THERMAL-EXPANSION CHARACTERISTICS OF SOME GROUND-COAT ENAMEL FRITS

By William N. Harrison, Benjamin J. Sweo, and Stephen M. Shelton

ABSTRACT

Thermal-expansion determinations were made on 11 sheet-iron ground-coat frits of the single-frit type, using the interferometer and also a quartz-tube dial-indicator apparatus. "Critical" temperatures for both heating and cooling were determined. Mean coefficients of expansion from 25° to 400° C, and total contraction from the critical temperatures to 25° C during cooling were correlated with variations in composition. Total differential contractions between enameling-type iron and the frits were also computed and correlated with variations in composition. Constants were determined which, when substituted in simple first-order equations, permit the computation of the expansivity of each frit at any temperature or temperature interval between 25° C and the critical temperatures.

The observed difference in the critical temperature on heating and that on cooling, the difference in the temperature-expansion curve of highly strained specimens below the critical temperature in heating, and the shrinkage of annealed specimens when held 30° C below the critical temperature for heating, are explained by the work of Tool, Lloyd, and Merritt on glass.

CONTENTS

I. INTRODUCTION

A series of 11 ground coats for sheet iron of the single-frit type were studied at this Bureau, and reports on their fusion properties,[1] strength, and elasticity [2] have been published. Subsequently, determinations on their thermal expansions were completed and considerable work done in comparing the results obtained by different methods of test and of analyzing the data. Further, some experiments were

---

[1] W. N. Harrison and B. J. Sweo, *Some fusion properties of ground coat enamels as influenced by composition.* BS J. Research **10**, 189 (1933) RP524.

[2] W. N. Harrison, S. M. Shelton, and W. H. Wadleigh, *Strength and Young's modulus of some ground coat enamels for sheet iron.* J. Am. Ceram. Soc. **18**, 100 (1935).

conducted to obtain confirmation of the logical presumption that the temperature-time-volume relations, which, according to the work of Tool, Lloyd, and Merritt [3] apply to glasses studied by them, also apply to the enamel frits used in this investigation, which were essentially homogeneous glasses. This paper is a report of these studies.

The method of preparation of the frits, and also their compositions, both as computed from batch weights and as determined by chemical analysis, have been published.[4] The scheme of variation in compositions is shown in table 1.

TABLE 1.—*Scheme of variation in composition of frits and data on critical temperatures and thermal-expansion characteristics*

Enamel designation	Variable constituents [1]				Coefficient of linear thermal expansion 25° to 400° C. ×10⁶		Critical [2] temperatures (heating)	Expansion constants from interferometer data		Coefficients of linear expansion ×10⁶ computed from constants		Total linear expansion, 25° C to "critical temperature on heating"	Total linear contraction from "critical temperature on cooling" to 25° C		
	Feldspar	Flint	Sodium oxide	Boric oxide	Dial	Interferometer		$a \times 10^5$	$b \times 10^5$	25° to 200° C	25° to 400° C		Enamel frit	Enameling-type iron	Difference
	%	%	%	%			°C					μ/cm	μ/cm	μ/cm	μ/cm
A	35	25	17	13	11.5	11.8	437	9.78	0.00484	10.9	11.8	49.6	41.3	47.9	6.6
B	35	25	14	16	10.7	10.9	475	9.08	.00431	10.1	10.9	50.6	42.8	53.9	11.1
C	35	25	11	19	9.6	9.9	483	8.45	.00347	9.2	9.9	46.7	39.8	55.1	15.3
D	30	30	17	13	11.4	11.6	438	9.75	.00440	10.7	11.6	48.7	40.6	48.0	7.4
E	30	30	14	16	10.5	10.7	480	9.10	.00387	10.0	10.7	50.2	42.7	54.7	12.0
F	30	30	11	19	9.4	9.7	490	8.57	.00262	9.2	9.7	46.1	39.5	56.2	16.7
G	25	35	17	13	11.0	11.3	447	9.38	.00444	10.4	11.3	48.4	40.5	49.4	8.9
H	25	35	14	16	10.2	10.4	482	8.92	.00351	9.7	10.4	48.9	41.6	55.0	13.4
I	25	35	11	19	9.1	9.5	488	7.92	.00362	8.7	9.5	45.3	38.5	56.0	17.5
J	27	27	17	19	11.0	11.5	450	9.66	.00427	10.6	11.5	49.8	41.7	49.9	8.2
K	33	33	11	13	9.6	9.9	488	8.84	.00249	9.4	9.9	46.8	40.2	55.8	15.6

[1] Each frit contained, in addition to the tabulated constituents, 7.7 percent of fluorspar, 1.7 percent of manganese oxide, and 0.6 percent of cobalt oxide.
[2] The values for cooling may be obtained by subtracting 60° C from those determined for heating, an approximation which is explained in the text.

II. METHODS OF TESTING

1. DIAL METHOD

The apparatus used was similar to that described by Hidnert and Sweeney,[5] with the following refinements. A sensitive dial indicator, which could be read to 0.0001 inch and estimated to an additional decimal, was used. To minimize temperature gradients, the furnace winding was tapped to divide it into three sections. The middle section was the same length as the specimen and inclosed it during a test. The two end sections were each about half the length of the specimen. Current could be shunted through variable resistances in parallel with the respective sections of the winding. Correction for the ex-

[3] *Dimensional changes caused in glass by heating cycles.* BS J. Research **5,** 632 (1930) RP219. Also J. Am. Ceram. Soc. **13,** 4 (Sept. 1930).
[4] W. N. Harrison and B. J. Sweo, *Some fusion properties of ground coat enamels as influenced by composition.* BS J. Research **10,** 189 (1933) RP524.
[5] Peter Hidnert and W. T. Sweeney, *Thermal expansion of magnesium and some of its alloys.* BS J. Research **1,** 771 (1928) RP29.

pansivity of the particular fused quartz used, and for temperature gradients in the quartz tubes during test, was made by calibration against a specimen of porcelain, the expansivity of which had been accurately determined at this Bureau. It was established that the expansivity of this specimen did not change in repeated determinations up to 400° C.

The dial was read when the furnace was at room temperature and at 100°, 200°, 300°, and 400° C, respectively. At each temperature the dial reading used in computing expansion had remained constant over a 20-minute period, during which the temperature of the furnace was held constant, the resistance being adjusted so that the temperature was uniform within 1° C from top to bottom of the specimen.

The requisite 8-inch specimens were cast in molds made from blocks of electrode carbon. Side-opening molds were used so that the vessel from which the molten frit was poured could be moved from one end of the mold to the other during the pouring process. Each mold was preheated to about 600° C and, after the specimen was cast, was returned to the furnace, held at 550° C for 1 hour and allowed to cool with the furnace. While in the furnace the molds were encased in sheet-iron jackets buried in mixtures of sand and graphite to retard oxidation. Expansion curves on specimens prepared in this way indicated a satisfactory quality of annealing.

2. INTERFEROMETER METHOD

The construction and operation of the apparatus used for measuring expansion by the interferometer method are described by Merritt.[6] The test specimens were made from rods approximately 3 mm in diameter drawn from the molten frit. A blunt point was formed at one end of each specimen, and three short legs formed on the opposite end, by grinding. These specimens were approximately 5 mm long, over-all. The temperature was increased continuously in these tests at the rate of 3° C per minute, as indicated by the average of two Chromel-Alumel thermocouples, the junction of one being placed just above the cover plate, and the junction of the other just below the base plate. The cup in which the specimens were placed during test was made of aluminum. Tests were made on unannealed specimens cooled from the molten state in air to determine their "softening temperatures."[7] They were then annealed by heating for 3 hours at a temperature about 5° C below their respective softening temperatures, and cooling in the furnace. These annealed specimens were used for expansivity determinations.

III. RESULTS AND DISCUSSION

1. EXPANSIVITY TO 400° C

The coefficients of linear thermal expansion from 25° to 400° C, as determined by both the dial and the interferometer methods, are given in table 1. The initial temperature in each case was approximately 25° C and the values were all corrected to 25° C in order that they might be comparable. The coefficient of expansion values given in

---

[6] G. E. Merritt, *The interference method of measuring thermal expansion.* BS J. Research **10**, 59 (1933) RP515.

[7] W. N. Harrison and B. J. Sweo, *Some fusion properties of ground coat enamels as influenced by composition.* BS J. Research **10**, 189 (1933) RP524.

this table represent averages of determinations on three separately prepared batches of frit. Individual deviations from the reported values averaged less than 0.1×10^{-6}, the maximum deviation being 0.3×10^{-6}.

The values obtained with the interferometer are 0.2 to 0.5×10^{-6} higher than those obtained with the dial apparatus. A number of experiments made to determine the source of this difference failed to reveal the cause of the discrepancy.

From table 1 it may be seen that the assumption commonly used in calculating expansivity from factors, namely, that the expansivity is an additive function of the constituent parts, held approximately true for these frits. Each of the six substitutions of 3 percent of boric oxide for 3 percent of sodium oxide, with other constituents unchanged, resulted in a decrease of about 1.0×10^{-6} in the coefficient of expansion, the extremes being 0.8 and 1.1×10^{-6}. The substitution of 10 percent of flint for 10 percent of feldspar produced a decrease of about 0.5×10^{-6}.[8] The *J-K* change in composition resulted in a substan tial reduction in the coefficient of expansion.

2. "CRITICAL" TEMPERATURES

It is recognized that the real importance of the thermal expansivity of enamels lies in the differential contraction between the enamel and the underlying metal as an enameled article cools after firing, and this differential depends not only upon the difference in expansivity but also upon the temperature at which the enamel becomes sufficiently stiff to set up strains in cooling. Hence it is obvious that the coefficient of expansion alone, whether computed or determined experimentally, does not give all of the required information.

The temperatures at which these strains were initiated were not determined directly. However, the "critical" temperatures [9] of the frits were determined because it was thought that a knowledge of the total contraction from these temperatures to room temperature would be helpful in estimating the relative amounts of residual strain after firing. In locating these critical temperatures, only the interferometer method was used. No attempt was made to carry the observations with the dial apparatus up to such temperatures, as the use of the large specimens, and the accompanying necessity for holding the temperature constant at each observation level, render this method unsuitable for the purpose. Data obtained during cooling were compared with those obtained during heating and, for greater accuracy, new determinations were made, using a more sensitive potentiometer, the precision of the new pyrometer being better than 0.01°C. The cooling rate of the furnace was approximately 2°C per minute through that temperature range which included the critical temperatures, becoming slower as the temperature decreased.

Figure 1 is indicative of the results that were obtained. In the upper curves, expansion and contraction with change of temperature are plotted in the usual manner. In the lower curves the rates (coefficients) of expansion (or contraction) for the small temperature intervals between pairs of adjacent interference bands are plotted against the corresponding mean temperatures. Since the lower curves

---

[8] This 10-percent change in batch composition entailed a much smaller change in chemical composition.
[9] C. G. Peters and C. H. Cragoe, *Measurements on the thermal dilatation of glass at high temperatures*, BS Sci. Pap. 15, 445 (1920) S393.

are the first derivatives of the upper ones, they accentuate changes in rate of expansion or contraction. Straight lines fitted the points on the derivative curves sufficiently well up to approximately the critical temperature, which may be defined for the purpose of this work as the temperature at which a smooth curve drawn through the plotted points diverges or "breaks away" from the straight line.[10] That this "break" was sharper and that it occurred at a substantially higher temperature on heating than on cooling, as shown in figure 1, held true for every frit tested.

Even with the breaks accentuated by this system of plotting the data, it was not possible to determine the exact temperature at which
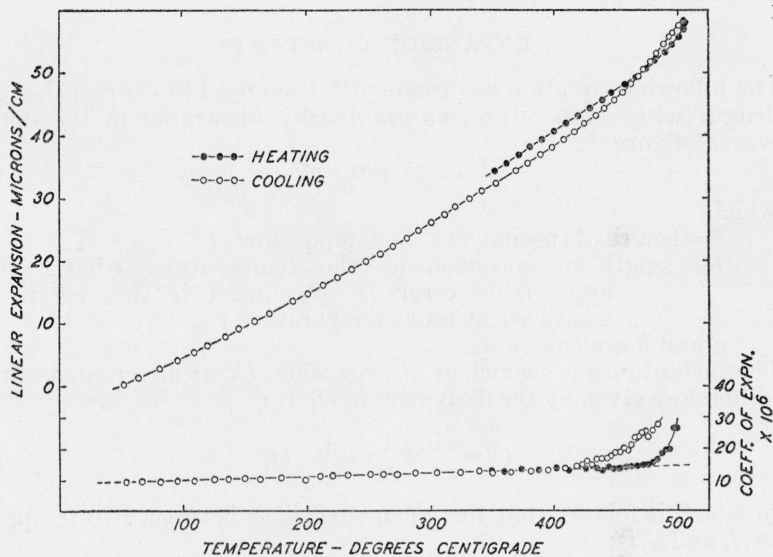

FIGURE 1.—*Curves showing the expansion and contraction of frit B.*

The upper curves show the expansion from 350° to 500° C and contraction from 500° to 50° C. The lower curves were obtained from the same data and show the change in coefficient of expansion (or contraction) with temperature under the conditions of test. To avoid confusion, not all of the data are plotted, except at the high-temperature end of the lower curves.

each break occurred, but it is thought that the uncertainty of the values obtained from the heating curves is within ±5° C. However, it is believed that the differences between the critical temperatures of different enamels were obtained with greater accuracy, since all were judged in the same way. The critical temperatures given in table 1 are those for heating data. Because of the greater difficulty in locating the critical temperatures for cooling from the data as plotted in figure 1, an estimate was made of the average difference, and this value (60° C) was subtracted from the critical temperature obtained from a heating curve to obtain the critical temperature for the corresponding cooling curve.

One correlation between change in composition and resultant change in critical temperature is very striking. The *A-B*, *D-E*, and *G-H*

---

[10] Although the points of divergence will not be accentuated to the same degree as in the described procedure, the same principle can be used by fitting a curve to expansion (or contraction) data from the constants referred to further on in this paper, and noting the temperatures at which smooth lines drawn through the data points diverge from such curves.

changes in critical temperatures (see table 1) are about four times as large as the B-C, E-F, and H-I changes, although the changes in composition are in the same direction and are of the same magnitude. The first three pairs all involve an increase of boric oxide from 13 to 16 percent and a reduction of sodium oxide from 17 to 14 percent. The second three pairs involve a further increase in the boric oxide to 19 percent, with corresponding decrease in sodium oxide to 11 percent. The average effect of increasing flint from 25 to 35 percent, at the same time reducing feldspar from 35 to 25 percent (the A-G, B-H,and C-I changes),was to increase the critical temperature only about 7° C.[11] The J-K change in composition resulted in an increase of 38° C in critical temperature.

3. EXPANSION CONSTANTS

The following equation has frequently been used to express changes of length with temperature, as graphically illustrated in the upper curves of figure 1.

$$L/L_0 = 1 + at + bt^2 \tag{1}$$

in which:

L=length of specimen at the temperature, t.

L_0=length of specimen at the temperature, 0° C. (No appreciable error is introduced if this length is measured at room temperature.)

a and b are constants.

The instantaneous coefficient of expansion, C_t, at any temperature, t, is therefore given by the derivative of eq 1.

$$C_t = \frac{dL}{dt} \times \frac{1}{L_0} = a + 2bt, \tag{2}$$

from which it follows that the mean coefficient between two temperatures, t_1 and t_2, is:

$$C_{t_1 t_2} = \frac{C_{t_1} + C_{t_2}}{2} = a + b(t_1 + t_2) \tag{3}$$

The constants, a and b, for the enamels studied are given in table 1. Although these constants are empirical, and small variations in the data may make relatively large percentage differences in their values, they are, nevertheless, useful in several ways. Various investigators have reported thermal expansions of enamels and similar materials between different limits of temperature, and hence it is sometimes difficult to compare the results reported by different authors. The constants given in table 1, when used in eq 3, make it possible to compute the coefficient of expansion of the enamels within any desired temperature range up to the critical temperature of a frit by a very simple calculation. Furthermore, unless elaborate precautions are taken, it is difficult to obtain accurate data on thermal expansion near room temperature when a schedule of continuous increase in temperature is used.[12] This difficulty may be largely remedied by use of the constants, as indicated in the following discussion.

11 See footnote 8, p. 130.

12 G. E. Merritt, *The interference method of measuring thermal expansion.* BS J. Research **10**, 59 (1933) RP515.

In this study determinations of total expansion from 25° to 400° C (and hence mean coefficient of expansion) were in satisfactory agreement whether obtained in heating or in cooling. However, the agreement was not satisfactory at the lower temperatures, notably from 50° to 150° C. Below 50° C no readings were taken in cooling. Since temperature measurements were made from two thermocouples, one above and one below the quartz plates, and a quartz thermometer was not used, it was concluded that the temperature readings may have differed significantly from the true temperature of the specimen during heating. In the cooling tests the average rate of change of temperature in the 50° to 150° C interval was about 0.3° C per minute, as compared with a rate of 3° C per minute in heating, and because of this slower rate, the temperature gradients were presumably smaller. When a very slow heating schedule was tried, a higher apparent rate of expansion was observed, as in cooling. Hence, in computing the constants given in table 1, the data obtained in cooling were used in establishing the lower end of the expansion curves down to 50° C. Extrapolations from 50° C down to 25° C by means of the constants used in eq 3, are thought to be more reliable than the observed data in that range.

In table 1, in addition to the constants for eq 3, the mean linear coefficients of expansion computed from these constants are given for the following temperature ranges: 25° to 200° C, 25° to 400° C, 25° C to the critical temperature, as determined from heating data, and 25° C to the critical temperature, as determined from cooling data.

Concerning the total expansions to the critical temperatures in heating, or total contraction from critical temperatures in cooling, a reversal of trend takes place as sodium oxide is substituted for boric oxide. Increasing the sodium oxide content from 11 to 14 percent and decreasing boric oxide from 19 to 16 percent (the *C–B*, *F–E*, and *I–H* changes shown in table 1) caused a substantial increase in total expansion to (or contraction from) the critical temperatures, as well as in the average coefficient of expansion. A further 3-percent increase of sodium oxide at the expense of boric oxide (the *B–A*, *E–D*, and *H–G* changes shown in table 1) increased the coefficient of expansion, as in the first substitution, but the accompanying reduction in critical temperatures more than compensated the effect of this increase in average coefficient of expansion on the total length change between 25° C and the critical temperatures.[13]

It would be a mistake, however, to deduce that the total differential contraction between iron and enamel in the temperature ranges under discussion undergoes a reversal, as boric oxide and sodium oxide are varied between the indicated limits. From values given in table 1 it is apparent that the differential contraction increases without reversal as the coefficient of expansion of the frits decreases. The total contraction of the iron to 25° C from the respective critical temperatures of the frits in cooling, given in table 1, was computed from constants which were experimentally established for one specimen of enameling-type iron in the range 25° to 400° C, namely, $a = 11.4 \times 10^{-6}$ and $b = 0.0055 \times 10^{-6}$.

---

[13] A nonlinear effect on the properties of glasses caused by intersubstitution of boric oxide for silica was noted by W. E. S. Turner, J. Glass Tech. **7**, 155 (1923).

4. APPLICATION OF CONCLUSIONS OF TOOL, LLOYD, AND MERRITT TO FRITS STUDIED

The described shift in the "critical" temperature obtained on cooling, as compared with that obtained on heating (fig. 1), has been explained by Tool, Lloyd, and Merritt.[14] The critical temperature observed on heating indicates a behavior analogous to that occurring in superheating and the critical temperature observed on cooling bears a similar analogy to under cooling. In either case the high rates of change of volume with respect to temperature illustrated by the lower curves in figure 1, between 400° and 500° C indicate drifts toward the equilibrium volumes, for the temperatures involved, which proceed at insignificant rates in lower temperature ranges, because of the higher viscosity of the specimens. The familiar dip in the expansion curve of highly strained specimens of enamel frit (or glass), which begins as much as 100° C below the critical temperature in heating, is also explained by those authors in the same way. Figure 2
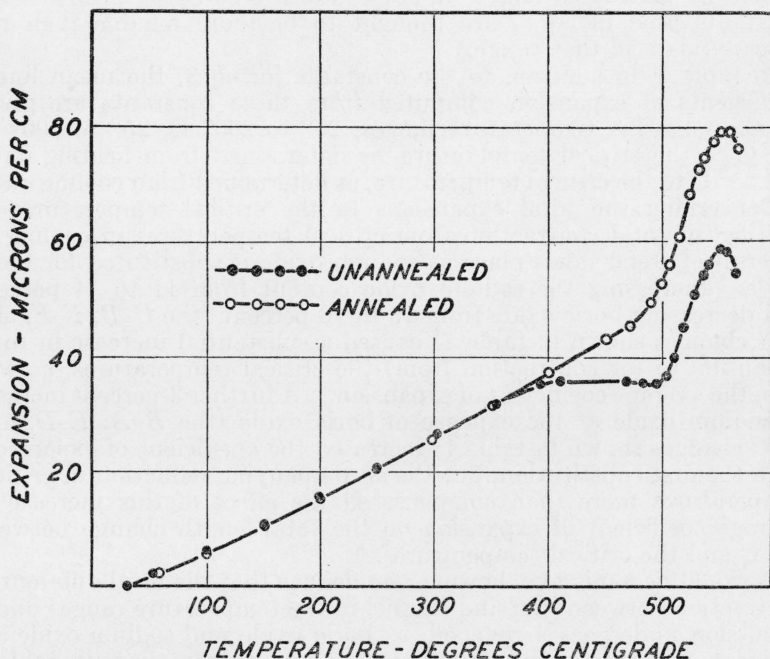

FIGURE 2.—*Thermal expansion curves for frit H.*

Drawn from molten frit and cooled in air (solid circles) and the same specimens after annealing (open circles).

shows typical heating curves for specimens of frit *H* in the annealed and the unannealed conditions. The relatively flat portion of the latter curve between 400° and 500° C reflects a drift toward the equilibrium volume-temperature line. The forces tending toward equilibrium volume are larger in the highly strained specimens and hence can operate more rapidly against high viscosities.

---

[14] *Dimension changes caused in glass by heating cycles.* BS J. Research 5, 627 (1930) RP219. Also J. Am. Ceram. Soc. 13, 4 (Sept. 1930).

The fact that even annealed specimens will undergo such drifts if given sufficient time was shown by Tool, Lloyd, and Merritt. In the present study, annealed specimens of enamel frit E were held for 5 hours at 450° C, which is 30° C below the critical temperature obtained on heating and 30° C above that on cooling. The drift toward equilibrium volume at that temperature resulted in a decrease in length equal to 13 percent of the expansion from 25° to 450° C (see fig. 3). Upon subsequent reheating no significant change in coefficient of expansion was detected.
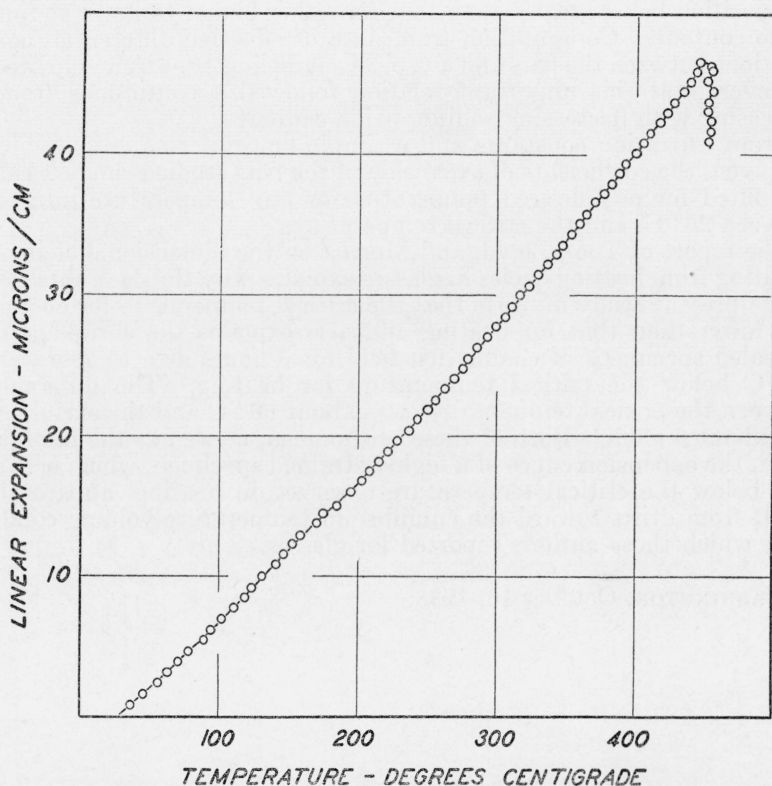

FIGURE 3.—*Curve showing the expansion of annealed specimens of frit E heated at 3° C per minute to 450° C and subsequent contraction on holding at that temperature for 5 hours.*

IV. CONCLUSIONS

A consistent difference of about 3 percent was observed between the expansivities from 25° to 400° C, as determined with the interferometer, using specimens 5 mm tall and 3 mm in diameter, and those determined with a quartz-tube and indicating-dial apparatus, using specimens 8 inches long and ⅜ inch square in cross section. Since interferometer specimens cut from the larger specimens gave the same difference in results, it was concluded that this difference was inherent in the methods of test and may have been related to the difference in size of the specimens. Because the smaller specimens are better

adapted for determining change of length with continuous change in temperature, especially through the "critical" range, the interferometer method is preferred.

Equal substitutions of boric oxide for sodium oxide in the range studied caused approximately equal decreases in coefficient of expansion, but caused unequal increases in "critical" temperature, the first 3-percent substitution causing about four times as much change in this property as a further 3-percent substitution in the same direction. The total expansion to critical temperature underwent an actual reversal in the same range of substitutions, that for the intermediate composition being greater than that for either higher or lower sodium oxide content. Computation from data of effective differential contractions between the frits and a typical enameling-type iron indicated, however, that this important relation followed a continuous trend, increasing with decreasing sodium oxide content.

From expansion constants and a simple first-order equation which are given, the coefficients of expansion of the frits studied can be easily computed for any desired temperature or any temperature interval between 25° C, and the critical temperatures.

The report of Tool, Lloyd, and Merritt on the dimensional changes resulting from heating cycles in glasses explains why the data obtained in the present study indicate that the critical temperature for cooling was lower than that for heating and also explains the shrinkage of annealed specimens of enamel frit held for 5 hours at a temperature 30° C below the critical temperature for heating. The difference between the critical temperatures was about 60° C and the shrinkage was about 6 μ/cm. Both of these phenomena, as well as the familiar dip in the expansion curve of a highly strained specimen, which occurs well below the critical temperature observed in heating, apparently result from drifts toward the equilibrium temperature-volume conditions which those authors reported for glasses.

WASHINGTON, October 16, 1938.