatment the whole of the dispersed phase is precipitated giving an opaque, strongly coloured glass.

Colour in Simple Glasses

Within the last year further studies have been published by a group of workers at the Pennsylvania State Univerity, which provide systematic information on the coloration imparted to glass by the platinum metals. The effect on a wide range of glasses has been studied, since a knowledge of the conditions under which they become coloured by platinum is of great interest in industrial glass manufacture.

The first paper in this group was published by Rindone and Rhoads (9) in 1956 on the colours of platinum, palladium and rhodium in simple alkali borate, phosphate and silicate glasses. The metals were introduced into the glass batches as aqueous solutions of their chlorides to give concentrations varying from 0.0005 to 0.4 per cent.

Palladium causes primarily yellow-brown ionic colours in all the glasses, but at higher concentrations dark grey and brown metallic colours are obtained. Rhodium also occurs mainly in the ionic form giving yellow, peach, orange and amber colours, with metallic greys at higher concentrations. Silicate glasses containing more than 0.05 per cent of rhodium exhibit grey colours due to the presence of rhodium crystals.

Platinum in both silicate and borate glasses gives either transparent or turbid grey colours, shown to be due to dispersed metallic particles, whereas in phosphate glasses yellow, orange and brown colours due to ionic platinum are obtained as well. This behaviour is in agreement with previous work (2) which showed that platinum ions were stable only in phosphate glasses.

Anomalous Behaviour in Phosphate Glasses

An apparently anomalous behaviour is observed in some phosphate glasses, namely those with the composition $Na_2O \cdot P_2O_5$ and $0.5\ Na_2O \cdot 0.5\ Li_2O \cdot P_2O_5$. As the platinum concentration increases, the colour in the glass changes from grey to yellow, and finally at concentrations above 0.1 per cent the metal crystallises out in the form of hexagonal plates of microscopic dimensions producing beautiful aventurine glasses. In the sodium metaphosphate glasses these effects are accompanied by partial devitrification of the glass when the platinum concentration lies between 0.002 and 0.008 per cent.

The reason for this change in colour from grey to yellow, which in effect means a change from metallic to ionic platinum in the glass, was investigated by melting in the presence of an oxidising or reducing agent and it was found that on oxidation the grey glasses became yellow, while by reduction the yellow glasses could be made grey. Since the platinum was introduced into the glass as chloride, the melt becomes more oxidising as the concentration of platinum increases, through the following reactions which produce a chlorine atmosphere:

$$PtCl_4 \xrightarrow{370^\circ} PtCl_2 + Cl_2 \quad \text{(i)}$$

$$PtCl_2 \xrightarrow{581^\circ} Pt + Cl_2 \quad \text{(ii)}$$

At low platinum concentrations (ii) proceeds to completion giving metallic platinum in the glass, but at higher concentrations the chlorine partial pressure of (i) is greater than that of (ii), so reaction (ii) is suppressed leaving platinum in the ionic form.

The explanation of the colour change by this mechanism is supported by the fact that grey platinum glass turns yellow when melted in a chlorine atmosphere.

This question of the mechanism of colour formation has been further studied in a paper presented by Ryder and Rindone (10) to the October 1956 meeting of the Glass Division of the American Ceramic Society. The effect of platinum in simple lead glasses was studied and although the paper is still in the press an abstract indicates that predominantly grey colours were obtained with borate glasses and yellow-red with phosphate glasses. Attempts were made to explain the formation of these colours on the basis of chloro-platinic reactions in the glass melt which are susceptible to oxidising and reducing agents.

The singular behaviour observed with platinum in sodium metaphosphate glass (9) is the subject of further study in a paper by Rindone and Ryder (11). The platinum was introduced into the glass melt as chloride giving concentrations of 0.002 to 0.006 per cent. In this instance grey colorations were obtained, while the platinum also caused the glass to devitrify when present in concentrations of 0.002 per cent and over. Electron micrographs indicated that the presence of platinum nuclei in the melt causes the molten glass to separate into two phases, thus enhancing its devitrification. X-ray diffraction analysis showed that the phase crystallising from the glass in the presence of platinum was different from that obtained by devitrification without platinum, and moreover could not be identified using any known diffraction data for sodium phosphate.

In a molten glass system it is normally thermodynamically impossible for separation into two phases to occur, but in the presence of platinum nuclei one phase is preferentially adsorbed and the free energy of the system is thus sufficiently lowered for the size of these adsorbed groups to grow and for phase separation to occur. The nature of the phase adsorbed on the platinum was investigated by studying the effect on the concentration of platinum needed to produce crystallisation of altering the ratio of Na_2O to P_2O_5 in the melt. It was found that as this ratio increased from 0.89 to 1.2 the concentration of platinum required to produce crystallisation decreased from 0.05 to 0.0005 per cent. This can be explained if the liquid phase which separates out through adsorption on the platinum particles is richer in P_2O_5 than the remainder of the melt.

Photosensitive Glasses

Nucleation by palladium leading to crystallisation is made the basis for a photosensitive glass process in a patent taken out by Stookey (12) for the Corning Glass Works in 1950. Palladium and either silver or gold are introduced into the glass as sensitising agents and it is desirable, though not essential, that cerium and antimony oxides be also present. If this glass is exposed to ultraviolet radiation, it develops a brown colour on subsequent heating at a lower temperature than it otherwise would if untreated. If the exposure is made through a photographic negative, a brown photographic image can be obtained in the glass by heat treatment at a suitable temperature. This discovery adds usefully to the colour range of photosensitive glasses. A normal concentration of palladium is about 0.01 per cent and the optimum concentration for gold or silver is about 0.02 per cent. A variant of this process involves the addition of an amount of Na_2SiF_6 to the glass melt giving sufficient fluorine to produce on heating an opal background to the picture.

Another patent (13) covers the use of ruthenium dispersed in glass to produce red and black coloured glasses, glazes and enamels. Lead borosilicate and lead silicate glasses containing ruthenium take on pink to reddish-black colours, whereas with all other glasses ruthenium gives a true black coloration. The value of the latter lies in the fact that it gives equivalent absorption of transmitted and reflected light at all wavelengths in contrast to commercial black glass produced in the normal way by dissolving several oxides to give overlapping absorptions at various wavelengths. Both the red and black colorations are obtained by mixing the desired concentration of ruthenium, preferably as its oxide, with the molten glass or enamel. A brown ceramic stain is also described in which ruthenium or its oxide is fused with, for example, titania or thoria.

Practical Aspects

The study of these effects is of more than theoretical interest. The mechanism of colour formation is of obvious importance in the manufacture of decorative glasses, but it is equally of interest to the maker of dense, colourless glasses. In the manufacture of optical glasses and of dense glasses for radiation shielding, platinum is, on nearly every count, the best container material, even for high-lead glasses. Although it is only when they contain alkali that colour is developed in these glasses by traces of platinum, any work which will lead to an understanding of the conditions in which the colour formation may be suppressed is of considerable practical importance in the glass industry.

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