Development of Selenium Black Glass

M. S. KHAN, M. A. KHAN, P. I. QAZI AND W. A. SHAH
Glass and Ceramics Research Centre
PCSIR Labs. Complex, Lahore - Pakistan

(Received 27th April, 2005, revised 26th January, 2006)

Summary: A black glass was made by melting a Soda-lime Silica glass under a reducing atmosphere with the addition of selenium and cobalt carbonate, $CoCO_3$. The light absorption of a specimen, (0.01 inch thick) in the range of 400 to 750 mų, was superior to that of commercial black glass. The maximum transmission was 27 % at 750 mų. The use of nickel and iron oxides is found less effective than cobalt oxide for obtaining black glass.

Introduction

In a general investigation on the role and uses of selenium in glass, the production of various coloured products is studied. Among these most interesting was the study of black glass of soda-lime-silica type with minor additions of colorants. The manufacturing of black glasses involves the addition of substantial amounts of colorants, such as oxides or sulphide of iron or oxides of manganese and iron and oxides of nickel and cobalt. Often these additions ranges from 10 to 15 % of the entire batch, adversely affect the working properties of the glass [1,2]. Therefore, a batch composition and a process to obtain a black glass containing only miner amounts of colour producing ingredients would be useful [3,4]. Combination of selenium and cobalt would result in development of excellent black glass [5].

Results and Discussion

(1) Oxidizing Vs Reducing Conditions.

Even in crucible melting where the conditions are most favourable, with 1 % selenium in the batch, the retention was practically zero when the melting conditions were oxidizing. The reason of selenium loss during the batch melting is that the metallic selenium boils at 688 °C and might be lost in this manner. An appreciable amount of selenium however, might be oxidized at lower temperatures and be lost by sublimation, in as much as selenium dioxide has a high vapour pressure and sublimes as low as 317 °C, before the boiling point of selenium is reached [6]. Particular emphasis, therefore, was placed on maintaining the reducing gaseous atmosphere during melting the glass batch to retain sufficient amount of selenium, that is having sufficient free carbon monoxide. For this purpose it is necessary to have a reducing agent in the glass batch to retain maximum possible amount of selenium. When some reducing agent is used in the batch ther slightly oxidizing atmosphere can be used safely [7].

Melt	Se in final glass (%)
Base batch + 1 % Selenium	0.013
Base batch + 1 % Selenium + 1 % C	0.69

the experiments showed that how rapidly selenium was lost even though the atmosphere above the melt was reducing. Selenium in the final glass is only 0.013 % (without reducing agent). But when 1 % carbon is used as a reducing agent, selenium in the final glass is 0.69 %. So addition of reducing agent is most necessary than the reducing atmosphere to retain the selenium contents.

(2) Effective Additants

The addition of oxides or oxide forming compounds of cobalt, nickel, or iron with selenium is effective in producing black glass. Cobalt is the most effective additive. The best black glass is obtained from a batch containing 0.6 % of selenium and 0.1 % of cobalt carbonate. Larger amount of selenium is not necessary when some reducing agent is present in the batch. The best procedure in making the black glass is to melt at about 1400-1450 °C [8, 9].

Figure 1 gives transmission curves of black glass which is made from a batch containing 0.6 % of selenium and 0.1 % of cobalt carbonate, and of a commercial black glass in the wave length range of about 400 to 750 mų [10, 11]. The specimens are approximately 0.01 in. thickness. The selenium cobalt glass is superior in optical properties. Its maximum transmission up to 750 mų is 27 %,

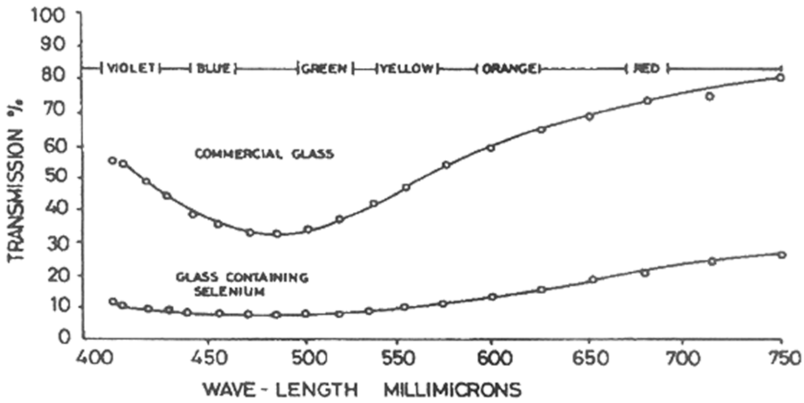

Fig. 1: Transmission curves, specimen 0.01 1N thick.

whereas the minimum transmission for the comercial glass is 34 % at 475 mų and at 750 mų, the transmission is 82 %.

(3) Effect of Amount of Selenium

It appeared necessary to use about 0.6 % of selenium in the batch. Addition of 0.4 % gave a black colour but not so opaque as with the 0.6 %. Above 0.6 % selenium makes no further improvement in black colour. So 0.6 % selenium is the optimum limit. In this connection, however, the retention of selenium in the final melt rather than the amount added in the raw batch is the governing factor. On the basis of the work done, it would be necessary to have at least 0.15 to 0.20 % of selenium in the final glass to obtain good black glass. This retention might be effected by the addition of a small amount of a reducing agent (upto 1 %) to the batch. If the atmosphere is oxidizing enough, selenium is not retained even when 0.6 % is added. After melting the resultant glass will not be black, but due to cobalt, it would be of a blue colour.

(4) Addition of $CoCO_3$

Addition of $CoCO_3$ in black glass batch is very important alongwith selenium. Many compositions of black glass has been melted with varying the amount of $CoCO_3$ while selenium contents kept at 0.6 %. All glass batches were melted under slightly reducing conditions alongwith carbon as a reducing agent. After a lot of experiments it is revealed that $CoCO_3$ should be about 0.1 %. Less than this amount black colour will not be developed. So the amount of $CoCO_3$ 0.1 % is the optimum amount for the development of black colour.

(5) Effect of Iron and Nickel Oxides

Oxide of iron and nickel are not effective as cobalt. Nickel oxide yielded an opaque black glass, but the colour was brownish-black [12]. It also appeared necessary to add more Ni_2O_3 than CoO. The colour from iron additions likewise was on the brownish-black side, and more Fe_2O_3 than CoO was used.

Experimental

The chemicals used for base glass are all commercial grade. Small crucibles made from imported grog and China clay were used for melting the glass samples. As the colouring chemicals used are in small quantities so intimate mixing with other glass materials is very essential for the development of uniform black colour.

All the results given here are on base glasses in the following composition ranges :

Ingredients	Weight (%)
SiO_2	69-74
Al_2O_3	1-4
$Na_2O + K_2O$	13-16
Cao + Cao MgO	7-13

However, our attention was mainly focussed on the base glass of the following composition :

Ingredient	(%)	Ingredient	(%)
SiO_2	72.5	Cao	6.6
Na_2O	12.5	MgO	4.4
K_2O	1.5	Al_2O_3	2.5

All the experiments were carried out in crucibles having 1000 gm batch capacity with natural gas as the fuel. Melting of glass batches were done at temperature between 1400 – 1450 ^{0}C. All the glass batches were melted in reducing atmosphere, because the selenium totally lost when batches were melted in oxidizing atmosphere. Selenium has the tendency to oxidize as it is sublimized. Selenium has low sublimation temperature i.e. 317 °C [13,14].

Conclusions

The results indicate that it is possible to get an excellent black glass with only minor additions of colorants. About 0.15 to 0.2 % of selenium and 0.1 % of cobalt (0.1 % of $CoCO_3$ = 0.05 % of Co in batch) seemed to be necessary in the final molten glass to get a good black colour. The batch must be melted under reducing conditions or with a reducing agent in the batch. The small amount of colorant does not affect the working properties of the glass.

Acknowledgement

The help of Mr. Mukhtar Ahmad J.T.O. in melting glass batches and Mr. Ahmad Din J.T.O, Mr. Muhammad Amin, P.T and Mr. Muhammad Ali, Sr. Tech. in experimental work and testing the glass samples is acknowledged.

References

1. J. Kocik, J. Nebrenshy and I. Fanderlik, *Sprechsaal,* **118**, 668 (1985).
2. L. P. J. Mait, *Glass.Tech.*, **40**, 99 (1990).
3. R. S. Samuel and H. Green, Modern Glass Practice. 7th Edit. P295 (1974)
4. D. Ahmed and M. Z. Hussain, *Pak. J. Sci.,* **30**, 1 (1977).
5. F. Novotny, *Silika.*, **2,** 67 (2003).
6. E. Rivera, H. Marquez and L.E. Celaya, *Mater. Lett.*, **13**, 27 (1992).
7. N. M. Bobkova and V. A. Zapol, *J. APPL. Spectrose.,* **56**,127 (2002).
8. T. H. Rehran, *J. Archry.*, **43**, 483 (2004).
9. K. B. Gross and J.Tikkinan, *J. Phys. Soc. JPN.,* **6**, 60 (2004).
10. R. D. Wright, *Glass Tech.*, **40**, 75 (1999).
11. A. C. L. Ramos and J. Petaiu, *J. Non. Cryst. Solid.,* **151**, 13 (1992).
12. T. Wenshulin, *J. Mat. Sci.*, **5**, 568 (2004).
13. S. Wen and F. Jingwei, *J. Non. Cryst. Solid.*, **80**, 190 (1986).
14. S. Y. Kanai, S. Y. T.Suchiya and M. Hasegawa, *J. Phys. Soc. JPN.,* **60**, 2477 (1991).