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SOME "SOFT" GLAZES OF LOW THERMAL EXPANSION

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ABSTRACT

Compositions in the ternary field $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ were studied as potential glazes both with and without the addition of 5 percent of Al_2O_3 . Compositions within a very small field (25 to 40 percent of PbO ; 15 to 30 percent of B_2O_3 ; and 40 to 55 percent of SiO_2) show promise as glazes maturing at temperatures below $1,150^\circ\text{C}$ on talcose bodies of relatively low thermal expansion. Low resistance to solution by weak acids may limit their application to wares which do not come in prolonged contact with food.

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I. INTRODUCTION

The need for glazes of relatively low maturing temperature and thermal dilatation, occasioned by the development of talcose bodies of similar characteristics,¹ was the incentive for a study of lead borosilicate glasses as a corollary of phase-equilibria determinations in the system $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$.² That glasses of this type might logically be expected to have a low thermal expansion is evident from the expansion coefficients of the constituents.³ The principal difficulty anticipated was that of low resistance to solution, as has been shown by numerous investigators, more recently by J. H. Koenig.⁴

II. MATERIALS AND METHODS

The materials for preliminary melts were sublimed litharge (PbO) containing 0.02 percent of total detected impurities; boric acid of reagent quality; pulverized quartz (SiO_2) containing 0.02 percent of nonvolatile residue; and Al_2O_3 of 99.95 percent purity. Commercial Pennsylvania "potter's flint", and Georgia kaolin containing 45.3 percent of SiO_2 and 39.1 percent of Al_2O_3 as the source of Al_2O_3 , were used in the larger batches, together with the litharge and boric acid described.

¹ R. F. Geller and A. S. Creamer. *J. Am. Ceram. Soc.* **20**, 137 (1937).

² A report of the first phase of this equilibria study has been published (R. F. Geller and E. N. Bunting, *The system PbO-B₂O₃*, *J. Research NBS* **18**, (1937) RP995).

³ F. P. Hall. *J. Am. Ceram. Soc.* **13**, 182 (1930).

⁴ Lead Frits and Fritted Glazes, Ohio State Eng. Exp. Sta. Bul. 95 (1937).

Preliminary melts were fused in platinum and ground in agate mortars. For larger batches, the frit was fused in clay crucibles, using a gas-fired pot furnace, and the glaze mixtures were ground in ball mills to pass a No. 100 sieve. Portions of the preliminary melts were used for determining initial softening temperatures (T_s), linear thermal expansions, and solubility in the powdered form. Portions of the larger batches were used to prepare glazed specimens for determining workability of the slip, maturing temperatures, solubility in situ, and appearance. For convenience, the small preliminary melts will be referred to as glasses (table 1), and the larger batches will be referred to as glazes (table 2). All materials in the glazes not introduced as clay were fritted. The glaze trials were "glost fired" in electrically heated ovens.

TABLE 1.—Compositions of glasses, softening temperatures, linear thermal expansion, and solubility in the powdered form

| Glass | Preliminary melts, composition G | | | Softening (T_s) | | Expansion, coefficient room temperature to 300° C | | | |
|-------|----------------------------------|-------------------------------|------------------|---------------------|--|---|--|-------------------------|--|
| | PbO | B ₂ O ₃ | SiO ₂ | G | G, plus 5% of Al ₂ O ₃ | G | G, plus 5% of Al ₂ O ₃ | Solubility ^a | |
| | | | | | | | | G ₂ | G ₂ , plus 5% of Al ₂ O ₃ |
| | % | % | % | °C | °C | ×10 ⁻⁴ | ×10 ⁻⁶ | % | % |
| 1 | 10.0 | 9.7 | 80.3 | 737 | 737 | 2.1 | | | 0 |
| 2 | 9.9 | 19.5 | 70.6 | 685 | 703 | 2.8 | 2.4 | 5 | 7 |
| 3 | 19.8 | 10.0 | 70.2 | 735 | 719 | 2.5 | 2.3 | tr | 0 |
| 4 | 8.9 | 29.1 | 62.0 | 624 | | 3.4 | | 80 | 91 |
| 5 | 19.8 | 19.2 | 61.0 | 722 | | 3.2 | | 5 | 34 |
| 6 | 29.5 | 9.9 | 60.6 | (b) | | 3.1 | | 9 | 4 |
| 7 | 8.7 | 30.7 | 51.6 | 535 | 561 | 4.7 | 4.6 | 100 | 100 |
| 8 | 19.4 | 28.9 | 51.7 | 655 | | 3.7 | | 68 | 94 |
| 8½ | 24.8 | 24.0 | 51.2 | 696 | 658 | 4.0 | 3.8 | 15 | 99 |
| 9 | 30.1 | 19.2 | 50.7 | (b) | | 3.9 | | 43 | 54 |
| 10 | 39.9 | 10.0 | 50.1 | (b) | 596 | 4.2 | 3.7 | 79 | 12 |
| 11 | 10.1 | 48.9 | 41.0 | 519 | | 5.4 | | | |
| 12 | 20.0 | 39.7 | 40.3 | 546 | | 4.3 | 4.4 | | 100 |
| 13 | 30.2 | 29.3 | 40.5 | (b) | 645 | 4.6 | 4.3 | 95 | 100 |
| 14 | 40.4 | 19.7 | 39.9 | (b) | 643 | 4.7 | 4.4 | 89 | 98 |
| 15 | 50.2 | 10.2 | 39.6 | (b) | | 5.3 | | 90 | 42 |
| 16 | 10.2 | 59.5 | 30.3 | 413 | ° 475 | | | | |
| 17 | 20.6 | 49.0 | 30.4 | 489 | | 5.9 | | | |
| 18 | 30.4 | 39.0 | 30.6 | 554 | | 5.5 | | | |
| 18½ | 35.3 | 34.0 | 30.7 | | ° 616 | | 5.0 | | 100 |
| 19 | 40.2 | 29.1 | 30.7 | (b) | | 5.4 | | | |
| 20 | 50.2 | 19.9 | 29.9 | (b) | | 5.3 | | | |
| 21 | 60.1 | 10.3 | 29.6 | 487 | 514 | 7.9 | 5.9 | 95 | 98 |
| 22 | 10.0 | 68.9 | 21.1 | 374 | | 7.8 | | 97 | 73 |
| 23 | 20.5 | 59.6 | 19.9 | 399 | | 7.1 | | | |
| 24 | 30.6 | 49.1 | 20.3 | 489 | | 6.3 | | | |
| 25 | 40.2 | 39.6 | 20.2 | 512 | | 6.0 | | | |
| 26 | 50.5 | 29.2 | 20.3 | 502 | | 6.2 | | | |
| 27 | 60.4 | 19.4 | 20.2 | 475 | | 6.3 | | | 97 |
| 28 | 69.9 | 10.2 | 19.9 | 460 | | 7.9 | | | 94 |
| 29 | 10.2 | 79.9 | 9.9 | 331 | 443 | | | | |
| 30 | 20.2 | 69.9 | 9.9 | 360 | | 8.9 | | | |
| 31 | 30.1 | 59.9 | 10.0 | 481 | ° 478 | 8.2 | 6.5 | | |
| 32 | 40.2 | 49.9 | 9.9 | 501 | | 6.9 | | | |
| 33 | 50.2 | 39.8 | 10.0 | 510 | | 6.4 | | | |
| 34 | 60.1 | 29.9 | 10.0 | 498 | 496 | 7.0 | 6.6 | | |
| 35 | 70.1 | 19.9 | 10.0 | 461 | | 7.6 | | | |
| 36 | 80.0 | 10.1 | 9.9 | 392 | 409 | 9.8 | 9.3 | | 100 |

^a Compositions G₂ were prepared using the same batch composition and procedure used in preparing compositions G, but were not analyzed. Solubility values show the PbO extracted, expressed as the percentage of total PbO in the glaze.

^b Samples crystallized before a normal softening temperature was reached.

^c Samples showed slight opalescence after the expansion test.

TABLE 2.—Compositions of prepared glazes

| Glaze | Chemical | | | | Empirical (molecular ratios) | | | |
|-------|----------|--------------------------------|-------------------------------|------------------|------------------------------|--------------------------------|-------------------------------|------------------|
| | PbO | Al ₂ O ₃ | B ₂ O ₃ | SiO ₂ | PbO | Al ₂ O ₃ | B ₂ O ₃ | SiO ₂ |
| | % | % | % | % | | | | |
| 5-9 | 23.8 | 5.0 | 18.8 | 52.4 | 1.00 | 0.49 | 2.73 | 9.02 |
| 6-9 | 28.5 | 5.0 | 14.1 | 52.4 | 1.00 | .39 | 1.66 | 7.15 |
| 8½ | 24.7 | 4.9 | 23.2 | 47.2 | 1.00 | .43 | 3.02 | 7.11 |
| 9 | 28.5 | 5.0 | 18.7 | 47.8 | 1.00 | .40 | 2.24 | 6.86 |
| 9½ | 33.6 | 4.9 | 14.0 | 47.5 | 1.00 | .34 | 1.50 | 5.70 |
| 8-13 | 23.7 | 5.0 | 28.5 | 42.8 | 1.00 | .52 | 4.34 | 7.58 |
| 9-13 | 28.5 | 4.9 | 23.1 | 43.5 | 1.00 | .38 | 2.67 | 5.99 |
| 9-14 | 33.3 | 5.0 | 18.8 | 42.9 | 1.00 | .35 | 1.91 | 5.29 |
| 10-14 | 38.4 | 5.0 | 14.0 | 42.6 | 1.00 | .28 | 1.17 | 4.13 |
| 13 | 28.5 | 4.8 | 27.5 | 39.2 | 1.00 | .37 | 3.09 | 5.12 |
| 14 | 38.1 | 5.0 | 18.8 | 38.1 | 1.00 | .29 | 1.58 | 3.72 |

To determine SiO₂ and R₂O₃, 0.5-g samples were fused with Na₂CO₃, dissolved in hot dilute HCl, evaporated almost to dryness, and the moist residue evaporated three times with 10 ml of C₂H₅OH saturated with HCl. This removed the B₂O₃. Silica was then determined in the usual way and the remaining R₂O₃ determined by double precipitation with NH₄OH.

PbO was determined on 0.5-g samples evaporated two or three times with HF and HNO₃ to remove SiO₂ and B₂O₃. HNO₃ was then added and PbO₂ deposited electrolytically. This deposit, after having been dissolved in dilute HNO₃ and C₂H₅OH, was converted to PbSO₄ and weighed as such.

B₂O₃ was determined by difference.

Data for establishing the T_s values and coefficients of linear thermal expansion were obtained by the interferometer method using specimens, approximately 3 mm in diameter, which had been fused in platinum capsules.

Resistance of pulverized glass samples to solution was determined by boiling 0.5 to 1.0 g of "through 200, on 325 mesh" material in 200 ml of a 4-percent acetic acid solution. The PbO dissolved was estimated by titrations with ammonium molybdate solution, using tannic acid solution as the external indicator.⁵ Specimens having approximately 12 in.² of glazed surface were subjected to the same treatment, but the amount of solution was estimated by precipitating the dissolved lead with H₂S and comparing the darkened solution with standards containing known amounts of Pb, also precipitated with H₂S. In addition, a limited number of tests were made by boiling glazed specimens in a 2-percent solution of potassium carbonate. In preparing glazed specimens for solubility tests, approximately 0.1 g of glaze was applied per square inch of surface.

III. RESULTS

1. GLASSES

Most of the Al₂O₃-free glasses become opalescent or opaque on cooling, only those of low PbO and high (60 percent or more) SiO₂ content, and those of high (60 percent or more) PbO with 20 percent or less of SiO₂ being clear. The addition of 5 percent of Al₂O₃ gave

⁵ This is the method used by Koenig. See footnote 4.

clear glasses, except with 60 percent or more of B_2O_3 and 10 percent of PbO .

Values for initial softening temperature (T_s) and for linear thermal expansion are given in table 1 and indicated by iso-lines in figure 1. For the sake of uniformity, average expansion coefficients are given for the range from room temperature to $300^\circ C$, because, in many instances, the first "break" or lower critical temperature (T_c) was found below $400^\circ C$.

In general, the expansions increase with increasing PbO or B_2O_3 content, but the relation is not linear. At a constant SiO_2 level, the addition of B_2O_3 in place of PbO at first reduces the expansion, becomes a minimum at approximately equal PbO and B_2O_3 content, and then increases again with increase of B_2O_3 . For example, at approximately 20 percent of SiO_2 and 20, 40, 60, and 80 percent of PbO , the expansions to $300^\circ C$ are 19, 16, 17, and $27 \mu/cm$, respectively. The corresponding average coefficients are 7.1, 6.0, 6.3, and 9.6×10^{-6} . At the 70-percent SiO_2 level, for 10 and 20 percent of PbO , the expansions are 7.6 and $6.8 \mu/cm$, the corresponding coefficients being 2.8 and 2.5×10^{-6} . The addition of 5 percent of Al_2O_3 to these glasses lowers the expansion by about 10 percent.

The softening point decreases with increasing PbO and B_2O_3 content but not in a linear manner. In most cases, the addition of 5 percent of Al_2O_3 raised the softening point, but in melts 3 and $8\frac{1}{2}$ (table 1) it was lowered, while melts 31 and 34 were practically unaffected.

Solubility values for pulverized samples are given in table 1 and indicated by lines of equal solubility in figure 2. All lead borate glasses (200 to 325 mesh) are completely dissolved by boiling in 4-percent acetic acid, while lead silicates containing over 83 percent of PbO have all the PbO extracted. At 60 percent of PbO and 40 percent of SiO_2 , only 9 percent of the PbO is extracted by this treatment and the addition of 5 percent of Al_2O_3 to this composition reduces the extraction to 1 percent. However, the addition of B_2O_3 increases the amount of extractable PbO ; for example, at 50 percent of SiO_2 , 40 percent of PbO , and 10 percent of B_2O_3 , about 75 percent of the PbO is dissolved. At 70 percent of SiO_2 , 20 percent of PbO , and 10 percent of B_2O_3 , only a trace of PbO is dissolved, whereas at 70 percent of SiO_2 , 10 percent of PbO , 20 percent of B_2O_3 , about 5 percent of PbO is extracted. The addition of 5 percent of Al_2O_3 has the unexpected effect of increasing the solubility of many compositions.

These values for solubility have significance in a relative sense only, probably because of the effect of surface area, which is very difficult (if not impracticable) to control in pulverized material. Determinations on portions of the same "grind" checked within ± 1 percent, but determinations on samples ground at different times varied as much as ± 15 percent. The shaded area in the right-hand diagram of figure 2 indicates the field of compositions chosen as potential glazes. This may appear unwarranted because of the high solubility in the pulverized form; however, their solubility as glazes in situ is much lower, as is shown by the values in table 5.

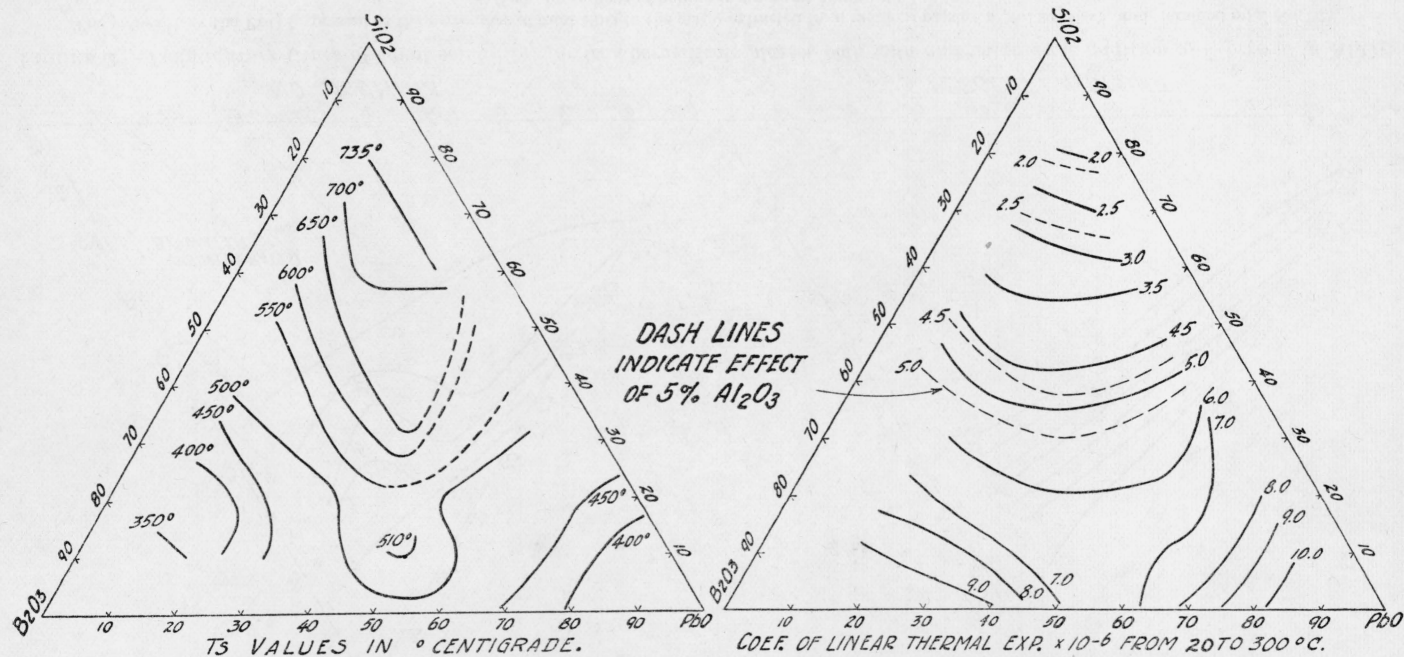


FIGURE 1.—Initial softening temperature (T_s) and linear thermal expansion of lead borosilicate glasses.

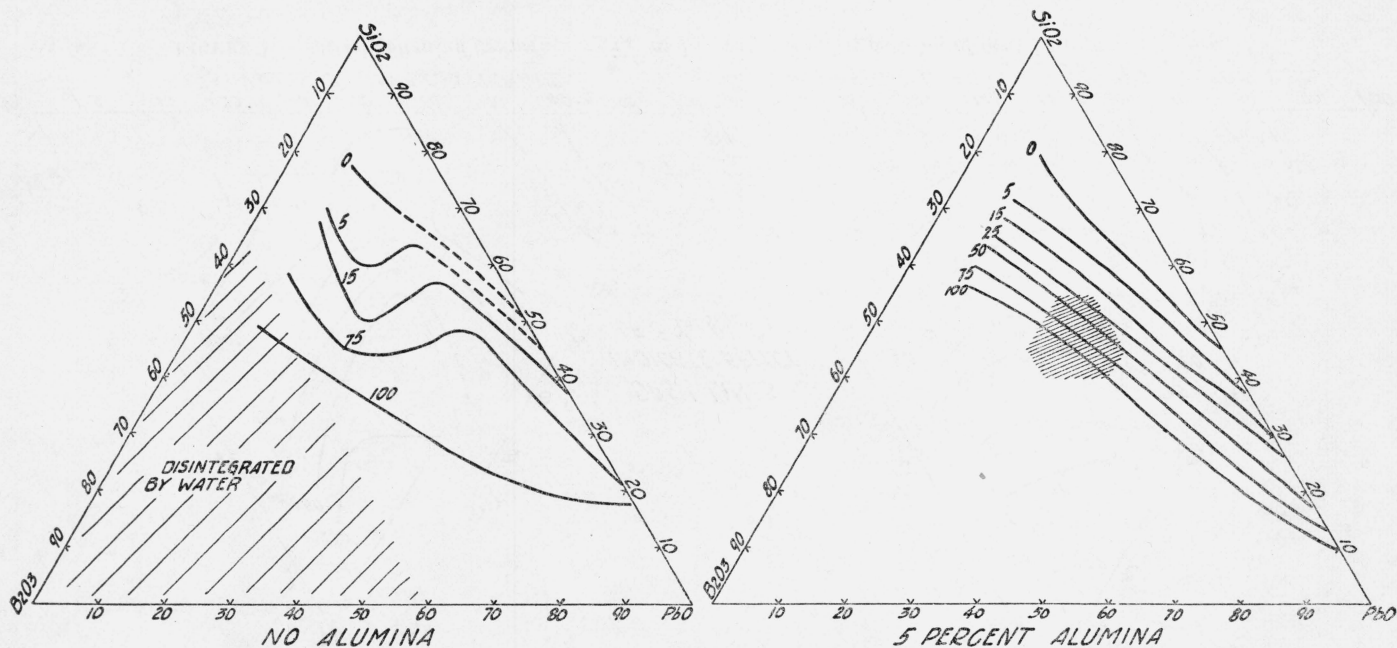


FIGURE 2.—Isolytic lines (lines of equal solubility) for lead borosilicate glasses both with and without the addition of 5 percent of Al_2O_3 .

The values show the PbO (expressed as the percentage of total PbO in the glaze) extracted from material passing a No. 200 sieve, and retained on a No. 325 sieve, by $\frac{1}{2}$ hour of boiling in 4-percent acetic acid.

2. GLAZES

Open circles in figure 3 indicate the theoretical compositions selected for study as glazes, while the actual compositions⁶ are indicated by filled circles and are given, also, in table 2. The compositions of the frits used in making these glazes are given in table 3.

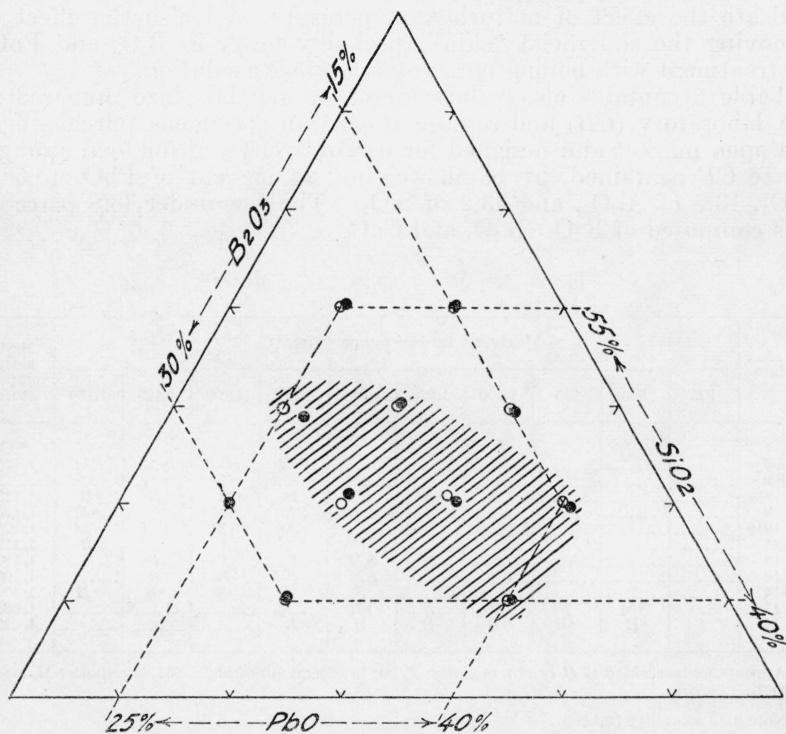


FIGURE 3.—Composition range of lead borosilicate glasses which show promise of being useful as glazes, the most promising lying within the shaded area.

These glasses contain 5 percent of Al_2O_3 .

TABLE 3.—Compositions of frits with which, singly or in combination, the various glazes were prepared

[Composition values are given in percentages by weight]

| Frit | Theoretical | | | Batch | | | Actual | | | |
|------|-------------|------------------------|----------------|-------|-------------------------------------|----------------|--------|-------------------------------------|------------------------|----------------|
| | PbO | B_2O_3 | SiO_2 | PbO | B_2O_3 ^a | SiO_2 | PbO | R_2O_3 ^b | B_2O_3 | SiO_2 |
| 5 | 21.30 | 21.35 | 57.35 | 21.2 | 23.3 | 55.5 | 21.2 | 0.3 | 22.7 | 55.8 |
| 6 | 32.00 | 10.65 | 57.35 | 31.8 | 12.0 | 56.2 | 31.5 | .4 | 11.8 | 56.3 |
| 8½ | 26.65 | 26.65 | 46.70 | 27.4 | 26.8 | 45.8 | 27.2 | .8 | 25.5 | 46.5 |
| 8-13 | 26.65 | 32.00 | 41.35 | 27.1 | 33.3 | 39.6 | 26.5 | .5 | 32.0 | 41.0 |
| 10 | 42.65 | 10.65 | 46.70 | 42.8 | 10.7 | 46.5 | 42.8 | .5 | 10.2 | 46.5 |
| 13 | 32.00 | 32.00 | 36.00 | 31.9 | 32.6 | 35.5 | 31.1 | 1.1 | 30.0 | 37.8 |
| 14 | 42.65 | 21.35 | 36.00 | 42.6 | 21.9 | 35.5 | 42.1 | .6 | 20.8 | 36.5 |

^a Added as boric acid.

^b Dissolved from crucible.

⁶ Actual compositions differ from the theoretical because of PbO and B_2O_3 lost by volatilization during the fritting process.

Maturing ranges of the glazes were judged by the observations recorded in table 4. A glost temperature of 1,150° C (cone 4) was not exceeded because it was considered that satisfactory glazes of comparatively low thermal expansions and maturing at higher temperatures were already available. The "solubility" of the more promising glazes (shaded area, fig. 3) is given in table 5. The values indicate the effect of maturing temperature, and also the effect of removing the superficial "skin" (probably lower in B₂O₃ and PbO) by treatment with boiling potassium carbonate solution.

Table 5 contains also values for a commercial glaze prepared in the laboratory (*CB*) and a glaze (*Com.*) on specimens purchased in the open market and designed for use in ovens and for food storage. Glaze *CB* contained, by batch weights, 24 percent of PbO, 10.5 of B₂O₃, 13.5 of Al₂O₃, and 43.2 of SiO₂. The remainder (8.8 percent) was composed of K₂O, Na₂O, and CaO.

TABLE 4.—*Maturing ranges of glazes*^a

| Glaze | Maximum furnace temperature, °C | | | | | | | | | | Best glost temperature |
|-------|---------------------------------|-----|-----|-------|-------|-------|-------|-------|-------|-------|------------------------|
| | 925 | 950 | 975 | 1,000 | 1,025 | 1,050 | 1,075 | 1,100 | 1,125 | 1,150 | |
| 5-9 | | | | | | | SM | SM | SM | SM | °C |
| 6-9 | | | | | | | | SM | SM | M | 1,125 |
| 8½ | | | | | SM | F | B | B | B | B | 1,125 |
| 9 | | | | | | | SM | SM | F | °B | 1,125 |
| 9½ | | | | | | | SM | SM | SM | SM | 1,125 |
| 8-13 | | | | | | P | SM | F | F | B | 1,150 |
| 9-13 | | | | | M | SM | F | F | F | | 1,100 |
| 9-14 | | | | | SM | SM | F | B | B | | 1,100 |
| 10-14 | | | | | | F | F | F | °B | °B | 1,100 |
| 13 | SM | SM | F | B | B | °B | | | | | 1,025 |
| 14 | F | B | °B | °B | B | B | B | | | | 1,025 |

^a Appearance is recorded as *B*, bright, or glossy; *F*, fair in general appearance; *SM*, semimatte; *M*, matte; *P*, poor.

^b Tendency to run.

^c Note high solubility (table 5).

TABLE 5.—*Solubility of glazes, estimated by comparing precipitated PbS suspension from solubility test with suspension of known PbO content and calculating to grams of PbO dissolved per 100 in.² of glaze surface*

| Glaze | Glost temperature | PbO dissolved | Glaze | Glost temperature | PbO dissolved |
|-------|-------------------|---------------|---------------|-------------------|---------------|
| | °C | g | | °C | g |
| 8½ | 1,050 | 0.0915 | 10-14 | 1,100 | 0.0018 |
| 8½ | 1,125 | .0005 | 10-14 | 1,150 | .0015 |
| 8½ | 1,125 | °.0025 | 14 | 975 | .0240 |
| 8-13 | 1,075 | .0008 | 14 | 1,000 | .0100 |
| 8-13 | 1,150 | .0005 | 14 | 1,025 | .0015 |
| 9 | 1,125 | .0005 | 14 | 1,025 | °.0400 |
| 9½ | 1,125 | .0025 | 14 | 1,075 | .0040 |
| 9-13 | 1,100 | .0010 | ° <i>CB</i> | 1,150 | .0005 |
| 9-14 | 1,100 | .0025 | ° <i>Com.</i> | ----- | .0005 |
| | | | ° <i>Com.</i> | ----- | °.0005 |

^a PbO dissolved in boiling 4-percent acetic acid, after having first treated glaze by boiling for 30 minutes in a 2 percent K₂CO₃ solution.

^b A commercial "cone 3" glaze prepared and applied in the laboratory.

^c Tests made on commercial "ovenware."

IV. DISCUSSION AND CONCLUSIONS

Although the laboratory work on this problem might have been prolonged by studying the effects of Al_2O_3 in percentages other than that reported on (5 percent), it is believed that the data obtained are sufficient to indicate the limited applicability of the lead borosilicate glasses as glazes.

Glasses containing over 55 percent of SiO_2 , or less than 25 percent of PbO and 15 percent of B_2O_3 , are too viscous to mature at or below $1,150^\circ\text{C}$ (approximately "cone 4"), and those containing less than 40 percent of SiO_2 , or more than 40 percent of PbO and 30 percent of B_2O_3 , are too soluble regardless of maturing temperature. Of the compositions within the relatively small, six-sided area (figs. 2 and 3) not covered by the above limitations, those within the shaded area in figure 3 were most promising. Of the six compositions in this area which were studied as glazes, only two could be applied easily and matured over a fairly wide temperature range. One (No. 8½) appeared best after maturing at $1,125^\circ\text{C}$ and the solubility was as low as that of two commercial glazes; the other (No. 14) matured best at $1,025^\circ\text{C}$, but the solubility would probably be too high for containers in which food might be stored.

The addition of Al_2O_3 to glasses in the ternary field $\text{PbO}-\text{B}_2\text{O}_3-\text{SiO}_2$ was necessary to prevent devitrification.

In terms of the "empirical formula" (molecular ratios with RO always equal to 1.0), the best glaze compositions were within the following limits:

PbO 1.0; Al_2O_3 0.28 to 0.43; B_2O_3 1.17 to 3.02; SiO_2 3.72 to 7.11.

W. M. Fickes,⁷ working with glazes in which PbO was the only RO constituent, found that the ratio of SiO_2 to Al_2O_3 should be as 6:1, or higher. C. W. Parmalee and G. A. Williams,⁸ after an exhaustive study of glazes containing B_2O_3 , found 8½ mole percent of B_2O_3 best, with the ratio of SiO_2 to Al_2O_3 as 8:1. In the present group of "best glazes," the mole percentage of B_2O_3 ranged from 17.8 to 26.6 and the ratio of SiO_2 to Al_2O_3 from 12.8:1 to 17.2:1.

Considerable argument may be found in the earlier ceramic literature over the question of considering B_2O_3 as basic or as acid in the empirical formula, which in turn affects the calculation of the "oxygen ratio."⁹ Preponderance of opinion appears to be in favor of considering B_2O_3 as basic.¹⁰ It is interesting that, with the present data, if B_2O_3 be considered as basic, the oxygen ratios of the most promising glazes fall within the narrow range of 1.1 to 1.5 but, if considered as acid, they range from 6.4 to 10.2, and many glazes with ratios within this range are decidedly not usable. Binns (footnote 10) recommends an oxygen ratio of 2 for glazes containing boron, but Stull (footnote 10) found that a ratio 2 or higher produced opalescent glazes, while a ratio of 1.5 produced clear glazes.

The thermal expansion of each of the compositions studied as a glaze is significantly lower than that of typical commercial "semi-porcelain" glazes. The average coefficient from room temperature to 300°C for the former ranges from approximately 3.7 to 4.4×10^{-6} , and from approximately 5.5 to 5.8×10^{-6} for the latter.

⁷ Trans. Am. Ceram. Soc. 3, 82 (1901).

⁸ Trans. Am. Ceram. Soc. 13, 812 (1916).

⁹ An arbitrary ratio between the oxygen in the acid radicals and the oxygen in the basic radicals.

¹⁰ C. F. Binns. Trans. Am. Ceram. Soc. 10, 158 (1908). R. T. Stull. Trans. Am. Ceram. Soc. 12, 129 (1910). F. G. Singer. Trans. Am. Ceram. Soc. 12, 676 (1910).

Glazes 8½ and 14 were applied successfully on each of the talcose bodies described by Geller and Creamer (footnote 1) with the exception of bodies 1 to 4, inclusive, which contained no feldspar. Specimens which were glazed withstood an autoclave treatment in vapor at 400-lb/in.² steam pressure for 4 hours without crazing and without perceptible loss of gloss. However, when immersed in the water, the gloss was affected.

The addition of Al₂O₃ increased resistance to solubility in some portions of the field, and decreased it in others.

The evaluation of laboratory data for relative solubility of lead-bearing glazes, for the purpose of establishing a maximum permissible without constituting a health hazard, is a complex problem. The following extract is from correspondence with W. B. White, of the Food and Drug Administration of the U. S. Department of Agriculture: "The writer's experience of some years on the contamination of foods with lead has left him somewhat skeptical of the value of any test other than actual trial of various types of foods under extreme conditions. This Administration has no official tolerances for Pb except in the case of fresh fruits, where, as yet, no less poisonous insecticides are available for pest control. Here the tolerance is 0.018 grain of Pb per pound of fruit, equivalent to 2.57 parts per million. This tolerance is a recognition that complete elimination by washing, though desirable, is impossible." W. P. Mason¹¹ states: "The writer believes that no water to be used for drinking purposes should contain lead compounds in quantity greater than what would correspond to half a part per million of metallic lead." Helpful information is contained in a report by G. W. Monier-Williams.¹² He found that 106 mg of lead per 100 in.² of glaze surface, or 0.732 part per million parts of food under the conditions of his tests, were extracted by 1-percent citric acid, while cooking rhubarb extracted only 0.58 mg, or 0.004 part per million parts of food. Any laboratory test for solubility, involving the use of food or dilute acid as the solvent, might require a glazed vessel of standardized dimensions. For example, 100 in.² of surface could be exposed conveniently to reaction in a vessel 4 in. in diameter and 8 in. deep by using approximately 1,400 g of dilute acid. Under such conditions the U. S. Food and Drug Administration's limit of 2.57 parts of lead (or 2.77 parts of PbO) per million of solvent would be equivalent to a maximum of 0.0039 g of PbO per 100 in.² of exposed surface. Several of the glazes tested met this requirement, with 4-percent acetic acid as the solvent (table 5).

WASHINGTON, November 16, 1937.

¹¹ Examination of Water, J. Wiley & Sons, Inc., New York, N. Y.

¹² Report on Public Health and Medical Subjects No. 29 of the Ministry of Health; London, England.