The Effect of Platinum in Lead Glasses

A FURTHER STUDY ON PROBLEMS OF COLORATION

The mechanical advantages of platinum and its immunity to chemical attack have led to a great increase in its use for handling molten glass. The presence of lead increases the solubility of noble metals in silicate glasses, and dense glasses that are handled in platinum equipment may dissolve significant traces of platinum. Since these glasses are mostly used for optical purposes or as radiation shields, the effect of platinum on their colour is of considerable importance and a number of studies have been carried out on this problem (*Platinum Metals Rev.*, 1957, **1**, 44–48).

A further paper on this subject by R. J. Ryder and G. E. Rindone of the College of Mineral Industries, Pennsylvania State University, has recently been published (*J. Amer. Ceram. Soc.*, 1958, **41**, (10), 415–422) entitled "Colour and Light Scattering of Platinum in Some Lead Glasses".

In the work described in this paper, platinum was introduced into sodium borate, silicate and phosphate glasses containing lead oxide, as a solution of platinic chloride ($PtCl_4$). The colours were similar to those obtained in the absence of lead oxide. In borate and silicate glasses only grey colours due to dispersion of metallic platinum were obtained, while in phosphate glasses yellow and orange colours from platinum ions were formed at high platinum concentrations, in addition to the more usual grey.

Effect of Lead Content

In the phosphate glasses where the transition from grey, metallic platinum to yellow, ionic platinum glass occurs with increasing platinum content, the effect of increasing lead content in the glass is to raise the concentration of platinum required before a yellow glass is obtained. In addition the presence of lead oxide greatly increases the stability of ionic platinum in these glasses. Under normal melting conditions no more than 0.10 per cent platinum can be retained in the ionic form in the $Na_2O.P_2O_5$ glass (above this concentration it is precipitated out as metallic crystals) but when the glass contains lead oxide as much as 0.80 per cent ionic platinum can be retained.

Influence of Oxidising and Reducing Conditions

The effect of oxidising and reducing conditions during the melting of phosphate glass on the colours caused by the presence of platinum have been studied previously. Similar results were obtained with lead-containing glasses, namely, on oxidation the grey glasses become yellow, while by reduction the yellow glasses can be made grey in colour.

Oxidising conditions were obtained by introducing CeO_2 or $NaNO_3$ into the melt or by bubbling oxygen or chlorine through the glass immediately after fusion of the batch was complete.

On extending the oxidation studies to borate and silicate glasses it was found that platinum could be retained in the ionic form in these glasses if they were melted under strongly oxidising conditions. The relative effectiveness of the oxidising methods varies with the type of glass due to the different stages in the melting process at which the particular oxidising agent is most effective.

Ceria is very effective in all cases investigated, since it dissolves slowly in the melt and its oxidising action continues throughout the melting period. The oxidising effect of sodium nitrate, on the other hand, occurs mainly during the initial fusion of the batch and it is lowered by prolonging the melting period or raising the temperature. Hence it is easily seen that sodium nitrate will be more effective in oxidising platinum in the borate glasses than in the higher-melting silicate glasses. Oxygen, which was bubbled through the melt only after fusion, was less effective in oxidising platinum in the borate and phosphate glasses than in the silicate glasses. This indicates that if the platinum becomes reduced in the early stages of melting it will be quite difficult to reoxidise, except in the silicate glasses.

In those glasses where ionic (oxidised) platinum can be retained, about 0.01 per cent platinum must be present to give a noticeable colour to glasses having a thickness of about 4 mm. In the reduced state, however, as little as 0.001 per cent platinum gives a noticeable grey colour. Hence, if platinum contamination is unavoidable, melting under oxidising conditions will reduce the visible evidences of the contamination.

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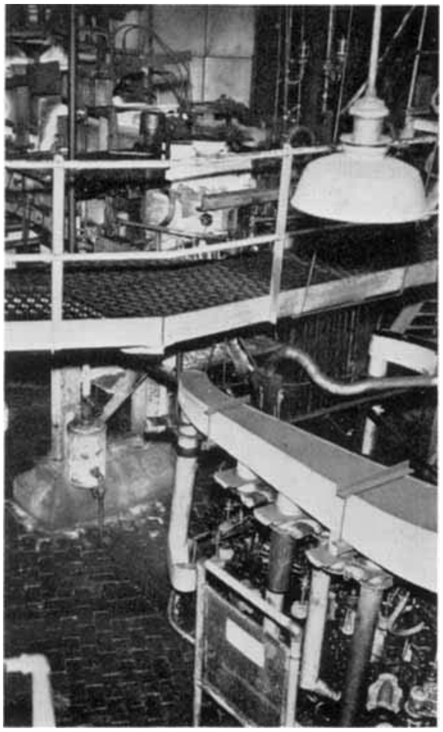
Temperature Control in Glass Manufacture

CONTINUOUS MEASUREMENT WITH PLATINUM THERMOCOUPLES

In the manufacture of glass bottles accurate control of temperature is necessary, and it is usual to check the temperature of the flowing glass in the channel and again in the feeder and to apply automatic corrections to the fuel supply. Continuous measurement with platinum : rhodium-platinum thermocouples is generally employed.

The thermocouple assemblies installed for this purpose by Honeywell Controls Ltd. at the works of Rockware Glass Ltd. are specially designed for instantaneous temperature measurement under severe conditions. They are fitted with platinum : 13 per cent rhodium-platinum couples in twin-bore refractory insulators and are housed in composite all-metal sheaths. These have a nickel stem passing through the tank wall, welded to a platinum or rhodium-platinum tip 0.2 inch thick, the tip projecting into the flowing glass.

A secondary sheath of impervious mullite protects the assembly for most of its length, but leaves the platinum tip uncovered. To provide the necessary sensitivity for rapid temperature control, the hot junction of the couple is held in contact with the inside of the sheath.



Platinum thermocouple assemblies installed by Honeywell Controls Ltd. at the Greenford works of Rockware Glass Ltd. are designed for instantaneous temperature measurement of flowing glass in severe conditions