SELENIUM BLACK GLASS*

By Chester R. Austin and John D. Sullivan

Abstract

A black glass was made by melting a soda-lime-silica glass under a reducing atmosphere with the addition of 0.6% of selenium and 0.1% of cobalt carbonate, $CoCO_3$. The light absorption of a specimen about 0.01 inch thick in the range of 400 to 750 mμ was superior to that of commercial black glass. The maximum transmission was 27% at 750 mμ. The use of nickel and iron oxides is less effective than cobalt oxide for obtaining selenium black glass.

I. Introduction

In a general investigation on the role and uses of selenium in glass, the production of various colored products was studied. One of the most interesting was black glass of the soda-lime-silica type with only relatively small additions of colorants. The present method of manufacturing black glasses usually involves the addition of substantial amounts of colorants, such as oxides or sulfide of iron or oxides of manganese and iron and oxides of nickel and cobalt. Inasmuch as these additions often amount to 10 to 15% of the entire batch, the working properties of the glass are often affected adversely. It would appear, therefore, that a batch composition and a process to obtain a black glass containing only minor amounts of color-producing ingredients would be useful.

II. Experimental Work

The authors have discussed the experimental procedure and results in producing a selenium ruby glass,[1] and as the general operations used were the same, they are not repeated here. All of the results given here are on base glasses in the following composition ranges:

Ingredient	Weight (%)
SiO_2	69–74
Al_2O_3	1– 4
$Na_2O + K_2O$	13–16
$CaO + MgO$	7–13

Most of the work was done with a 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 of the experiments were made in crucibles up to 3000-gm. batch capacity with natural gas as the fuel. The term "reducing atmosphere" above the melt as used in this paper indicates one which contains no free oxygen and from 1 to 4% of free carbon monoxide, CO. The importance of reducing conditions in the retention of selenium has been pointed out in the previous paper.[1] In the present work on black glass, experiments were made with oxidizing and reducing atmospheres. Reducing agents were not added to the batch in most cases, but they are even more effective in retaining selenium than reducing atmospheres.[1]

(1) Effective Additants

The addition of oxides or oxide-forming compounds of cobalt, nickel, or iron with selenium was effective in producing a black glass. Cobalt was the most effective, and the best black was obtained from a batch containing 0.6% of selenium and 0.1% of cobalt carbonate. Larger amounts of selenium were not necessary. The best procedure in making the black glass was to melt at about 2700°F., cool, and form.

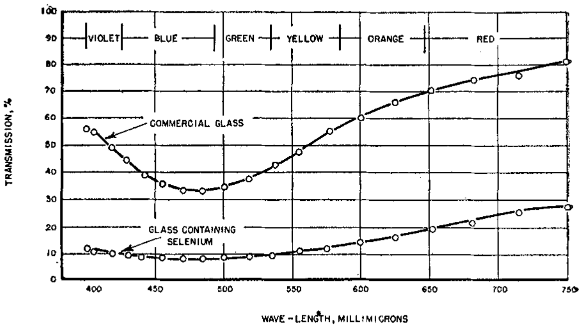

Fig. 1.—Transmission curves; specimen 0.01 in. thick.

Figure 1 gives transmission curves of black glass, which was 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 mμ. The specimens were approximately 0.01 in. thick. The experimental glass contained 0.18% of Se. The selenium-cobalt glass was superior in absorption in the "black range." Its maximum transmission up to 750 mμ was 27%, whereas the minimum transmission for the commercial glass was 34% at 475 mμ, and at 750 mμ, the transmission was 82%.

(2) Effect of Amount of Selenium Added

In the crucible melts with reducing atmospheres of the type used, it appeared necessary to use about 0.6% of selenium in the batch. Additions of 0.4% gave a black color but one not so opaque as with the larger addition. In this connection, however, the retention of selenium in the final melt rather than the amount

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[1] J. D. Sullivan and C. R. Austin, "Selenium Ruby Glass," this issue, pp. 123–27.

added in the raw batch is the governing factor. On the basis of the work done, it would appear to be necessary to have at least 0.15 to 0.20% of selenium in the final glass. This retention might be effected by the addition of a small amount of a reducing agent to the batch even if less than 0.6% of selenium is used initially. If the atmosphere is oxidizing enough, selenium is not retained even when 0.6% is added. In a test maintaining 3% of free oxygen in the atmosphere above the melt and with no reducing agent in the batch, the final glass had 0.02% of selenium. This glass was not black, but due to the cobalt, it had a blue color.

The work also indicated that 0.05% of $CoCO_3$ was not enough to produce a black color when 0.4% of selenium was used in the batch.

(3) Iron and Nickel Oxides

Oxides of iron and nickel were not so effective as cobalt. Nickel oxide yielded an opaque black glass, but the color had a brownish-black cast. It also appeared necessary to add more Ni_2O_3 than CoO. The color from iron additions likewise was on the brownish-black side, and more Fe_2O_3 than CoO was necessary.

III. Discussion

The results indicate that it is possible to get an excellent black glass with only minor additions of colorants. Less than 0.2% of selenium and less than 0.1% of cobalt (0.1% of $CoCO_3 \approx$ 0.05% of Co in batch) would seem to be necessary in the final melt to give a black color. 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. There should be commercial applications both in pressed ware and in structural type of glass.

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ZIRCONIUM OXIDE AND THORIUM OXIDE IN CERAMICS*

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ABSTRACT

The properties of the most important zirconium compounds are correlated to the main ceramic applications of these compounds, namely, refractories, ceramic bodies, binders, cements, glazes, glasses, and enamels. A brief survey of the information available on the systems $MgO-ZrO_2$, TiO_2-ZrO_2, $SiO_2-Na_2O-ZrO_2$, and several other systems is included. The more specific ceramic properties are summarized in short descriptions of the applications to each single ceramic field. The ceramic uses of thorium oxide are listed.

I. Introduction

Engineering is predominantly responsible for the progress of the ceramic industries. Energy-saving mass production has not only increased the importance of these industries but has also financed ceramic research and has stimulated new pioneer branches of ceramics. This present development might be called the third period of ceramic knowledge. The first is the hit-and-miss period of valuable traditions which covers several thousand years, and, in many branches of ceramics, it reaches well into the present century. The second period is closely related to the chemical achievements of the 19th century. Chemistry and physics first analyzed the traditional experience of the preceding period, and then, rapidly and systematically, introduced elements, compounds, processes, and research methods to achieve an admirable expansion. The development of optical glasses and of ceramic colors is an example of this period.

In the present period, chemical and physical research is continuing as the faithful servant of ceramic engineering. Apart from the perpetual value of continued fundamental research, another lasting task of chemical and physical investigations of immediate service to these industries is the utilization of raw materials of local importance or of low cost and the development of rarer materials.

Are all rare materials definitely applicable to the ceramic industry, or must they be excluded from it? Can it be that rarity, an unchangeable attribute of certain forms of matter, is sometimes confused with the fluctuating attributes of availability and cost? A chart of the occurrence of some elements in the earth's crust (Fig. 1) proves that there is a tendency to consider some elements as being rare which do not belong in this classification. The height of the twelve steps on the chart symbolizes the occurrence of a number of elements on a logarithmic scale. The lowest step represents an occurrence of 10^{-10}%, the highest an occurrence of 10%.

Zirconium, thorium, cerium, and the rare earths are so-called rarer materials. These elements, which can be useful for ceramic ware, are the subject of this discussion. None will be found on any of the lower steps; rather, all of them occur in an abundance of $^1/_{1000}$ to $^1/_{100}$%. Beryllium precedes such familiar ele-

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