Platinum in the Glass Industry

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In the glass industry of today platinum and its alloys are accepted as essential tools in the successful production of a wide variety of glass-ware, from the humble bottle to the finest optical glass, from the electric light bulb to the fibre glass insulating material. This article, to be published in two parts, reviews the most important of these applications of platinum and outlines some newer developments.

It would not be unfair to suggest that to most managements and technicians engaged in glass manufacture today the use of platinum and its alloys to assist in the melting and working of glasses is a comparatively modern development.

Equally, they could be forgiven for believing that the first use of this metal and its alloys was in the laboratory in the form of crucibles and other chemical ware for the analysis of glass, and that subsequently its first entry into the glass factory proper was in the form of thermocouples for the control of the melting and working operations. In fact, as far as the glass industry is concerned it was rather the other way round. The connection of platinum with the process of glass melting dates from 1829 when Michael Faraday, in the Bakerian lecture of that year, gave his account of the successful production of a number of new optical glasses of exceptional purity. He obtained them by melting in small trays of "platina", as the metal was then called. This was hardly production on a

One of the major uses of platinum in the glass industry is in the production of glass fibre in electrically heated platinum vessels or bushings. This photograph of the drawing section of the ASEA glass-fibre mill at Robertsfors, Sweden, shows the battery of bushings, operating at a temperature of around 1400°C.

One of the platinum bushings producing continuous filament glass fibre in the ASEA plant. The base of each bushing contains either 102 or 204 orifices through which the molten glass is drawn on to a spool. The fibre diameter is dependent upon the speed of drawing, the diameter of the orifice, and the temperature.

factory scale, but Faraday obtained the glasses in amounts sufficient for him to determine their more important optical properties.

To this day one of the major uses in the glass industry of platinum and its alloys is in the manufacture of optical and other special glasses requiring to be free from contamination by iron oxide or from the effects of the solution of the refractory materials of the fireclay or sillimanite pots in which they would otherwise have to be melted. This is undoubtedly to be considered as the commercial development of the technique the possibilities of which were first demonstrated by Faraday.

It is not, however, by any means the only major use. Among others to be described in this article are the cladding of furnace refractories with platinum in order to avoid contamination of the glass by corrosion products, and – one of the most fascinating of modern industrial developments – the production of fibre glass through a series of closely dimensioned orifices in a platinum bushing at a working temperature of around 1400° C.

The important properties of platinum and platinum alloys that render them of particular value in all forms of glass manufacture today are their high melting points, their extreme resistance to oxidation at glass melting temperatures, their virtual insolubility in all molten glasses, all combined with the fact they can be produced under such carefully controlled conditions that their chemical compositions and physical properties remain constant within very close limits.

In general, platinum and its alloys are used in the glass industry because they are "refractory metals", they are indestructible, and their thermo-electric properties enable them also to be used as the most accurate means of temperature control. The sections which follow give a brief account of the varied applications of these metals in widely different sections of the industry.

It is a significant fact that the use of these so-called "precious metals", admittedly high in initial cost, has always resulted in the production of the particular types of glass to which they have been applied at a more economic price. This is due entirely to the production of a purer glass, or a glass with greater freedom from defects from whatever cause.

The metals that find greatest application in the glass industry are platinum and its alloys with rhodium up to a maximum of 10 per cent. Alloys containing higher percentages of rhodium have been employed on occasion but they are not in general use and at the moment it is doubtful if it is necessary to go beyond 10 per cent rhodium.

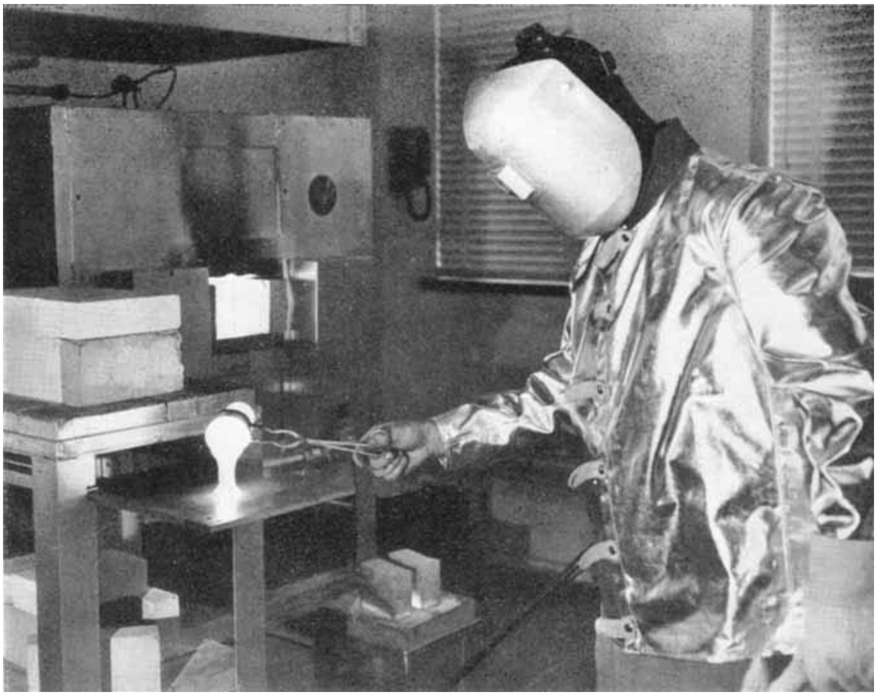
Platinum and rhodium form a continuous series of solid solutions in which the liquidus temperature gradually rises from the melting point of platinum, 1769°C, to that of rhodium, 1966°C. As the proportion of rhodium present in the alloy increases so also does the mechanical strength of the alloy, and, a most important feature, the resistance to creep stresses also rises. In applications where pure platinum is considered to be too soft, then one or other of the alloys is employed containing usually 5 or 10 per cent rhodium. However, the mechanical strength of platinum at high temperatures is by no means insignificant, and at 1000°C it requires a pull of more than two tons per square inch to cause fracture. As will be seen from the table, this is increased to some six tons per square inch in the 10 per cent rhodium alloy.

The ductility of platinum and the ease with which it can be shaped and welded, which are also features of the harder alloys, greatly facilitate its industrial applications. In the case of the glass industry these properties allow any shape to be covered with a comparatively thin "overcoat" of platinum or alloy to protect the underlying material from corrosion by the molten glass.

The value given in the table below for the coefficient of linear thermal expansion may be surprising to glass technologists who are more familiar with the value 9.1. For one of the earliest applications of platinum was as a conductor which sealed easily into glass, making a strain-free seal with a glass of approximately the same thermal expansion, namely 9.0 to 9.1×10^{-6}. Indeed it was this

Properties of Platinum and Rhodium-Platinum Alloys

	Pure Platinum	5 per cent Rhodium-Platinum	10 per cent Rhodium-Platinum
Density, g per cc	**21.4**	**20.8**	**20.0**
Melting point, °C	**1769**	**1820**	**1850**
°F	**3216**	**3318**	**3362**
Coefficient of linear expansion, (20°—1000° C) $\times 10^6$	**10.2**	**10.3**	**10.4**
Ultimate tensile strength (annealed) at room temperature, lb per square inch	**18,000**	**35,000**	**48,000**
Ultimate tensile strength at 1000°C (1832°F), lb per square inch	**4,500**	**8,000**	**14,000**
Resistivity, microhm-cm at 0° C	**9.8**	**17.3**	**18.4**
Thermal conductivity, CGS units	**.17**	**.11**	**.09**



A laboratory worker at Corning Glass Works, Corning, New York, pouring a sample of a new glass composition from a platinum-lined crucible

easy matching of the expansions of glass and platinum that allowed the early lamps and radio valves to be manufactured by sealing the conductors through lead oxide containing glass. Even today, the substitute which was quickly developed, copper-clad, is still often referred to as "red platinum".

In common with many other materials, including glasses themselves, the coefficient of linear thermal expansion is not constant throughout the entire temperature range, the plot of expansion against temperature being a curve and not a straight line. In the range 20° to 320°C the linear thermal expansion of pure platinum is almost exactly that of a glass containing 30 per cent lead oxide, i.e. 9.1×10^{-6}.

It is difficult to state a "safe" temperature at which platinum and its alloys may be employed, for much depends upon the conditions, chemical and physical, into which the metal is to be introduced. In some cases, as in thermocouples, 1600°C is a perfectly safe temperature over long periods, while 1450°C could be said to be a generally safe temperature in which to employ platinum and its alloys in glass working operations, but appreciably higher temperatures are commonly encountered.

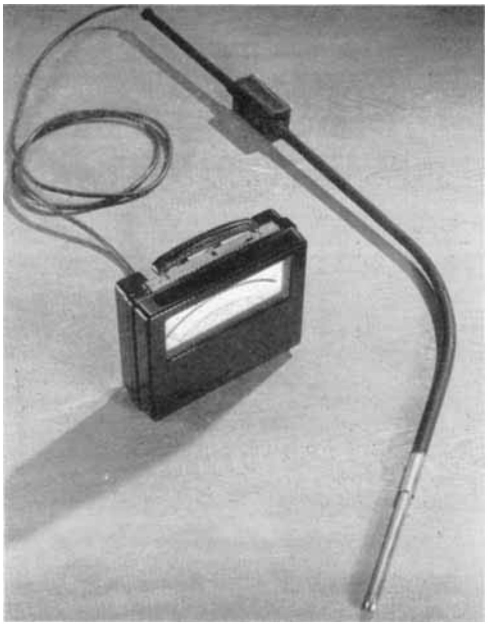
Laboratory Uses

The glass technologist first becomes aware of the value of platinum to the industry in the laboratory where he is called upon to carry out chemical analyses of the glasses which would be quite impossible without platinum crucibles and dishes, and also many physical tests that require special platinum apparatus. Although not the greatest amounts of platinum are employed here it is the section of the factory where platinum and its alloys will be universally found.

In addition to these, many special pieces of apparatus in platinum or its alloys are often required. Tests devised for the control of the devitrification temperatures of glasses are carried out in 10 per cent rhodium boats measuring approximately $6 \times \frac{1}{2} \times \frac{1}{2}$ inches. For the determination of the viscosity of glass at high temperatures concentric cylinders of platinum alloy are required or sometimes a variation of the falling ball technique is used, employing a platinum ball and rod. In the larger glass-works laboratories such equipment is part of the routine control employed in glass manufacture and it is here in this vital section of the factory that the young technician appreciates the refractory, insoluble nature of the platinum metals and then naturally seeks to apply them in production.

Temperature Measurement and Control

The value of platinum : rhodium-platinum thermocouples to industry is too well known to require further elaboration. Today they are accepted without question, and it is a tribute to the extreme care and control exercised in the production of the wires to give products of constant thermo-electrical properties that there are so many temperature measuring and recording devices whose scales and charts require no alteration when new batches of thermocouple wire are put into service. For all practical purposes today these properties remain constant and allow temperature control of glass-making processes to $\pm 1^{\circ}$C without difficulty. This degree of control is necessary in many high-speed modern glass forming operations.

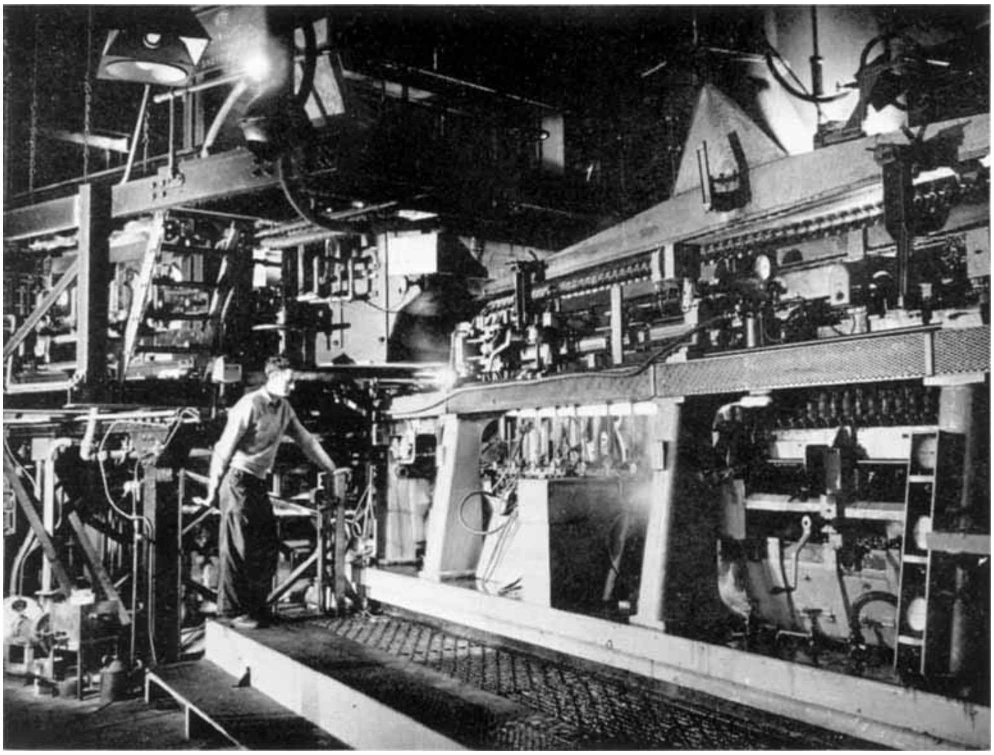


For the measurement of temperature in molten glass, this platinum : rhodium-platinum thermocouple has been developed by the Foster Instrument Co. Ltd. The former refractory sheath has been replaced by a platinum sheath

Not many years ago one thermocouple would have been regarded as adequate as giving "the melting temperature", but today furnace technicians are much more conscious of the need not only for constancy of temperature at the measured point but for constancy of temperature distribution within the melting and working compartments of a tank furnace if glass of consistent properties and quality is to be produced.

In a moderate sized tank for the manufacture of the commonplace bottle it would not be unusual to find as many as a dozen platinum thermocouples, both in the combustion space and within the glass itself, and in a glass works having three such tanks as many as fifty or sixty such couples in operation would be found for measuring not only the furnace and glass temperatures, but in the feeders conveying the molten glass to the machines, in the annealing furnaces and pot arches. In the huge sheet glass furnaces of today as many as fifty may be found in a single furnace.

For the measurement of temperature in the combustion space, and above the glass surface, the old forms of refractory sheathed couple still survive, but for the measurement of temperatures within the molten glass itself they are obviously at a disadvantage. The refractory sheath is attacked by the glass and gradually dissolved, and frequent replacements are necessary. This is not an easy operation, especially if they are inserted through the siege of the furnace. To meet this requirement a more rigid type of couple,



Accurate temperature measurement and control are vital in the operation of modern glass-forming machines. This "ribbon" machine produces more than one and a quarter million electric lamp bulbs a day at the works of Glass Bulbs Ltd. at Harworth, Yorkshire, where more than fifty platinum thermocouples are installed

illustrated on page 6, has been devised. The former refractory sheath is replaced by a sheath of platinum or rhodium-platinum alloy, and the unit is practically indestructible, with the added advantage of a much quicker response to any temperature variations.

This form of couple finds application not only in the melting and refining compartments of tank furnaces but in the feeder channels where it is even more vital to have accurate and rapid temperature control for the most efficient operation of the modern high speed glass forming machines. A typical example is in the production of electric lamp bulbs by the ribbon machine, where from a single feeder more than 1.25 million bulbs are produced each 24 hours and where a variation of 2 degrees in the glass temperature would completely upset the operation of the machine.

For intermittent and experimental exploration of glass temperatures a form of this couple has been devised based on the immersion thermocouple familiar in steel works operations, in which the expendable silica sheath has been replaced by one of platinum. Such a portable thermocouple for the rapid determination of glass temperatures in pots, or for the exploration of glass temperatures in tank furnaces and feeders, has now been made available. After a year's operation it is calculated to be no more expensive than the similar form with the expendable sheath.

It is not unlikely that in the future thermocouples of this type with the platinum-sheathed end will replace the old refractory sheaths, for the latter, even in the furnace space, are often so attacked by the products of combustion that they are burnt through, to the detriment of the couple inside and in consequence they have to be replaced from time to time.

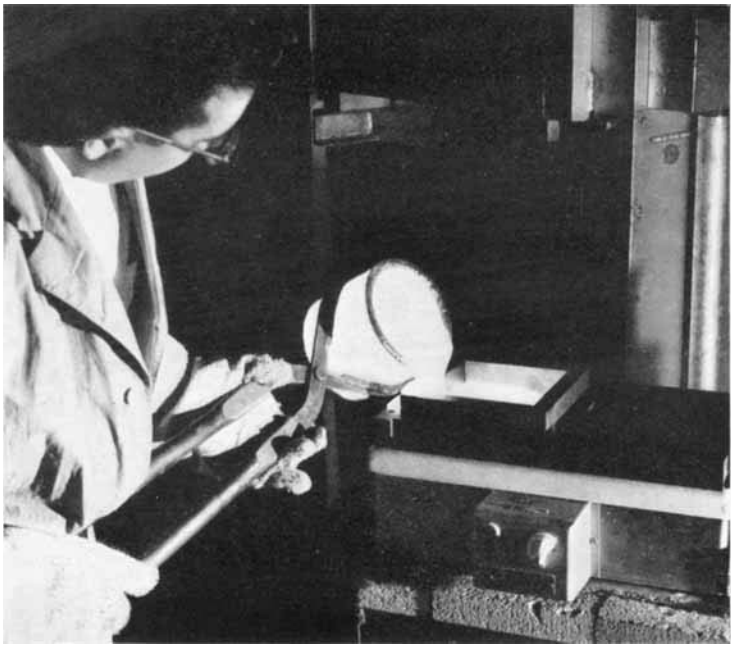
Replacing a thermocouple through the crown of a furnace operating at 1500°C and higher is not a pleasant task, and the newer all-metal sheath should not require replacement and would have the very important advantage of following more rapidly the temperature fluctuations in the combustion space and thereby allowing the fuel and air controls to react more quickly.

Glass Melting in Platinum Pots

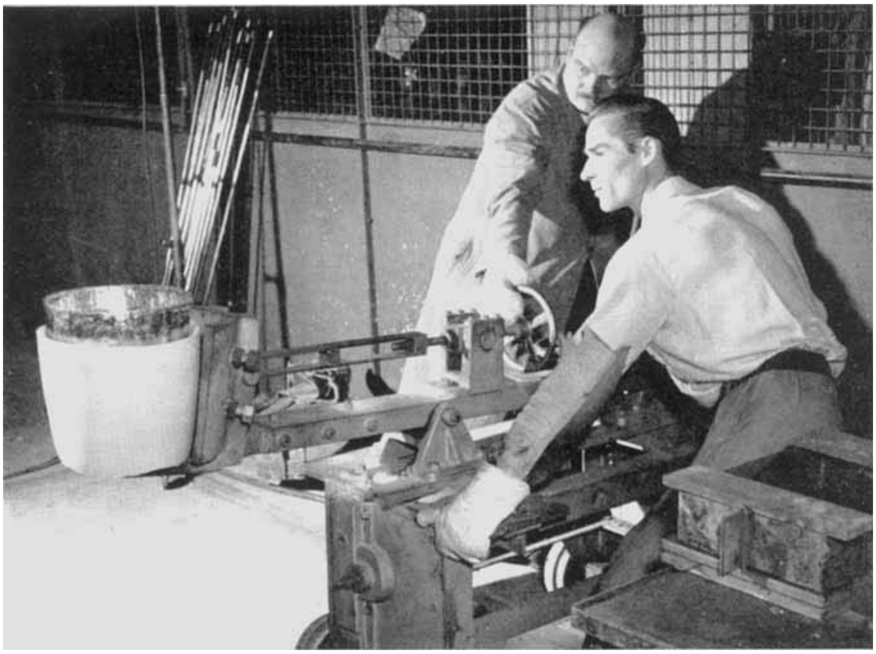
Apart from the melting of optical glasses, which must in the chronological sequence be accorded first place, one of the most important applications of platinum to the factory production of glasses is for the electrical industries. Some twenty-five years ago it became obvious that discharge lamp lighting was far more efficient in terms of light output for watts input than tungsten filament lighting. The individual lighting units however were expensive but were ideally suited to public lighting systems. One of the earliest of these systems to be developed was the sodium-vapour lamp. For a time it was perhaps a little over-shadowed by the mercury-vapour lamp but today there appears to be a strong preference for sodium-vapour lighting of main thoroughfares.

For the successful production of a sodium-vapour lamp the essential unit is a tube of glass which is itself resistant to the attack of sodium vapour. This is achieved by producing a tube the internal surface of which is coated with a layer of sodium-resistant glass. It would be far too costly to produce the entire tube in this glass, so a very small quantity of the sodium-resistant glass is covered with a much larger mass of ordinary soda glass and the whole drawn out into a tube having a thin layer on the internal surface of a glass inherently resistant to sodium vapour. To be successful this internal layer must be absolutely free from contamination by iron oxide. The only way of ensuring this is to melt the glass in platinum pots.

The first platinum pot for this process was supplied about twenty-five years ago and the technique for the production of this glass



Optical glass is produced by Bausch and Lomb of Rochester, New York, both in continuous-flow furnaces, portions of which are lined with platinum, holding 5 to 8 tons of glass, and in platinum-lined crucibles each holding up to 200 lb of glass. The platinum-lined pot shown here is pouring a small experimental batch of optical glass



Removing a platinum pot, supported in a refractory crucible, from the furnace at the Birmingham works of Chance Brothers Ltd. The pot holds 12 litres of optical glass

remains the same, although the pots have grown in size and number. These pots relied entirely on their own mechanical strength and were usually in 10 per cent or 5 per cent rhodium-platinum alloys. Their life before reshaping was required was, and remains, upwards of one year.

It is true to say that the vast majority of sodium-vapour lamps employed in street lighting today contain glass melted in platinum alloy pots.

In the optical glass industry although there is a longer history of the use of platinum pots the tonnage involved is not quite so great. Here it is a question of even greater chemical purity. Although the platinum alloys are virtually insoluble in molten glass it is true that minute quantities of rhodium can be detected in the resulting glass, and as optical glasses are required to be of the highest possible purity they are generally melted when required in pure platinum pots. We have seen that the mechanical strength of pure platinum at high temperatures is only about one-third to one-quarter that of the 10 per cent rhodium alloy so that when pure platinum is employed it is wise to give it added strength by supporting the pot in an external refractory crucible. This technique is exemplified in the illustration above, which clearly shows the platinum pot supported by its refractory outer case. Optical glasses of the highest degree of purity and freedom from colour are produced by this means.

Apart from the production on a commercial scale in the factory of such glasses melted in platinum or rhodium-platinum alloys, there continues daily the experimental development of glasses melted in platinum on a laboratory scale. The overriding requirement is to keep the glasses free from colouring oxides such as iron resulting from the solution of the normal alumino-silicate refractories in which they would otherwise have to be melted.

The concluding part of Dr Preston's article will be published in the April issue of 'Platinum Metals Review'.