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EFFECT OF AL_2O_3 AND B_2O_3 ON SELENIUM RUBY GLASSES FOR RED SIGNALS

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This paper presents the results of some investigations on the melting of selenium ruby glasses, 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. To this glass 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 and 2.0% and having B_2O_3 2.0 to 3.0% alongwith 1.0% Al_2O_3 have been found suitable for the development of red signal glasses. Pilot Plant meltings also gave satisfactory results.

Key words: Selenium glass, Ruby glass, Red signal glass.

Introdution

Signal glasses are special kind of glasses 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 glasses. 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 glasses. Selenium ruby glass is a typical signal glass, the manufature of which requires special expertise. Selenium and cadmium sulphide alongwith appreciable amount of zinc oxide are the important constituents of these glasses. Reducing conditions are essential for the retention of selenium and cadmium in the final glass. These glasses may be red or pot red on melting. The colour of the articles will depend on the rate at which 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.

Kirk Patrick and Roberts (1919) were the first who used a glass batch consisting of sand 100, potash 30.3, soda ash 30.3, zinc oxide 21.2,borax 1.51, cadmium sulphide 1.51 and selenium 1.51 for making red lenses. The chemical durability of this glass was not good. Lamon and Robinorich (1950) recommended the use of CaO 1.5 -2.0% for getting suitable colour. Stanworth (1941) also developed a suitable batch for the production of red bulbs having sharp cut off. Sullivan and Austin (1942) worked on the retention of selenium during melting and refining operations. A few more workers (Pavlish and Austin 1947; Pelikam 1952; Kokoler 1954) investigated the melting of this glass but glass compositions and melting conditions were not been mentioned in detail. Shulin and Jingwer (1987) investigated the mechanism of colouration of selenium by HREM X-ray dispersive spectroscopy. Their results indicated that the colour is emitted by both non crystalline and crystalline forms of CdSe particles. Most of the workers (McMillan 1979) are of the view that colouring agents in the ruby red glasses 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).

The previous works have shown that glass composition, furnace atmosphere (reducing or oxidizing), melting and fabrication conditions play important role in the development of selenium signal glasses. In view of this, present study was carried out to find out suitable glass compositions for selenium red signal glasses. A base glass of composition w% 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 was selected and studies were carried out by substituting B_2O_3 and Al_2O_3 for Na_2O up to 3.0%. Melting behaviour, colour development and striking temperature have been determined. Pilot plant meltings were also carried out to confirm the laboratory studies.

Experimental.

It is prerequisite that raw materials and chemicals for selenium red glasses should be free of iron as far as possible.

Washed graded silica sand from Daud Khel 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 made from imported grog and china clay were used for melting the glasses. It was observed that due to bad mixing instead of a uniform colour, streaks of red colour were seen in the glass. As the colouring chemicals are always in small quantities therefore homogeneous mixing with other glass materials is very essential for the development of uniform red colour. Inview of this, Se and CdS were first mixed with zinc oxide and boric acid and then with other materials. Mixed batch was charged to crucible in two stages. Glass melting temperature was kept at 1400°C ± 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 technique was required for this purpose. However, special techniques are used when glass melting is done in electric furnace.

At the end, temperature was lowered gradually 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 540 °C for 15 - 20 minutes. Most of the glasses did not turn red at 540°C and hence temperature was raised slowly till full red colour appeared.

Results and Discussion

Present work as well as the work of other researchers have shown that selenium losses are increased in the presence of highly oxidizing conditions (Sullivan and Austin 1942). Similarly excessive reducing conditions are not also beneficial to the development of ruby glass due to too much loss of cadmium sulphide. 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 (Sullivan and Austin 1942).

Glass compositions showing the effect of alumina and boric oxide on the development of red colour are pesented 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. It was noted that glasses containing alumina upto 1.5% were easy to melt and refine but as the percentage of alumina was increased, glasses became hard causing difficulty in melting and refining. Both striking temperature and time also increased (Table 1).

A-3 and A-4 glasses have better weather/chemical resistance as compared with first three glasses in this group. It is because alumina assumes tetrahedral coordination rejoining Si-O bonds broken by the addition of alkali. It is noted that glass A-5 do not refine completely even at 1430°C. With the increase of alumina content (3.0%) higher melting temperature and more time are needed for melting and refining. As a result, a considerable quantity of selenium and cadmium sulphide is volatilized, therefore higher temperature is required for the development of red colour. Glass samples are also deformed in this process, formats are used in such cases to avoid deformation of glass samples. Therefore, low melting glass composition with moderate chemical resistance are preferred. In view of the melting behaviour, A-2, A-3, A-4 glass compositions are quite suitable for selenium ruby glasses as far as colour, chemical resistance and other properties are concerned. Glasses containing alumina more than 2.5% are not recommended due to high melting temperature and high losses of Se and CdS, as both are costly chemicals.

Table 2 shows the glass compositions where Na_2O has been replaced by B_2O_3 from 0.5 to 3.0% while 1% Al_2O_3 is kept constant. Melting and refining behaviour of these glasses is much better than that of alumina containing glasses. It is because boric acid and borax both act as fluxing and refining agents. In these glasses melting temperature do not exceed beyond 1400°C ± 10°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 with 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 to be suitable for selenium ruby glasses. So 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 alumina containing glasses. In the light of the preceding discussion, it may be concluded that partial substitution of both B_2O_3 and Al_2O_3 for Na_2O is beneficial but substitution of B_2O_3 is more effective than that of Al_2O_3.

As mentioned above, too much oxidizing and reducing conditions prevailing in the furnace have been reported to spoil the ruby colour. This fact was also observed during the present investigation and it was noted that whenever there were excessive oxidizing conditions in the furnace, ruby colour did not develop easily as considerable amount of selenium was volatilized during melting. Reducing conditions are conducive for the retention of a large percentage of the selenium in the glass, but when conditions are highly reducing, cadmium is eliminated almost completely. A balance must be maintained so that the batch and the atmosphere above the batch

Table 1

Effect of Al_2O_3 on selenium red glasses 65.0 SiO_2, xAl_2O_3, (15.5-x) Na_2O, 5.3 K_2O,1.0 B_2O_3 ,12.0 ZnO, 0.6 CdS 0.6 Se (Wt%).

Glass No.	X/Wt%	Colour on annealing (525°C)	Colour on heat treatment for 15-20 minutes	Remarks
1.	-	Yellowish	Light red at 500°C	Well refined
A-1.	1.0	Slightly red	Transparent red at 550°C	Refined
A-2	1.5	Yellow with red streaks	Red at 560°C	Refined
A-3	2.0	Slightly redish yellow	Red at 565°C	Seed free
A-4	2.5	Slightly yellowish	Almost red at 670°C	Bubble free with a few seeds, hard glass
A-5	3.0	Slightly Yellowish	Just red at 580°C	Bubble free with many seeds, hards

Table 2

Effect of B_2O_3on selenium red glasses 65.0 SiO_2,1.0 Al_2O_3, (15.5-x) Na_2O, 5.3 K_2O, xB_2O_3, 12.0 ZnO, 0.6 CdS, 0.6 Se (Wt%).

Glass No.	x/Wt%	Colour on annealing (525°C)	Colour on heat treatment for 15-20 minutes	Remarks
B-1	1.5	Light red	Light red at 540°C but full red at 550°C	Almost free of bubbles and seeds
B-2	2.0	Light Yellow	Just red 540°C, completly red at 550°C	Almost free of bubbles and seeds
B-3	2.5	Redish yellow	Transparent red at 550°C	Free of seeds
B-4	3.0	Redish yellow	Full red at 560°C	Free of seeds

are sufficiently reducing to hold enough selenium in the melt but not so much reducing as to eliminate cadmium. Rapid melting of selenium glass batches has been found helpful in the retention of colouring materials in the finished glass.

Transmittance of the glasses is measured and representative curves are given (Fig. 1) alongwith the transmission of an imported signal glass. The difference in transmittance of the imported sample and laboratory samples is not significant between 650 and 740 nm. High percentage of iron in the indigenous raw materials and also iron contributed from crucible during melting are 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 as in the case of imported sample. Transmittance curves were also compared with the curves of Se-ruby glasses in literature (Sullivan and Austin 1942; Samuel *et al* 1974)) and a close agreement was observed.

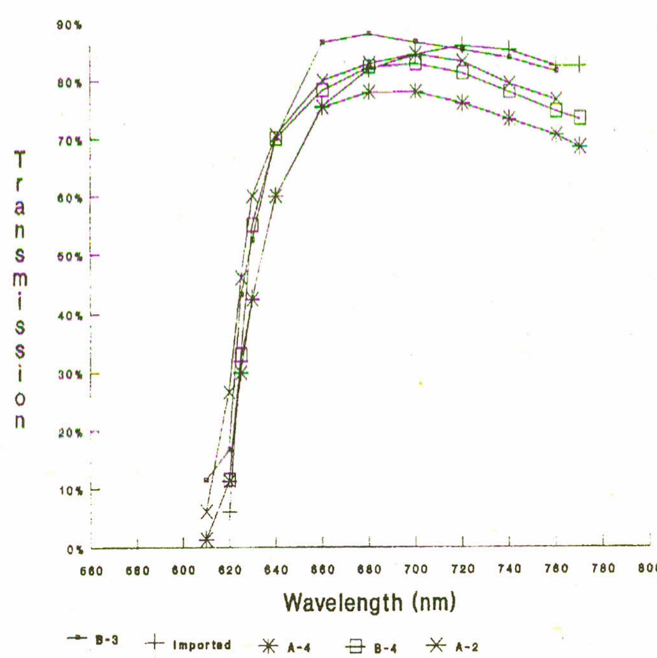

Fig 1. Transmission curves for selenium red glasses for signals.

Exact mechanism of colouration of ruby glasses is not known. It has been planned to carry out these studies in detail as equipments like atmosphere controlled electric furnace, platinum crucibles for glass melting, DTA, scanning electron microscope are being made available in this Centre. Scanning electron microscope equipped with EDS facility is very useful equipment for the identification of crystals in red ruby glasses. In view of this very useful and interesting results would be obtained regarding the mechanism of colouration of red glasses.

The quality of glass melted in a tank furnace is always much superior than a glass melted in a smaller furnace or in a crucible. It is due to the convection currents which are developed in tank furnace and intermixing during melting resulting in a homogenous refined glass. Although the losses of selenium and cadmium are comparatively much higher in tank furnaces, these are compensated by increasing the percentage of colouring material in the batch and above all quality of glass is improved significantly.

Pilot Plant Melting. 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. Selected glasses of both series gave satisfactory results on pilot plant melting. Glass indicators and signal glasses were supplied to private parties for marketing and quality evaluation. So far as the quality is concerned, product has been accepted by the end users. Orders received from time to time have been met successfully. Pilot plant prodution has been very useful in improving the quality of the glass.

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