ORIGINAL PAPERS AND DISCUSSIONS

THE COMPOSITION OF BARIUM GLASS¹

BY ROBERT J. MONTGOMERY

ABSTRACT

In this paper the relation between the composition of barium glasses and the optical constants is discussed as well as the general rules for proportioning batches. The important results and conclusions are given by the figures. After the required amounts of BaO and B₂O₃ have been obtained from figures 2 and 3, the amount of SiO₂ can be obtained from figure 5, the alkali and ZnO from figure 7 and the Al₂O₃ from figure 8. If the total exceeds 100, the ZnO and the Al₂O₃ may be reduced. The proportions cannot be as definitely expressed as in the case of lead glasses and more experience is required to enable one to change the optical properties at will.

Introduction

In a previous paper,² the optical glasses whose main component is lead were discussed. The present paper covers another section of the optical glass field and includes those glasses whose properties are dominated by their barium oxide content. The composition of barium glasses is not as easily covered as that of lead glasses, because of the greater complexity of the batch. With lead glass we have essentially a three component system of alkali, lead and silica, while in barium glasses we have a second acid (B₂O₃) introduced, as well as Al₂O₃ and a more complicated RO containing zinc and calcium in addition to alkali and barium. The zone covering the relation of optical properties to composition, which is narrow in the case of the lead glasses, is here much wider with a dispersion, as expressed by the ν value, ranging from 54 to 61 and an index of refraction for the D line, from 1.50 to 1.63. The composition is further complicated by the use of lead in the baryta flint

¹ Received April 2, 1921.

² THIS JOURNAL, 3, 900 (1910)

glasses. These lie between the typical barium glasses and the lead glasses proper and their composition will not be discussed in this paper. In the paper on lead glasses referred to above the compositions were discussed on the equivalent weight basis because of their simplicity. With barium glasses it was found that little or nothing was gained by employing the equivalent weight basis because of the complexity of the glasses. There are no simple relations between composition and optical properties and the relations observed have to be expressed in more general terms. For this reason the composition will be given in weight per cents

$$\nu = \frac{N_D - 1}{N_F - N_C}$$

of the oxides present. The optical properties referred to are the refractive index for the D line, N_D , and the reciprocal dispersion or constringence ν , defined by the equation.

In figure 1 are plotted the optical properties of 28 typical barium glasses whose compositions are given in table 1. These extend from the ordinary crown glass as a base through the barium silicate crowns, and the dense barium crowns to the densest barium crown. The relation of these glasses to the general field may be seen by referring to the chart given in a previous paper.¹ The baryta

¹ THIS JOURNAL, 3, 404-10(1920).

TABLE I

No.	SiO ₂	B ₂ O ₃	K ₂ O	NaO	BaO	CaO	ZnO	As ₂ O ₃	Al ₂ O ₃	PbO	Nb
1	71.56	...	9.01	8.08	2.61	8.02	...	0.72	...	...	1.5160
2	68.50	3.50	5.00	12.00	9.70	...	1.00	0.20	...	...	1.5179
3	64.60	2.70	15.00	5.00	10.20	...	2.00	0.40	...	...	1.5179
4	67.00	3.50	5.00	12.00	10.60	...	1.50	0.40	...	...	1.5171
5	59.13	3.04	9.70	3.16	19.25	0.13	5.00	0.34	0.11	...	1.5409
6	49.57	4.51	8.49	1.01	26.06	...	10.03	0.34	...	...	1.5666
7	48.10	4.60	8.00	2.00	26.05	2.00	8.40	0.50	...	...	1.5755
8	48.10	4.50	7.50	1.00	28.30	...	10.10	0.40	...	...	1.5726
9	48.00	4.50	6.10	2.00	29.50	...	10.00	1.40	...	...	1.5754
10	48.45	3.65	7.55	0.95	32.63	...	6.46	0.32	...	...	1.5727
11	37.23	6.02	...	3.19	40.40	...	10.79	0.37	1.98	...	1.6167
12	37.30	6.00	...	3.20	40.50	...	10.80	...	2.00	...	1.6097
13	37.50	15.00	...	...	41.00	...	...	...	5.00	...	1.5899
14	34.50	10.10	...	...	42.00	...	7.80	0.50	5.00	...	1.6088
15	39.63	6.04	...	...	42.08	...	9.24	0.50	2.50	...	1.6054
16	36.28	5.57	3.20	...	43.62	0.21	10.73	0.39	...	...	1.6147
17	37.00	5.00	2.60	...	44.00	...	7.70	0.70	...	3.00	1.6242
18	39.60	5.00	...	...	44.00	2.00	7.70	0.40	...	3.00	1.5905
19	39.00	5.00	...	...	45.00	2.60	7.00	0.40	1.00	...	1.6145
20	37.80	5.69	3.50	...	45.04	...	7.56	0.40	...	...	1.6085
21	34.56	10.96	0.09	0.21	46.91	...	1.14	0.59	5.02	...	1.6091
22	37.00	5.00	2.60	...	47.00	...	7.70	0.70	...	...	1.6177
23	32.27	12.90	0.33	...	47.20	...	1.12	0.20	6.10	...	1.6139
24	38.29	5.76	2.84	...	47.60	...	5.11	0.41	...	...	1.6085
25	38.12	7.18	2.40	...	49.37	...	2.54	0.41	...	...	1.6062
26	36.58	11.60	0.10	0.22	49.66	...	1.21	0.62	...	...	1.5991
27	36.46	8.91	1.21	...	52.88	...	...	0.39	...	...	1.6091
28	36.51	8.93	1.22	...	52.96	...	...	0.39	...	...	1.6138

References—C. N. Fenner, *This Journal*, 2, 102(1919).Williams and Rand, *Ibid*, 2, 422(1919).Allen and Zies, *Ibid*, 1, 739(1918); Doelter's "Handbuch der Mineralchemie."

light flint, telescope flint and soft silicate crown are omitted because of the lead content although they contain considerable barium. Only one barium silicate crown glass was available but the others used are selected from a great many obtained from experimental melts in our plant, and from published information. On first consideration the scattered positions of the points seem to show little regularity. A further study reveals certain underlying relations and these will now be discussed.

BaO vs. Optical Properties

When it is desired to increase the index of refraction in a soda-lime glass without lowering the ν value, barium is used. The dispersion is not affected to any extent by the barium and we may have more than 40 per cent BaO in glasses whose ν values vary only from 53 to 60. The line A-A in figure 1 shows the effect of the addition of barium to a soda-lime glass. The ν value decreases not because of the increased barium but because of the decrease in SiO_2 which the barium displaces. The normal index of refraction of a soda-lime glass is about 1.51, largely due to its content of silica which has an index of 1.4585. It may be raised as high as 1.52 to 1.53 by the addition of lime, but above this point we have to

resort to barium if the ν value is not to be lowered. The relation between the increase of index and the barium content is very nearly a straight line as the barium increases up to 40 or 42 per cent. This relation is shown graphically in figure 2. Above 42 and up to 54 per cent, which is about the maximum in these glasses, very little change in index is noted, the line becoming practically horizontal. The points do not lie as closely to the line as could be wished, but as the index is affected by the other constituents the variation is not unexpected. Glass number 17 contains 3 per cent of PbO which is responsible for its rather high index. Barium cannot be studied without the introduction of B_2O_3 , since with the higher percents of BaO, boric acid is necessary in order to prevent crystallization on cooling. The effect of B_2O_3 will therefore be shown next in conjunction with SiO_2 as both have to be considered together in a discussion of optical properties.

B_2O_3 and SiO_2 vs. Optical Properties

In considering the effect of these two materials their optical properties must be kept in mind. They are as follows: Boric acid glass N_D 1.463, ν 59.4; Silica glass N_D 1.4585, ν 67.9.

Their influence on the optical properties of glass are quite consistent except in one case. In a high BaO glass, SiO_2 will lower the index more than will B_2O_3 . For some unknown reason an addition of B_2O_3 will often *raise* the index of refraction in both barium and lead glasses when the index is about 1.60. It very seldom causes a drop in index although the index of boric acid glass is low.

Soda-lime glasses and glasses of this general type containing small amounts of barium are dominated by the properties of silica, and have an index of about 1.518 and a ν value of about 58 to 60. The effect on the dispersion, of the B_2O_3 which may be present up to 5 per cent, is not noticeable. In the glasses high in BaO, which have a correspondingly low SiO_2 content, the effect of B_2O_3 is more easily seen. It is quite apparent when the index is 1.59 or above. The line B-B in figure 1 shows the tendency of B_2O_3 to increase the ν value when the SiO_2 content is constant. In figure 3 the relation between B_2O_3 and the dispersion is given. Glasses with an index of 1.59 or above are indicated by crosses and the heavy line curve passes through these points. The

glasses containing less than 6 per cent B_2O_3 evidently fall into another group indicating that the higher ν value may be obtained with silica as well as with B_2O_3 . A dash line passes through this group. The variation in dispersion is evidently limited by the optical properties of SiO_2 and B_2O_3 and the amount of each which can be introduced into a commercial glass.

Figure 4 shows the relation between SiO_2 and the ν value in those glasses containing less than 6 per cent B_2O_3 . This includes the group through which the dash line is drawn in figure 3.

There are a number of general relations referring to the proportioning of the constituents of the batches which may be shown in curve form. These are as follows:

SiO_2 vs. BaO

The relation between the barium and silica content is clearly shown in figure 5. The required proportions are quite well defined, a decided drop in the silica content as the barium increases being noticeable.

SiO_2 vs. Alkali

As would be supposed, the amount of alkali in the glass increases with the silica. The curve in figure 6 shows this relation. While the points are not all very close to the curve drawn the general relation is beyond question. It must be remembered that in these complex barium glasses a comparison of any two constituents will be affected, often to a considerable extent, by the other constituents present. Only general relations can be established.

The Proportioning of the RO Bases

In figure 7 the relation between BaO and the other RO bases is shown. The solid line goes through the total RO bases except BaO and includes K₂O, Na₂O, CaO, ZnO and PbO. The dash

line runs through the points representing the alkali content including K_2O and Na_2O . The positions of the two curves are fairly well defined except when the BaO is over 40 per cent. Some of the glasses contain no alkali while others contain 2 to 3 per cent. Alkali is not necessary to obtain the desired optical properties and when used it is for the purpose of controlling the melting and working properties of the glass.

The Al_2O_3 Content

It is hard to determine just what the Al_2O_3 content depends on. It is not necessary to use alumina to control the optical properties but it is almost invariably used and the amount seems to depend upon the B_2O_3 content, at least an interesting comparison can be obtained between the amounts of these two constituents. Alumina would tend to increase the viscosity of the glass and reduce the attack upon the pot.

In figure 8 the Al_2O_3 and B_2O_3 contents are plotted against each other and an average curve is given. Al_2O_3 is seldom used until the glass contains at least 5 per cent B_2O_3 and then it increases quite rapidly with the addition of B_2O_3 reaching a maximum at about 6 per

cent. Points 25, 26, 27, and 28 are not on the curve and they are rather abnormal in this respect. They prove that the optical properties do not depend upon the Al_2O_3 .

The ZnO Content

Zinc oxide may run as high as 11.0 per cent in these glasses but it has little effect upon the optical properties. It is used largely to fill in when it is undesirable to increase any of the other constituents. Zinc oxide may replace BaO to lower the index of refraction or replace B_2O_3 to lower the ν value.

Alkali

Potassium is the alkali almost invariably used because the sodium compounds give greater color. The amount used depends upon the flux required after the SiO_2 , BaO, B_2O_3 contents are adjusted to give the proper optical constants.

BAUSCH & LOMB OPTICAL CO.,
ROCHESTER, N. Y.