Influential Role of Al_2O_3 and B_2O_3 on Selenium Ruby Glass

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(Received 27th December 2006, revised 26th April 2008)

Summary: This paper represents the results of investigations on the melting of selenium ruby glass, particularly on the effect of Al_2O_3 and B_2O_3 on ruby colour. A glass of base composition (wt. %) SiO_2 65.0, Na_2O 15.5, K_2O 5.3, ZnO 12.0, B_2O_3 1.0, CdS 0.6, Se 0.6 has been chosen for these studies. In this study Al_2O_3 and B_2O_3 are systematically substituted for Na_2O in small amounts from 0.5 to 3.0 %. Effects of these substitutions on melting, refining, colour, striking temperature *etc.* have been recorded. Transmittance of some representative samples has been determined. Glasses containing Al_2O_3 1.5 to 2.5 and B_2O_3 2 to 3.0 % have been found suitable for the development of red signal glass. Pilot plant meltings also gave satisfactory results.

Introduction

Signal glass is special kind of glass giving selected transmission at various wavelengths of light. Red, green, yellow, amber and blue are the usual signal colours. They are required in various shapes and sizes for the regulation and control of traffic on land, sea and in air. In Pakistan, railway and road traffic are the main consumers of signal glass. Besides this a considerable quantity is consumed by all types of auto-vehicles and for decoration purposes.

This paper describes the laboratory studies carried out for the development of selenium red signal glass. Selenium ruby glass is a typical signal glass, the manufacturing of which requires special expertise. Selenium and cadmium sulphide along with appreciable amount of zinc oxide are important constituents of this glass. Reducing conditions are essential for the retention of selenium and cadmium in the final glass. The glass may be red on melting or pot red in each case the colour depends on the rate at which the molten glass is cooled during fabrication. In practice, it is found easier to control colour by reheat treatment (*i.e.* striking) which produces brighter red and economises the use of selenium.

W. Shulin and F. Jingwer investigated the mechanism of colouration of selenium by HREM X-ray dispersive spectroscopy. Their results indicate that the colour arises from both non crystalline and crystalline forms of CdSe particles. Most of the researchers are of the view that colouring agents in the ruby red glass appear to be crystals of colloidal dimensions. These crystals can be described as cadmium sulphoselenide representing members of a series of mixed crystals between cadmium sulphide (CdS) and cadmium selenide (CdSe) [1,2].

Experiments proved that glass composition, furnace atmosphere (reducing or oxidizing), melting and fabrication conditions play important role in the development of selenium signal glass. In view of this, present study was carried out to find out suitable glass compositions for selenium red signal glass. A base glass of composition SiO_2 65.0, Na_2O 15.5, K_2O 5.3, ZnO 12.0, B_2O_3 1.0, Se 0.60, CdS 0.60 (wt. %) was selected and studies were carried out by substituting B_2O_3 and Al_2O_3 in place of Na_2O upto 3.0 % [3]. Melting behavior, colour development and striking temperature were determined. Selenium ruby glass, on commercial scale is virtually made in pots or in small tank furnaces. Most of the experimental work presented in this paper was carried out in clay crucibles. Pilot plant meltings were also conducted to confirm the laboratory studies.

Results and Discussion

The chief purpose of this discussion is to show that the entire chemistry of the glass batch must be kept in mind in any work on the production of selenium ruby glass.

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In the customary commercial methods of making selenium ruby glass, 1 % or more by weight of selenium, usually in metallic form, is added to the batch. Cadmium and sulphur are usually added as cadmium sulphide, frequently in amounts of 0.6 % or more by weight of the raw batch.

Experiments showed that selenium, cadmium and sulphur must be present in the final glass to get a ruby colour. Melting conditions are very important for the development of the ruby colour. Strong reducing conditions which are conducive to retain selenium in the melt may effect a substantially complete loss of the cadmium, glass containing even more than 0.5 %of selenium in the final glass will not produce a ruby colour if cadmium is absent or too low. Past researchers and operators have neglected the consideration of retaining cadmium in the melt, and they have also incorrectly placed the blame for failure to develop colour on the loss of selenium rather than on the loss of cadmium [4,5]. But experiments have shown that oxidizing conditions are conducive to high selenium losses. Selenium is expensive and the production of cheap glass requires that its loss be not too great. This problem is aggravated further when making a selenium ruby glass in a tank furnace because the losses are higher than when pots are used. Even if the gases over the melt are reducing, the selenium losses are great because of the high vapour pressure of selenium. The rapid sweeping of combustion gases over the melt intensifies the removal of selenium [6,7]. Both selenium and cadmium sulphide must be present in sufficient amount in the final glass to get good ruby colour. It must not be less than 0.06 % in the final glass. So, during melting slightly reducing conditions are beneficial. The time required for melting the glass sample should be between 3 to 4 hours. Because if the melting time is more the volatilization losses of Se and CdS will be more.

Glass compositions alongwith striking temperatures are given in Tables-1 and 2. Light transmission of some representative glasses is shown in Fig. 1.

As it has been shown in Tables-1 and 2, Al_2O_3 and B_2O_3 play a vital role in the development of selenium ruby glass.

In common soda-lime-silica glass, weather and chemical attack cause the leaching of alkalies through the glass which tarnishes the surface of glass. That effect is more serious in signal glass which is exposed to severe weather conditions. This defect of selenium ruby signal glass is successfully removed by the substitution of Al_2O_3 and B_2O_3 in glass batch. Although Al_2O_3 and B_2O_3 play a vital role on the stabilization and homogenisation of colour in the glass the major influence of these oxides is to make the glass resistant against chemical and weather attack. Substitution of Al_2O_3 and B_2O_3 also affect the glass coloration, viscosity, melting temperature and time striking temperature and structure of glass.

Light transmission of the glass was measured and representative curves are given in Fig. 1 along with the transmission of an imported signal glass. It can be seen that transmissions of these glasses are comparable with the imported signal glass. The difference in transmittance of the imported sample and laboratory samples is not significant between 650 and 740 nm [8,9]. High percentage of iron in the indigenous raw materials and also from crucible during melting is responsible for low transmittance. This difference in transmittance can be minimized by using raw materials, especially sand, having low iron content and by melting the glass in furnaces made from AZS refractories [10,11].

The quality of glass melted in a tank furnace is always much superior than a glass melted in a

Table-1: Effect of Al_2O_3 on selenium ruby glass.

Glass No.	Ingredients Oxide wt. % SiO_2	K_2O	B_2O_3	ZnO	CdS	Se	Na_2O	Al_2O_3	Colour on annealing (525°C)	Colour on heat treatment for 15-25 minutes.	Remarks
A-1	6.5	5.00	1.00	12.00	0.6	0.6	14.3	1.0	Yellowish red	Transparent light red at 550°C colour is slightly more uniform than 1	Refined
A-2	-	-	-	-	-	-	13.8	1.5	Slightly red	Red at 560°C. Colour is almost uniform	Refined
A-3	-	-	-	-	-	-	13.3	2.0	Light red	Good red colour at 570°C. Colour is uniform	Seed free. Glass is slightly hard.
A-4	-	-	-	-	-	-	12.8	2.5	Light red	Beautiful red colour at 575°C. Colour is uniform.	Bubbles free with a few seeds, glass is hard.
A-5	-	-	-	-	-	-	-	3.0	Light red	Good red colour like A-4 at 585°C. Colour is uniform	A few bubbles and lot of seeds. Glass is very hard.

Table-2: Effect of B_2O_3 on selenium ruby glass.

	Ingredients Oxide wt. %										
Glass No.	SiO_2	K_2O	ZnO	Al_2O_3	CdS	Se	Na_2O	B_2O_3	Colour on annealing (525°C)	Colour on heat treatment for 15-25 minutes.	Remarks
B-1	6.5	5.00	12.00	2.50	0.6	0.6	12.8	1.5	Light red	Good red at 560°C	Almost free of bubbles. But a few seeds.
B-2	-	-	-	-	-	-	12.3	2.00	Light red	Good red at 560°C	Almost free of bubbles and seeds
B-3	-	-	-	-	-	-	11.8	2.50	Light red	Transparent red at 550°C .	Free of seeds. Glass is slightly soft.
B-4	-	-	-	-	-	-	11.3	3.00		Beautiful transparent red at 550°C	Free of seeds. Glass is soft.
B-5	-	-	-	-	-	-	10.8	3.50		Good red at 550°C	Free of seeds. Glass is soft but some surface cords appear.
B-6	-	-	-	-	-	-	10.3	4.00		Red at 550°C but not as transparent as B-4	Glass is soft but lot of surface cords.

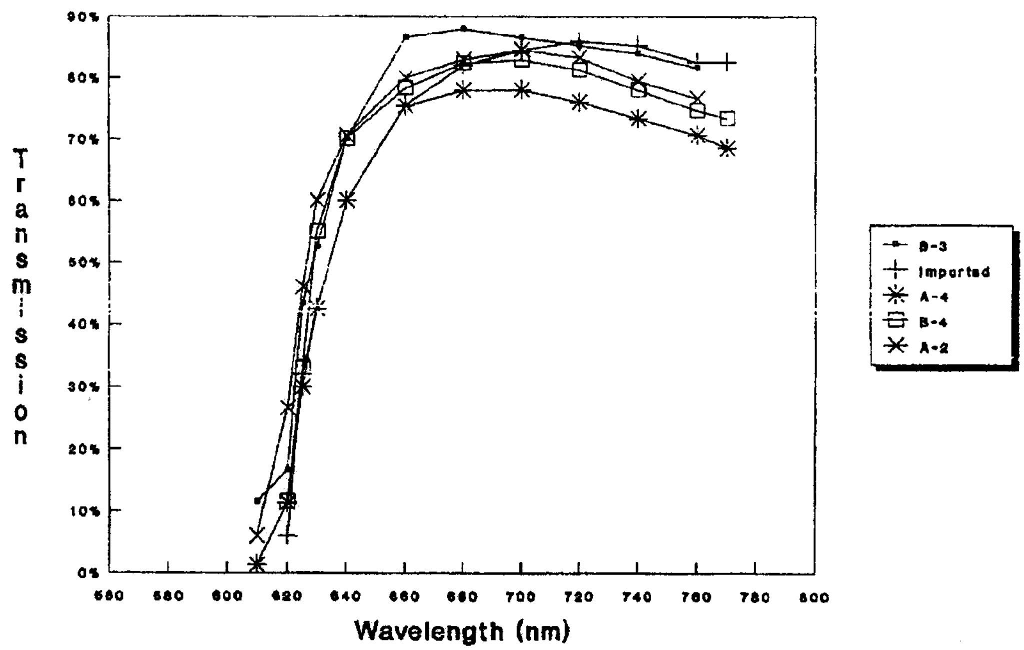

Fig. 1: Transmission curves for selenium red glass for signals.

smaller furnace or in a crucible. It is due to the convection currents which are developed in tank furnaces and intermixing during melting which result in a homogenous refined glass [12]. Although the losses of selenium and cadmium are much higher in tank furnaces, it is compensated by increasing the percentage of colouring material in the batch and overall quality of glass is improved significantly.

Pilot plant meltings were done in a tank furnace of 100 kg capacity per day. Amounts of selenium and cadmium sulphide were increased slightly to compensate losses during melting. Pilot plant production produced superior quality glass which was according to requirements.

Effect of Al_2O_3

Glass compositions showing the effect of alumina and boric oxide on the development of red colour are presented in Tables-1 and 2 respectively, alongwith striking temperature and time. It was observed that in most cases annealed samples were yellowish but turned to red on heat treatment due to the presence of Al_2O_3. Table-1 shows that intensity and uniformity of ruby coloration depends upon the contents of Al_2O_3. It was noted that glass batches containing alumina upto 1.5 % were easy to melt and refine but as the percentage of alumina was increased, glasses became hard and therefore difficult to melt and refine. Both striking temperature and time are increased as is evident from Table-1.

A-3 and A-4 glasses have better weather and chemical resistance as compared to first three glasses in this group. It is because alumina assumes tetrahederal coordination rejoining Si-O bonds broken by the addition of alkali [8]. It was noted that glass A-5 did not refine completely even at 1500°C. With the increase of alumina content (3.0 %) the melting temperature was increased and more time was needed for melting and refining. As a result, a considerable quantity of coloring agents selenium and cadmium sulphide were volatilized and therefore the striking temperature for the development of red colour was increased and glass samples were also deformed in this process. Therefore, low melting glass compositions with moderate chemical resistance are preferred to control the volatilization of coloring agents.

Keeping in view the results of Table-1, glass A-4 is quite suitable for selenium ruby glass. Glasses containing alumina more than 2.5 % are not recommended due to high melting temperature and higher losses of Se and CdS, as both are very costly chemicals.

Effect of B_2O_3

Table-2 shows the glass composition where Na_2O has been replaced by B_2O_3 from 0.5 to 3.0 % while Al_2O_3 has been kept constant at 2.5 %. Melting and refining behaviour of these glasses found much better than that of alumina containing samples. It is because boric acid and borax both act as fluxing and refining agents [13]. In these glasses melting temperature did not exceed beyond 1450°C, to get well refined seed free samples. It can also be seen from Table-2 that the striking temperature has decreased considerably as compared to alumina containing glasses. Striking temperature of alumina glasses is 550 to 580°C, whereas boron glasses were striked at 550 to 560°C. All the glass compositions of this group have been found suitable for selenium ruby glass. As far as weathering effect and thermal shock resistance are concerned, the glasses containing 2.0 to 3.0 % B_2O_3 (B-2, B-3, B-4) are better than only alumina containing glass. But B_2O_3 contents should not be more than 3 % because beyond 3 % the surface cords start to appear on the glass surface. In the light of experimental study, it may be concluded that partial substitution of both Al_2O_3 and B_2O_3 in place of Na_2O is beneficial for the development of selenium ruby glass.

So a modified glass composition SiO_2 65 %, K_2O 5 %, ZnO 12 %, Al_2O_3 2.5 %, CdS 0.6, Na_2O 11.3 %, B_2O_3 3 % is more suitable for the development of selenium ruby glass.

Experimental

It is prerequisite that raw materials and chemicals for selenium red glass should be free of iron as far as possible. Washed graded silica sand having Fe_2O_3 0.03 to 0.05 % was used in these experiments. Other chemicals were of commercial grade, almost free of iron. Small crucibles (of 1kg. melting capacity) made from imported grog and China clay were used for melting these glasses [14]. As the colouring chemicals are always in small quantities the intimate mixing with other glass materials is very essential for the development of uniform red colour. It was observed that due to bad mixing instead of uniform colour, streaks of red colour were seen in the glass. A base glass of composition SiO_2 65 %, Na_2O 14.8 %, K_2O 5 %, ZnO 12 %, B_2O_3 1 %, Al_2O_3 1 %, Se 0.6 %, CdS 0.6 % was selected and studies were carried out by substituting B_2O_3 and Al_2O_3 in place of Na_2O. Mixed batch was charged to crucible in two stages. Glass melting temperature was kept at 1450°C $\pm$ 10°C throughout these meltings. A well refined melt was usually obtained after 3 to 4 hours melting. Mild reducing flame was maintained as both excessive reducing and oxidizing flames badly affect red colour. Reducing or oxidizing conditions were achieved easily by increasing air/gas ratio in the furnace. Pressure gauges and other adjustments were used to achieve these conditions and no special techniques were required for this purpose. However, special techniques are used when glass melting is done in electric furnace [15].

After melting the glass, temperature was lowered readily to 1150°C and test samples were prepared for the determination of properties. Glass samples were annealed at 525°C. Later on all glass samples were heat treated at temperatures from

550°C to 585°C for 15 to 25 minutes. Different glass samples have different heat treatment temperatures and times which have been shown in Tables-1 and 2.

Conclusions

The experimental study shows that it is possible to develop an excellent, durable and economical selenium ruby glass with minor additions of coloring agents Se 0.06 % and CdS 0.6 % in the batch. Glass melting is done at 1450°C but the melting conditions are kept slightly conductive to reducing to control the volatilities of Se and CdS. It has been proved that addition of Al_2O_3 upto 2.5 % and B_2O_3 upto 3 % in the glass batch is very essential. The development of ruby coloration is not possible without Al_2O_3 and B_2O_3. Presence of Al_2O_3 and B_2O_3 in glass batch cause the homogenization of ruby coloration, resistance to chemical attack and severe weather conditions.

Acknowledgement

The help of Mr. Mukhtar Ahmad, JTO (in melting glass batches) and Mr. Ahmad Din, JTO, Mr. Muhammad Amin, PTO, and Mr. Muhammad Ali, Sr. Tech., in experimental work and testing glass samples is acknowledged. The help of Mr. Shakil Ahmad in compilation is also acknowledged.

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