

DEVELOPMENT OF ECONOMICAL BLACK GLASS FOR TABLEWARE WITHOUT SELENIUM

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ABSTRACT: This paper presents the experimental study for the production of economical black glass without inclusion of highly expensive material selenium metal powder. Most of the work reported in this paper was done on the soda-lime-silica glass of composition, 73% SiO₂, 2% Al₂O₃, 15% Na₂O, 7%CaO, 1.5% B₂O₃ and 1.5% K₂O. The black glass was developed with the addition of 2.5% K₂Cr₂O₇ and 2.5% MnO₂, while CaO and NiO are added in minute quantities characterization of properties like transmission of light and thermal expansion proved it to be a superior quality black glass.

INTRODUCTION

Coloured glasses for tablewares have probably been manufactured since seventeenth century. In Pakistan coloured tablewares are being manufactured on small scale. But their quality is not upto the imported products. Similarly, the quality of black colour glass is not being manufactured in the country. The present investigations were therefore, undertaken to develop suitable formulation for exploitation by indigenous glass industry.

Usually, the main constituents have been used for the development of black colour in glass are, selenium metal powder and cobalt oxide. Both are expensive chemicals, especially selenium metal powder is too much expensive that it can not be used for ordinary coloured glasses. So it was need of the time to search out the alternate of these chemicals. After comprehensive study and experimentation, alternate colouring agents are sort out.

Among these main the alternate colouring agents are pot dichromate and manganese dioxide which are very much cheap as compare to selenium metal powder. Selenium also has draw back that when it is used as a colouring agent, controlled reducing conditions are required in the furnace to melt the glass batch. Because selenium volatilises at high temperature. This volatilization process increases when melting conditions are oxidizing. So prolonged oxidizing melting conditions causes complete elimination of selenium in the final glass is a big problem. For this purpose either melting conditions are kept reducing or some reducing agent is included in the glass batch (Cernoskora &

Holubova, 2005). On the other hand, Cr₂O₃ (which is obtained after the decomposition of K₂Cr₂O₇ at high temperature) is most stable compound. Similarly MnO₂ is also very stable compound. These oxides do not require any kind of oxidising or reducing melting conditions. Also they do not evaporate at high temperature. So the intensity of colour does not reduce with the fluctuation of melting conditions or with prolonged melting period (Hebenz and Frenz, 2006).

MATERIALS AND METHODS

The base glass composition selected for the experimentation is as (73% SiO₂, 2% Al₂O₃, 15% Na₂O, 7%CaO, 1.5% B₂O₃ and 1.5% K₂O) while colouring agents were used as Cr₂O₃ 1.5%, MnO₂ 2.8%, NiO 0.2%, CoO 0.06% (Henry, 1986). All chemicals used were of commercial grade. Mixing of chemicals was done in a mixer of capacity 10 Kg. After mixing the batches were sieved through 30 mesh screen. All meltings were done in 1 Kg. clay crucibles. Natural gas was used as a fuel for melting the glass batch. Pot furnace was used to melt all samples of black glass. The melting temperature was maintained in the temperature range from 1450 to 1500°C. Melting of the samples took 5 to 6 hours. Six batches were prepared by varying the amount of colouring oxide to develop high quality black glass. The results of different batches are shown in Table-1.

Table-1: Chemical compositions of black glass

S. #.	Wt.%										Remarks
	SiO ₂	Na ₂ O	CaO	Al ₂ O ₃	K ₂ O	B ₂ O ₃	NiO	CoO	Cr ₂ O ₃	MnO ₂	
1	71.0	14.50	6.0	2.0	1.5	1.74	0.2	0.06	1.0	2.0	Deep purple
2	71.0	14.50	6.0	2.0	1.5	1.54	0.2	0.06	1.1	2.1	Deep purple
3	71.0	14.50	6.0	2.0	1.5	1.34	0.2	0.06	1.2	2.2	Purple black
4	71.0	14.50	6.0	1.7	1.5	1.34	0.2	0.06	1.3	2.4	Light black
5	71.0	14.50	6.0	1.4	1.5	1.34	0.2	0.06	1.4	2.6	Black
6	71.0	14.50	6.0	1.10	1.5	1.34	0.2	0.06	1.5	2.8	Excellent dark black colour

RESULTS AND DISCUSSION

Conventionally selenium had been used the main ingredient for the development of selenium ruby and selenium black glass. But due to extraordinary high prices of selenium, it is impossible to use selenium in ordinary coloured glasses. Other than its high prices, it also has some draw back to use in colored glasses especially selenium ruby and selenium black glass. At high temperature selenium reacts with sodium carbonate to form sodium selenide compound which is unstable at temperature 1200°C and above.

So within few minutes all selenium volatilized through glass batch and the required colour in the glass does not develop (Kocin & Nebrenshy, 2004). For this purpose melting conditions are kept reducing to retain selenium in the final glass or some reducing agent is added in glass batch to minimize the volatilization of selenium at high temperature. This problem is aggravated further in melting the glass in a direct fired tank furnace because the losses of selenium contents 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 intensified the removal of selenium (Liang & Marshall, 1985). So it was required to sort out alternate chemicals to develop black glass. After comprehensive study and experimentation, Potassium dichromate and manganese dioxide are found as alternate of selenium.

Potassium dichromate (K₂Cr₂O₇) which is very cheap as compare to selenium gives Cr₂O₃ after decomposition at high temperature which is most stable oxide. When it is used alone in glass it gives green colour in glass. Cr₂O₃ is immiscible in molten silica but its solubility increases with the increase of alkali contents in silicate glasses. Chromium oxide forms a series of chromium compounds, of colours varying from green to blue

and even dark red, depending on the types of glass and melting conditions of glass (Mait, 2002).

Similarly, manganese dioxide (MnO₂) is one of the cheapest glass colouring oxide, Manganese usually gives purple colour in ordinary glass composition. The purple colour is produced by the trivalent manganese oxide, Mn₂O₃. The colour of manganese glasses is caused by the absorption of the Mn⁺³ ions. Manganese ions have greater tendency to absorb oxygen in surrounding and change into deeply coloured Mn₂O₃ glass (Race, 1980).

At about 500°C its decomposition starts and oxygen is liberated. Above 700°C another reaction is superimposed on the decomposition of pyrolusite-namely, a reaction between MnO, alkali and the oxygen of the air leading to alkali manganates. In order to obtain an intensive manganese colour the melting conditions should be oxidizing (Shulin & Jingwei, 1986). While all kinds of reducing agents destroy the (original) purple colour of manganese. On the other hand in selenium black glass reducing agents are necessary to retain selenium in the final glass for the development of black colouration.

Chromates have a higher oxidation potential than Mn₂O₃, so that intensive colour can be obtained by combination of manganese dioxide and potassium dichromate (Stadler and David, 1972). NiO and CoO are used in minor quantities to intensify the black colour. Although they are not cheap as K₂Cr₂O₇ and MnO₂ but they are used in so minor quantity that there is no appreciable increase in the price of glass.

Characterization of properties: Properties of black glass like light transmission and thermal expansion were studied and found upto the standard.

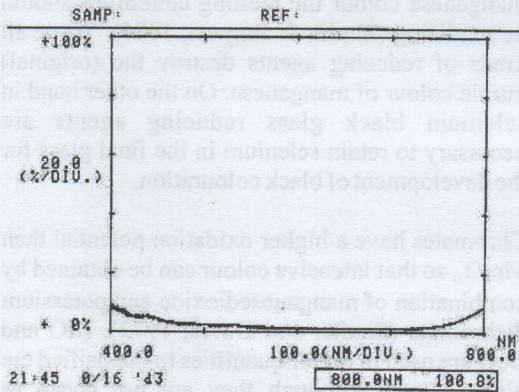
Light Transmission: It was studied on spectro

photometer. Specimens of size 15mmx8mmx1mm were prepared and examined. The maximum transmission of light was 8.6% at wave length 800NM and minimum was 1.0% at 700NM (Wen & Kanai, 2006). The results obtained are excellent and upto the standard. The result of experiment is shown in Fig. 1.

Table-2: Percentage of light transmission at various wavelengths

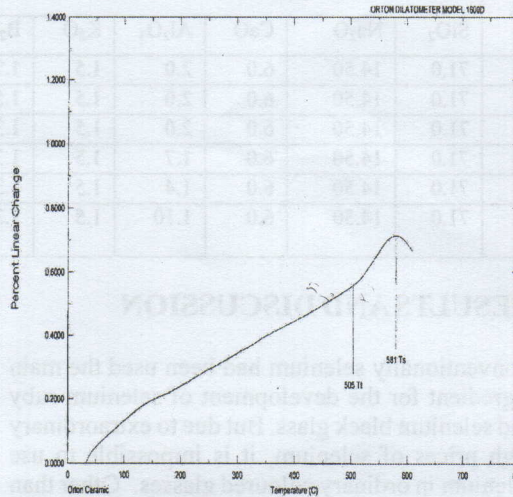
LIGHT TRANSMISSION			
*** DATA PRINT ***			
λ	T%	λ	T%
800.0	8.6	780.0	5.0
760.0	2.0	740.0	1.8
720.0	1.4	700.0	1.0
680.0	1.0	660.0	1.1
640.0	1.0	620.0	1.2
600.0	1.1	580.0	1.2
560.0	1.5	540.0	1.7
520.0	2.0	500.0	2.1
480.0	2.7	460.0	3.5
440.0	4.7	420.0	5.8
400.0	8.5		

Table-1: Light transmission curve at various wavelengths



Thermal Expansion: Specimens of size 25mm length and 5mm diameter were prepared and studied on the apparatus called dilatometer. After calculations, the thermal expansion of the best sample was determined as 101×10^{-7} which is upto the standard. The result of experiment is shown in Fig. 2.

Fig-2: Thermal expansion of the sample with gradual increase of temperature



Conclusion: It is concluded that it is possible to manufacture economical high quality black glass without addition of highly expensive selenium metal powder. Alternate colouring agents are Cr₂O₃ 1.5%, MnO₂ 2.8%, NiO 0.2%, CoO 0.06%. These ingredients do not increase appreciably the cost of glass. The colour of glass does not impair at high temperature or by prolong heating. Excessive oxidizing or reducing melting conditions are not required as are required when selenium is used.

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INTRODUCTION

The mobility of a natural clay or soil as a barrier against the migration of contaminants towards the groundwater is usually assessed by evaluating mineral parameters such as mineralogical composition, specific surface area (SSA) and cation exchange capacity (CEC) (Rosen and Canda, 1977). The actual form of fraction of sorbed contaminants to the components of the clay soil is not considered (Baron and Roman, 1988). The objective of the presented laboratory study was to compare the evaluation of retention processes of heavy metals in natural clays with the separation of the sorbed metals by using sequential extraction procedures. Knowledge of chemical speciation is important in evaluating the mobility and toxicity of heavy metals. In general, the organic forms of metals are more toxic than their inorganic forms. In environmental samples such as soils or sediments, it is important to ascertain the availability and distribution of metals. Foster et al. (1977) developed a method for sequential extraction that separates metals in sediments into five different metal fractions: (1) Exchangeable, (2) bound to carbonates, (3) bound to iron and manganese oxides, (4) bound to organic matter and (5) Residual heavy metal fractions. In each of these fractions have different (or) mobilization behaviors under specific environmental conditions. This well established method has been