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<https://doi.org/10.18297/etd/1677>

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NAME OF STUDENT: Robert C. Boyd

TITLE OF THESIS: THE RELATIVE INFLUENCE
OF RAW MATERIAL COMPONENTS
UPON THE THERMAL EXPANSION
OF VITREOUS ENAMEL

APPROVED BY READING COMMITTEE COMPOSED OF THE
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DATE: May 24, 1940

UNIVERSITY OF LOUISVILLE

THE RELATIVE INFLUENCE
OF RAW MATERIAL COMPONENTS
UPON THE THERMAL EXPANSION
OF VITREOUS ENAMEL

A Dissertation

Submitted to the Faculty

Of the Graduate School of the University of Louisville

In Partial Fulfillment of the

Requirements for the Degree

Of Master of Science

Department of Chemistry

by

Robert C. Boyd

1940

THE RELATIVE INFLUENCE
OF RAW MATERIAL COMPONENTS
UPON THE THERMAL EXPANSION
OF VITREOUS ENAMEL

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ACKNOWLEDGMENT

The author wishes to express his
sincere appreciation to Dr. H. E. Carswell
for his generous assistance in the preparation
of this thesis.

INTRODUCTION

INTRODUCTION

Vitreous enamel is an inorganic glass, similar to the glass used in making windows or bottles, and is often called porcelain enamel to distinguish it from organic paint enamels. The designation, vitreous enamel, is most generally associated with opaque glass coatings on metal, although applying equally well to opaque glazes used on pottery. The distinctions between glass, glazes, and enamels are in use and application, not in properties.

The constitution of glass has been and still is the subject of considerable controversy. One hypothesis is that glass is composed of crystals so small as to be indistinguishable by any means now available. A more generally accepted theory is that which designates glass as an undercooled liquid (1). The basis of this theory is that molten glass is similar to any other liquid solution, but when it is cooled to the highest temperature at which one of its components would tend to crystallize, it has become so viscous that such crystallization is impossible.

One of the characteristic properties of glass is that it has no well defined melting point, nor does it show any definite break in heat capacity at or near the

softening point, as do crystalline substances. When molten glass is cooled it gradually becomes more viscous until it is apparently solid and can be shattered by sudden mechanical stress. However at this point and for an appreciable temperature range downward, the glass may be permanently deformed by stress slowly applied over a sufficient period of time. This temperature range for any particular glass is called its annealing range, where internal strains will adjust themselves providing the time is sufficient. Theoretically the annealing range has no lower limit, but in practice the time necessary for release of strain increases so rapidly with decrease in temperature that the useful limit is soon reached. This limit is of considerable importance in the application of enamels to metal, since at all lower temperatures the enamel must respond dimensionally to temperature very nearly the same as does the metal to which it is bonded. This results from the fact that all vitreous enameling processes involve fusing particles of enamel in contact with the metal at temperatures well above the annealing range. While cooling, the enamel will deform in accordance with any differential shrinkage of the metal, until the lower temperature limit of the annealing range is reached. If at this point the enamel is shrinking more rapidly than

the metal, fine cracks will occur. This is called crazing. If the enamel shrinks less rapidly than the metal the resultant compression may become so great that pieces of the coating break loose, particularly at edges and convex surfaces. This result is called chipping.

When the thermal expansion and contraction of enamel and metal are in such close agreement that chipping and crazing are negligible, the enamel is said to fit the metal. The necessity for control of this fit has been recognized from the earliest application of enamel to metal, but often without any conception of the principles involved. It was known that increasing a certain raw material in the enamel tended to stop crazing, and decreasing it would stop chipping. With a different raw material the reverse might be true. Such empirical methods of control were in use until comparatively recent times, when the availability of raw materials of standard and uniform composition, and the rapidly expanding use of enameled metal, made more accurate means of control not only possible but essential.

HISTORICAL

HISTORICAL

The first systematic investigation of the thermal expansion of glasses was that of Winkelmann and Schott (2). They found that the physical properties of glass, including thermal expansion, are approximately additive in proportion to the relative amounts of the component oxides. After an extensive investigation they were able to express their results in terms of oxide factors, each factor representing the effect of one per cent of the particular oxide. In order to calculate the coefficient of thermal expansion of a glass, the factor for each oxide was multiplied by the per cent of that oxide in the glass and the results added together. They called attention to the fact that such results are only approximately correct and that the factors shown apply only to the range of compositions within which they worked.

Mayer and Havas (3), working with enamels, checked the results of Winkelmann and Schott and added many factors not included in the original investigation. Gehlhoff and Thomas (4) working with glasses, pointed out that any set of oxide factors is accurate for only a limited field of composition. English and Turner (5) assumed that silica carries the thermal expansion of fused quartz into glass

and on this basis determined a set of oxide factors that show an appreciable departure from those previously derived. Their results indicate that boron oxide does not give the additive values characteristic of the other oxides, but that over a certain range its effect decreases to a minimum and then increases again. They found further that the magnitude of the oxide factors was influenced by the composition of the glass and emphasized the fact that they worked in the comparatively narrow temperature range of 25°C to 90°C. Fetterolf and Parnalee (6) making the same assumption as to silica, calculated oxide factors for Na_2O , ZnO , and BaO . Hall (7) investigated the physical properties of glasses and determined expansion factors for several oxides.

Andrews and Smith (8) determined the coefficients of thermal expansion for compositions systematically varied through the field of sheet iron ground coat enamels, checked these against calculated results using different sets of oxide factors, and concluded that the factors of Mayer and Havas are most accurate for this type of enamel. In a later paper, Andrews and Howe (9) concluded that the coefficient of thermal expansion of sheet iron cover coat enamels cannot be calculated accurately from any previously determined set of oxide factors although those

of Mayer and Havas were most nearly applicable. They showed that the error may have been due in part to the high fluoride content of such enamels. Kinsie and Commons (10) compared results obtained by different methods of measuring the coefficient of thermal expansion of enamels with measurements of the chipping tendencies of the same enamels, and concluded that other properties than the expansion were of importance in determining the fit.

It seems evident from the references cited that an ideal set of oxide factors for calculating the coefficient of thermal expansion of glasses, which will be accurate for all temperature and composition ranges, does not exist. In nearly every investigation a statement is made that the findings apply only to the specific range of compositions studied.

The earlier investigators determined thermal expansion by measuring the amount of mercury expelled from a bulb of the glass composition being tested, when the temperature was increased through a definite interval. This method severely limited the temperature range which usually did not extend above 100°C. More recent workers in this field, overcoming temperature limitations with improved methods, have confined their experiments to

relatively simple glasses, or else have checked measured expansions with calculated results obtained by using one or more of the predetermined sets of oxide factors. Where a number of oxide factors have been determined, the method employed has been to substitute successively definite quantities of several different oxides for an equivalent quantity of one of the components of a simple glass. Knowing the oxide factor of the replaced component, and the coefficients of thermal expansion of the two glasses, it was possible to calculate the oxide factor of the replacing oxide. Such values may not be accurate for the same oxides coexistent in a complex glass.

The field of dry process enamels for cast iron has been rather neglected in thermal expansion investigations. This is particularly true of acid resisting enamels which have been developed largely in recent years. While the various sets of oxide factors have been found very useful in working with such enamels, inaccuracies are often noted. For instance, in working with two different types of enamels, both having a satisfactory fit to the same metal base, the calculated coefficients of thermal expansion may show a pronounced difference. It is evident that the actual coefficients must be very nearly the same.

Consideration of such occurrences, together with the discussion in the previous paragraph, lead to the conclusion that an investigation in the field of dry process acid resisting enamels for cast iron should yield oxide factors which will be more applicable to such compositions than any available from previous investigations.

PREPARATION OF ENAMELS
AND TEST RODS

PREPARATION OF ENAMELS
AND TEST RODS

In order to narrow the field, the basic enamel composition was limited to the ingredients which experience has proved to be both necessary and sufficient for the production of a satisfactory acid resisting dry process enamel. A base formula of one hundred parts was used, so proportioned among the different ingredients that a variation of from three parts less to three parts more for each ingredient carried it through the range in which it normally occurs in such compositions. A further consideration was that variations of this magnitude should not appreciably alter the type of the resulting enamel.

The enamel compositions used in these tests are shown in Table 1, the basic enamel composition being designated "X". Each ingredient in the basic enamel was varied in turn, from three parts less to three parts more than its proportion therein. This variation was believed to be the maximum which could be used without danger of altering too greatly the enamel characteristics, when applied to those ingredients which occur in relatively small proportion.

Commercial raw materials were used in preparing

Table 1
Composition

	X	A1	A2	B1	B2	C1	C2	D1	D2
SiO_2	40	<u>37</u>	<u>43</u>	40	40	40	40	40	40
TiO_2	6	6	6	<u>3</u>	<u>9</u>	6	6	6	6
B_2O_3	6	6	6	6	6	<u>3</u>	<u>9</u>	6	6
Na_2O	15	15	15	15	15	15	15	<u>12</u>	<u>18</u>
PbO	15	15	15	15	15	15	15	15	15
CaO	6	6	6	6	6	6	6	6	6
Na_2SiF_6	6	6	6	6	6	6	6	6	6
Sb_2O_3	6	6	6	6	6	6	6	6	6
	X	E1	E2	F1	F2	G1	G2	H1	H2
SiO_2	40	40	40	40	40	40	40	40	40
TiO_2	6	6	6	6	6	6	6	6	6
B_2O_3	6	6	6	6	6	6	6	6	6
Na_2O	15	15	15	15	15	15	15	15	15
PbO	15	<u>12</u>	<u>18</u>	15	15	15	15	15	15
CaO	6	6	6	<u>3</u>	<u>9</u>	6	6	6	6
Na_2SiF_6	6	6	6	6	6	<u>3</u>	<u>9</u>	6	6
Sb_2O_3	6	6	6	6	6	6	6	<u>3</u>	<u>9</u>

Variations from basic composition are underlined.

Formulae are not in per cent except for "X".

A1, B1, etc. have 97 parts.

A2, B2, etc. have 103 parts.

the enamels. With the exceptions noted later, their purity is not less than 99%. It is known that some of the materials used have an appreciable vapor pressure at the temperatures used in smelting enamels. This results in a small but definite decrease in the proportion of these materials as supplied by the raw batch.

Soda Ash (Na_2CO_3) is slightly hygroscopic. The soda ash used in preparing these enamels was dried in an enclosed, ventilated oven for three hours at 150°C , and allowed to cool to room temperature before weighing.

Boron oxide was introduced in the form of commercial anhydrous borax. It is believed to be less volatile in this form than when added as a compound containing combined water, and there is certainly less mechanical loss. Since anhydrous borax varies slightly from the theoretical composition, the lot used for this work was thoroughly mixed and a representative sample analysed. The analysis showed, B_2O_3 65.89%, Na_2O 31.73%, and an ignition loss of 2.34%.

Sodium Fluosilicate, when heated by itself, decomposes into sodium fluoride and volatile silicon tetrafluoride at temperatures lower than those reached in smelting enamel. There may be reactions within the melting enamel batch which tend to limit the loss of

silicon tetrafluoride; since it is known that the effect of sodium fluosilicate upon the properties of an enamel, when compared to more stable fluorides such as cryolite and fluorspar, is greater than would be apparent on the basis of its sodium fluoride content only.

Antimony oxide gives the enamel opacity. It is supplied as the relatively volatile trioxide and requires addition of sodium nitrate to the batch to oxidize it to the pentavalent form which is stable. Theoretically a disperse phase in a glass should have no effect on its thermal expansion. However it is known that antimony oxide has a very definite effect. Whether this results from combination with other ingredients of the enamel, or from partial solution, or both, is not known.

It is evident from the foregoing considerations in regard to raw materials that a precise determination of oxide factors for any of the physical properties of an enamel would require a complete and accurate quantitative analysis of each composition after smelting. However, since the purpose of this investigation is to determine the relative effect of the raw materials upon the finished enamel, following a procedure which can be correlated with that obtaining in the preparation of commercial enamels,

such analyses were not made. The only stipulation in respect to the finished enamels is that their physical properties shall have a definite and uniform relationship to the proportions of raw materials used. The raw material compositions of the enamels prepared for this investigation are shown in Table 2.

Preparation of Enamels

The batches of raw material were proportioned to give a calculated weight of 1000 grams when melted. Each material was weighed to the nearest 1/10 of a gram. The weighed batch was screened through a twenty mesh sieve to insure the absence of lumps, and thoroughly mixed. Three batches were made of the basic enamel composition and two of each of the others. The enamels were smelted in a heavy duty, gas fired crucible furnace, the same fire clay crucible being used throughout. A Leeds and Northrup optical pyrometer was used in controlling the temperature which was held at 1093°C, (2000°F). Each batch of enamel was allowed to melt until evolution of gas had ceased. It was then stirred thoroughly with an iron rod of sufficient weight to prevent its becoming hot enough to scale and contaminate the enamel. After five minutes the stirring

Table 2
Raw Material Composition

	X				
SiO_2	40.00	A1	37.00	A2	43.00
TiO_2	6.00	B1	3.00	B2	9.00
$\text{Na}_2\text{B}_4\text{O}_7$	9.11	C1	4.55	C2	13.66
HNO_3	5.00				
Na_2CO_3	17.58	C1	20.05 ^a	C2	15.11 ^a
		D1	12.45	D2	22.70
PbO	15.00	E1	12.00	E2	18.00
CaCO_3	10.71	F1	5.35	F2	16.06
Na_2SiF_6	6.00	G1	3.00	G2	9.00
Sb_2O_3	6.00	H1	3.00	H2	9.00

aa. Soda ash varied to compensate for changes in sodium oxide content caused by varying borax.

The composition of enamel X is given completely. The other compositions differ from enamel X only in respect to the materials for which the amounts are shown.

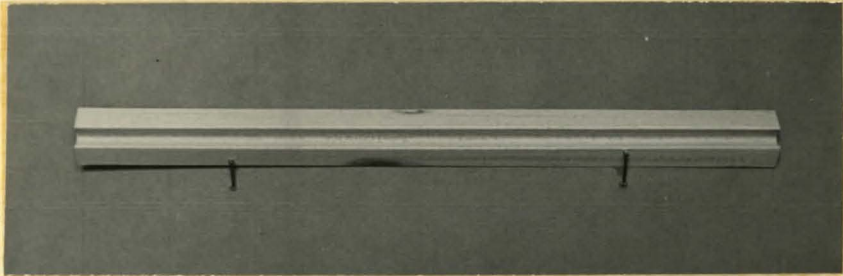
was repeated and after another five minutes the batch was quenched by pouring it into cold water. The first two batches of the basic enamel (X) were used to rinse and glaze the crucible, and discarded after smelting. The first batch of each of the other enamels was used as a rinse batch to insure against carry over from one composition to another. The final batch of each enamel was quenched and then dried in an enclosed oven.

Preparation of Samples

Sample bars of enamel to be used as test rods were prepared in machine pressed, trough shaped, sheet iron molds; which had been coated with a clay suspension to prevent the enamel from sticking when heated. Figure 1 shows a clay coated mold. To insure uniformity, each mold was filled to capacity with enamel particles which had passed a twenty mesh sieve. In order to permanently identify each test rod very small portions of differently colored enamel powders were applied to the surface of the enamel heaped in the mold. In the subsequent treatment colored dots were formed on the surface of the rods.

The molds which contained enamel were heated in

Figure 1
Mold for Test Rods



an electric furnace to a temperature of 675°C which was sufficient to fuse the enamel. The furnace was then shut off and allowed to cool. Due to heavy insulation the cooling rate was slow enough to insure satisfactory annealing of the rods. After cooling they separated easily from the molds. The finished test rods were seven and one half inches long and about three sixteenths of an inch in diameter. One end of each was ground on an abrasive wheel to a hemispherical shape. The other end was notched and broken to make the length of the rod approximately seven inches. This end was also ground to a hemispherical shape. With a room temperature of 70°F the length of each test rod was determined to the nearest ten thousandth of an inch by means of a micrometer caliper calibrated to read correctly at that temperature. These lengths were recorded in the data.

APPARATUS

APPARATUS

Thermal expansion measurements were made by means of a dilatometer. This instrument consists essentially of a fused quartz outer tube which has one end closed, and a shorter inner tube of the same material, closed at both ends. An Ames Dial calibrated in ten thousandth of an inch divisions was clamped to the open end of the outer tube with its appendix centered in the end of the tube.

A heavily insulated, vertical electric tube furnace was used for heating the dilatometer, the rate of temperature increase being controlled by a rheostat. An iron-constantan thermocouple and a Leeds and Northrup potentiometer were used to measure temperatures. The thermocouple was made from 22 B&S gage wire, and when calibrated against a standard platinum, platinum-rhodium couple, was found to have negligible deviation from theoretically correct E. M. F. values over the range from 20°C to 500°C. A recent paper by Dahl (11) shows data indicating that a thermocouple of this type will have no significant changes in its characteristics for temperature ranges and durations equivalent to those used in these tests. A mercury in glass laboratory thermometer was used

to measure cold junction temperatures.

Since the diameter of the test rods was small compared to the diameter of the outer dilatometer tube, it was necessary to support them in the correct coaxial position. A support was formed from stainless steel and so constructed that the rod and support could expand and contract independently.

PROCEDURE

PROCEDURE

The junction end of the thermocouple was contained within a three inch porcelain insulator, with the tip of the junction projecting slightly. It was fastened to the enamel rod to be tested by means of a wire wrapped around the insulator and rod. The alignment was such that the tip of the thermocouple junction was at the center of the test rod. The rod with attached thermocouple was placed in the stainless steel support as shown in Figure 2. This combination was inserted in the outer dilatometer tube so that the lower end of the test rod rested against the closed end of the tube. The inner dilatometer tube was then placed within the outer tube with its lower end in contact with the upper end of the test rod and its upper end just within the open end of the outer tube. The thermocouple wires were positioned between the two tubes in a manner to prevent an accidental short circuit, and to allow free movement of the inner tube. Figure 3 illustrates the assembly at this stage. The dilatometer assembly was then placed in the vertical tube furnace and secured with adjusting screws at the top of the furnace. The Ames Dial was adjusted so that its appendix rested against the top of the inner dilatometer tube with sufficient pressure to rotate the indicating

needle through ten to twenty divisions. Consideration of this assembly makes it obvious that the expansion of quartz need be taken into account for only that length of tube occupied by the sample rod, since the expansions of the two dilatometer tubes were self compensating above the rod.

The thermocouple wires, which had been made long enough to eliminate the necessity for supplementary leads, were connected to the potentiometer. The zero setting of the latter was adjusted, the cold junction temperature read from the adjacent thermometer, and the cold junction compensator set accordingly. The calibrated face of the Ames Dial was adjusted to show a zero reading. The complete expansion apparatus is shown in Figure 4.

The furnace was started and the expansion read and recorded at intervals of 50°F , from 100°F to 750°F inclusive. The use of the English length units and the Fahrenheit temperature scale was due to the calibration of the dilatometer and to the availability of printed data sheets incorporating the correction factors for the expansion of quartz in these units. Under the circumstances it was simpler to proceed with these units and calculate the results to the metric equivalents.

The rate of temperature increase was held as nearly

Figure 2
Test Rod and Support
Thermocouple Attached to Rod

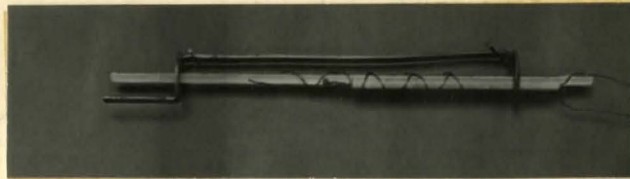


Figure 3
Dilatometer Assembly

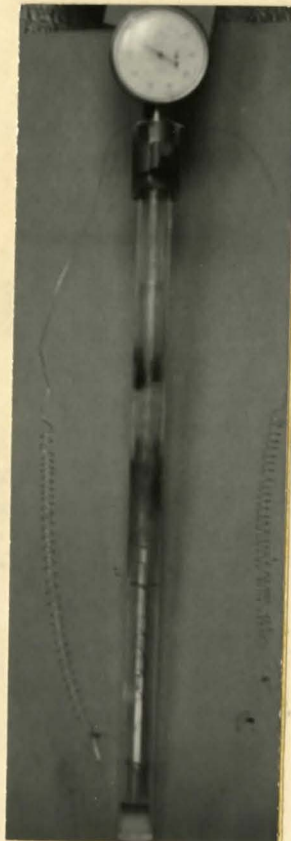


Figure 4
Thermal Expansion Apparatus

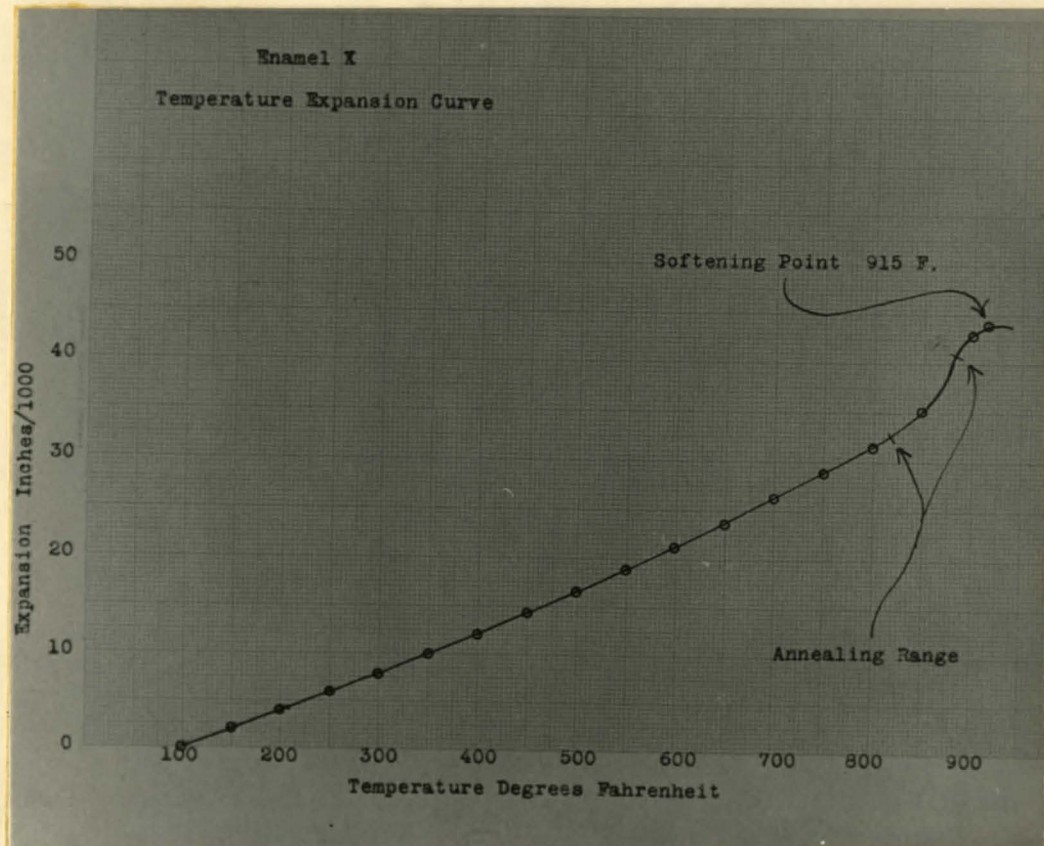


Dilatometer and Furnace toward the Rear -
Potentiometer, Front Left under Desk Lamp
Rheostat, Front Right (only partly showing)

as possible to 50°F in eight minutes, by rheostat regulation. This rate was selected because it is appreciable lower than the allowable rate of temperature decrease recommended for annealing glass of a thickness corresponding to that of the rods. An analogy was drawn from the necessity for having a negligible temperature gradient through the section in each case.

The lower temperature limit of 100° F was selected to be above the maximum room temperature likely to be encountered. The upper temperature limit of 750°F was based on consideration of the complete temperature expansion curve illustrated in Figure 5, showing the expansion of Enamel X from 100° F to the softening point at 915° F. It will be noted that the rate of expansion increased rather uniformly to a point about 75° F below the softening point where it became much more rapid. This type of curve is characteristic of glasses and it is within the range of rapid expansion that annealing takes place. Due to the fact that internal strains are self adjusting in this range it should be excluded from data to be used in determining fit of enamel to metal. The 750° F limit was believed to be safely below any shifts in the annealing range which might occur in the series of enamel compositions tested.

Figure 5
Enamel X. Complete Temperature Expansion Curve



Expansion determinations were made successively on the series of test rods representing the different enamel compositions, and then repeated. Duplicate tests which did not check within five one-hundred-thousandths of an inch for the temperature interval, 100° F to 500° F, were repeated a third time. In order to avoid repetition of an error in assembly, duplicate tests were never made successively on the same sample.

SOURCES OF ERROR

SOURCES OF ERROR

Considerable difficulty was encountered in arranging the thermocouple wires so that they would not interfere with the free movement of the inner dilatometer tube. The latter fits loosely within the outer tube in order to allow clearance for the wires, and if the assembly was not quite right, differential expansion of these wires during the expansion determination caused a slight shifting of the inner tube which was sufficient to lead to inaccurate results. In spite of every care used in assembly, this occurrence could not be positively prevented, and is believed to account for most of the unsatisfactory determinations.

The equivalence of Thermocouple Potential, Temperature, and Thermal Expansion are roughly in the ratio of 1.5 Millivolts to 50° F to 20 Ten-thousandths of an inch. Expansion readings were made to the nearest one half scale division on the Ames Dial, that is, to the nearest five one-hundred-thousandths of an inch expansion. Settings on the potentiometer cold junction compensator, and on the lower temperature scale, 0° F to 500° F, were accurate to within plus or minus 0.01 millivolt, and on the upper temperature scale, 550° F and above, to within plus or minus 0.02 millivolt. A possible error of plus

or minus 0.03 millivolt could have resulted from these sources. This would be equivalent to one degree fahrenheit or to one third of a ten-thousandth of an inch expansion. Exceptional care used in making the settings for the first and final expansion readings, upon which the calculations were based, should have reduced the error with respect to these readings.

Cold junction temperatures were read at intervals during each test and the compensator reset if necessary. Here again every precaution was taken to insure correct settings for the first and final readings of each run.

Errors in connection with enamel batch compositions have been discussed previously. It is believed that consideration of the data will support the conclusion that the sources of error enumerated are sufficient to account for such discrepancies as exist.

DATA

DATA

The Ames Dial was set at zero for the start of each run. Since the initial furnace temperature differed for the different runs, the temperature intervals up to the first reading at 100° F varied considerably, and the recorded readings at this temperature varied accordingly. It will be observed that numerical values of specific readings are unimportant, since only the intervals between the first and final readings have significance. Therefore, in order to facilitate comparison of the expansion runs, the data were corrected to initial readings of zero at 100° F. Table 3 includes all thermal expansion data.

Figure 6 is a graphical representation of the effect on the thermal expansion of Enamel X when each raw material is varied in turn, the curves having been derived from the data in Table 3. Solid lines represent the expansion of enamels containing three parts less of the material shown than is contained in Enamel X. Broken lines represent the expansion of enamels containing three parts more. The degree of separation of the lines represents the magnitude of the effect on expansion, while their relative position shows its direction.

Table 3

Data

Test Rod	Expansion Inches/1000					
	X			A1		
Length Inches	6.995			6.995		
Run No.	1	2	3	1	2	3
Temp. °F.						
100	0.00	0.00	0.00	0.00	0.00	0.00
150	1.80	1.80	1.80	1.85	1.85	1.85
200	3.90	3.80	3.80	3.95	3.90	3.90
250	5.90	5.85	5.85	5.95	5.90	6.00
300	7.80	7.80	7.75	7.95	7.85	7.90
350	9.75	9.80	9.80	9.90	10.00	10.00
400	11.85	11.90	11.90	12.05	12.05	12.10
450	14.00	14.05	14.00	14.25	14.30	14.30
500	16.30	16.35	16.30	16.55	16.60	16.60
550	18.55	18.60	18.45	18.95	18.95	19.00
600	20.95	21.10	21.00	21.45	21.50	21.55
650	23.45	23.55	23.50	24.05	24.00	24.05
700	25.95	25.95	25.85	26.65	26.55	26.60
750	28.50	28.55	28.50	29.15	29.30	29.30

Test Rod	Expansion Inches/1000					
	A2			B1		
Length Inches	7.026			7.027		
Run No.	1	2	3	1	2	3
Temp. °F.						
100	0.00	0.00		0.00	0.00	0.00
150	1.70	1.75		1.80	1.85	1.85
200	3.65	3.75		3.85	3.90	3.90
250	5.55	5.60		5.90	5.90	5.95
300	7.45	7.50		7.85	7.90	7.90
350	9.45	9.50		9.85	9.90	9.95
400	11.45	11.55		11.95	12.05	12.00
450	13.50	13.65		14.10	14.25	14.20
500	15.80	15.90		16.50	16.60	16.50
550	17.95	17.95		18.90	18.90	18.85
600	20.35	20.45		21.35	21.30	21.35
650	22.85	22.95		23.80	23.90	23.85
700	25.15	25.20		26.40	26.40	26.40
750	27.80	27.80		28.95	29.10	29.05

Table 3 (continued)

Data

Test Rod	Expansion Inches/1000					
	B2			C1		
Length Inches	7.015			7.017		
Run No.	1	2		1	2	3
Temp. °F.						
100	0.00	0.00		0.00	0.00	0.00
150	1.90	1.80		1.90	1.85	1.85
200	3.75	3.80		3.95	3.90	3.95
250	5.70	5.75		6.05	6.05	6.00
300	7.60	7.65		8.00	8.00	8.00
350	9.65	9.65		10.20	10.10	10.15
400	11.65	11.65		12.30	12.25	12.30
450	13.75	13.75		14.55	14.45	14.55
500	15.95	16.00		16.90	16.85	16.90
550	18.10	18.15		19.25	19.15	19.30
600	20.60	20.65		21.85	21.75	21.85
650	23.20	23.05		24.40	24.25	24.45
700	25.55	25.50		26.95	26.80	27.00
750	28.10	28.10		29.60	29.50	29.65

Test Rod	Expansion Inches/1000					
	C2			D1		
Length Inches	7.052			7.025		
Run No.	1	2	3	1	2	3
Temp. °F.						
100	0.00	0.00	0.00	0.00	0.00	0.00
150	1.80	1.75	1.80	1.60	1.70	1.65
200	3.70	3.75	3.75	3.55	3.60	3.55
250	5.65	5.65	5.55	5.35	5.45	5.45
300	7.50	7.50	7.55	7.15	7.25	7.25
350	9.45	9.55	9.55	9.15	9.20	9.15
400	11.40	11.55	11.55	11.10	11.10	11.05
450	13.50	13.60	13.65	13.05	13.05	13.10
500	15.70	15.85	15.90	15.20	15.25	15.20
550	18.00	17.95	18.05	17.35	17.15	17.25
600	20.45	20.40	20.50	19.50	19.50	19.55
650	22.95	22.90	22.95	21.85	21.85	21.90
700	25.30	25.30	25.25	24.15	24.10	24.15
750	27.75	27.50	27.80	26.55	26.40	26.45

Table 3 (continued)

Data

Test Rod	Expansion Inches/1000					
	D2		E1		E2	
Length Inches	7.024		7.020		7.005	
Run No.	1	2	1	2	1	2
Temp. °F.						
100	0.00	0.00	0.00	0.00	0.00	0.00
150	1.95	2.00	1.90	1.85	1.80	1.85
200	4.10	4.10	3.85	3.85	3.85	3.90
250	6.25	6.25	5.85	5.90	5.80	5.90
300	8.40	8.30	7.75	7.80	7.75	7.85
350	10.55	10.50	9.85	9.90	9.90	9.90
400	12.75	12.70	11.90	11.95	11.95	11.95
450	15.10	15.00	14.05	14.10	14.20	14.15
500	17.50	17.45	16.35	16.40	16.40	16.45
550	20.05	19.95	18.60	18.65	18.65	18.65
600	22.65	22.60	21.15	21.15	21.20	21.25
650	25.30	25.20	23.70	23.60	23.70	23.70
700	28.00	27.90	26.10	26.10	26.15	26.15
750	30.70	30.70	28.60	28.60	28.75	28.80

Test Rod	Expansion Inches/1000					
	F1			F2		
Length Inches	7.016			7.022		
Run No.	1	2	3	1	2	3
Temp. °F.						
100	0.00	0.00	0.00	0.00	0.00	0.00
150	1.85	1.85	1.85	1.85	1.85	1.85
200	3.90	3.90	3.85	3.95	3.90	3.90
250	5.95	5.85	5.85	5.95	5.90	5.90
300	7.90	7.80	7.75	7.90	7.90	7.90
350	9.85	9.85	9.80	10.00	9.95	9.95
400	11.90	11.90	11.90	12.10	12.05	12.05
450	14.00	14.05	14.00	14.30	14.20	14.20
500	16.30	16.25	16.25	16.60	16.55	16.55
550	18.55	18.50	18.45	18.90	18.80	18.80
600	20.95	20.90	20.95	21.35	21.35	21.35
650	23.45	23.30	23.35	23.90	23.85	23.85
700	25.90	25.75	25.75	26.40	26.35	26.35
750	28.35	28.30	28.30	29.00	29.05	29.05

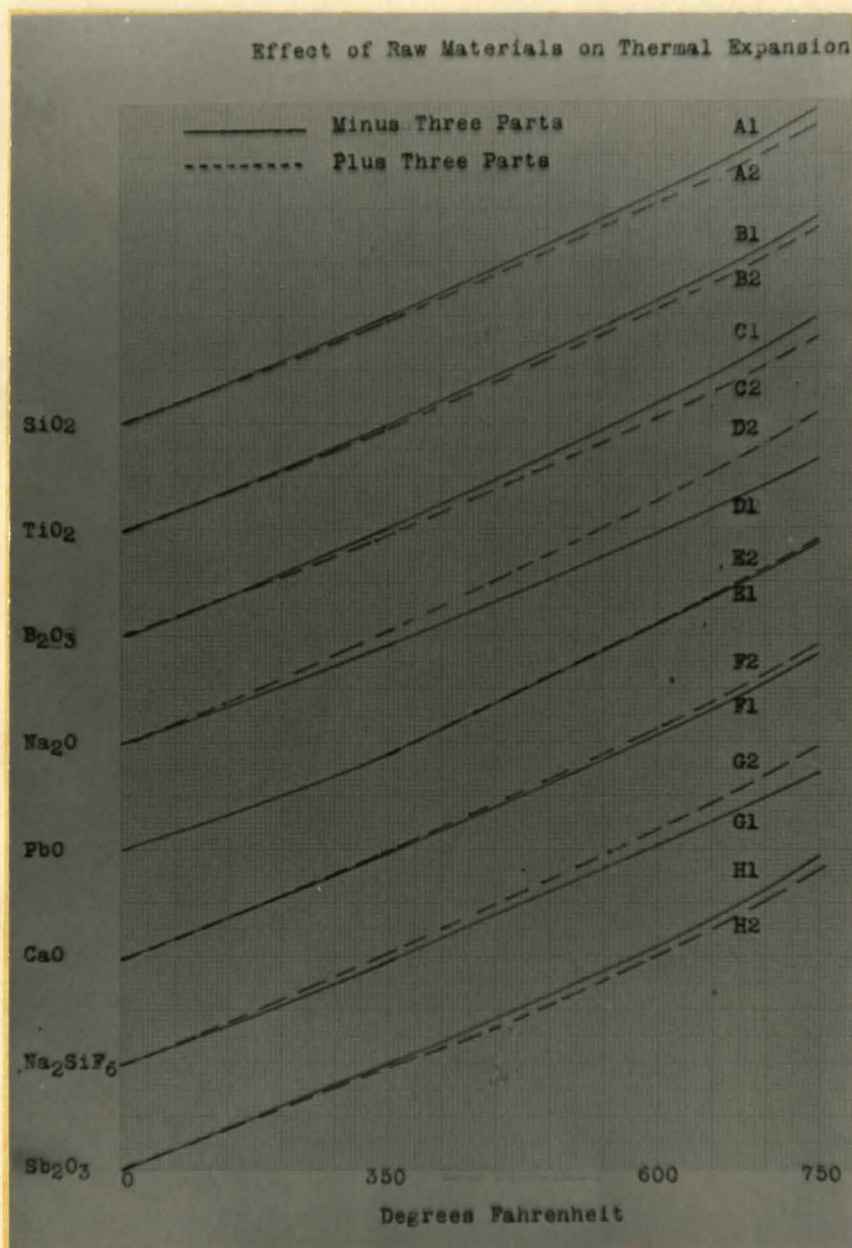
Table 3 (continued)

Data

Test Rod	Expansion Inches/1000					
	G1			G2		
Length Inches	7.032			7.005		
Run No.	1	2	3	1	2	
Temp. °F.						
100	0.00	0.00	0.00	0.00	0.00	
150	1.65	1.75	1.75	1.95	1.90	
200	3.65	3.70	3.75	4.05	4.05	
250	5.50	5.65	5.65	6.15	6.15	
300	7.30	7.50	7.55	8.15	8.15	
350	9.40	9.50	9.60	10.30	10.35	
400	11.50	11.50	11.60	12.45	12.45	
450	13.55	13.60	13.70	14.70	14.65	
500	15.70	15.85	15.90	17.15	17.05	
550	17.85	17.90	18.00	19.50	19.45	
600	20.15	20.35	20.40	22.05	21.95	
650	22.45	22.75	22.85	24.55	24.45	
700	24.90	25.15	25.20	27.00	27.05	
750	27.40	27.70	27.75	29.65	29.65	

Test Rod	Expansion Inches/1000			
	H1		H2	
Length Inches	7.000		7.030	
Run No.	1	2	1	2
Temp. °F.				
100	0.00	0.00	0.00	0.00
150	1.85	1.85	1.75	1.80
200	3.80	3.95	3.75	3.80
250	5.95	6.00	5.70	5.75
300	7.90	8.00	7.60	7.65
350	10.00	10.05	9.60	9.70
400	12.10	12.15	11.60	11.70
450	14.35	14.40	13.70	13.80
500	16.70	16.70	16.00	16.05
550	19.10	19.05	18.25	18.25
600	21.55	21.60	20.65	20.70
650	24.05	24.10	23.10	23.15
700	26.60	26.65	25.50	25.50
750	29.20	29.25	28.05	28.05

Figure 6
Graphical Representation of Data



CALCULATIONS

CALCULATIONS

Results of the early investigations of the thermal expansion of glasses were expressed as the Volume Coefficient of Thermal Expansion per Degree Centigrade. Later workers have followed the same practice in order to make direct comparisons. The volume coefficient may be obtained with negligible error by multiplying the linear coefficient by three. The volume coefficient of thermal expansion was obtained for each enamel included in this investigation, the following formula being used:-

$$\text{CTE} = \frac{\Delta L}{L_0 \times \Delta T} \times \frac{9}{5} \times 3$$

Where CTE is the Volume Coefficient of Thermal Expansion.

L_0 is the length of the test rod at 70° F.

ΔL is the expansion between 100° F and 750° F.

ΔT is the temperature interval, 650° F.

9/5 is the conversion factor Fahrenheit to Centigrade.

3 is the conversion factor from linear units to volume units.

Oxide Factors were calculated from the enamel coefficients by means of the formula shown below, in which the additive character of the oxides is assumed:-

$$F = \frac{C'(W + \Delta W) - (W \times C)}{100 \Delta W}$$

Where F is the Oxide Factor for the oxide which has been varied to change the thermal expansion.
 C is the CTE value of the original enamel.
 C' is the CTE value of the enamel which has been altered.
 W is the number of parts by weight of the original enamel, 100 in the case of Enamel X.
 ΔW is plus or minus 3, representing the number of parts by weight of the oxide which has been added to or subtracted from the original enamel. It is multiplied by 100 in the denominator in order that the resulting factor will represent the effect of one per cent of the oxide.

The calculated volume coefficients of thermal expansion for the enamel compositions tested are shown in Table 4, together with the corresponding calculated oxide factors. The two values obtained for each oxide factor were averaged and the average values are also included in Table 4. In Table 5 the oxide factors obtained in this investigation are shown in comparison with oxide factors, for the same oxides, which have been taken from the literature.

Table 4

Volume Coefficients of Thermal Expansion
and Oxide Factors

Multiply all values by 10^{-7}

Enamel	CTE	Oxide	Oxide Factor	Average Oxide Factor
X	338.5			
A1	348.0	SiO ₂	0.31	0.17
A2	328.7	"	0.02	
B1	343.7	TiO ₂	1.70	1.57
B2	332.8	"	1.43	
C1	350.7	B ₂ O ₃	-0.56	-0.53
C2	327.2	"	-0.50	
D1	312.5	Na ₂ O	11.79	11.81
D2	363.1	"	11.83	
E1	338.5	PbO	3.39	3.87
E2	341.3	"	4.35	
F1	335.1	CaO	4.48	4.78
F2	343.4	"	5.07	
G1	327.5	Na ₂ SiF ₆	6.94	7.41
G2	351.6	"	7.88	
H1	346.8	Sb ₂ O ₃	0.70	0.84
H2	331.5	"	0.98	

Table 5
Comparison of Oxide Factors

Multiply all values by 10^{-7}

Oxide	B	W&S	M&H	E&T	F&P	Hall
SiO_2	0.17	0.8	0.8	0.15	0.15	0.96
TiO_2	1.57	---	4.1	----	----	----
B_2O_3	-0.53	0.1	0.1	-1.98	----	----
Ba_2O	11.81	10.0	10.0	12.96	12.50	7.60
PbO	3.87	3.0	4.2	3.18	----	1.50
CaO	4.78	5.0	5.0	4.89	----	3.00
Na_2SiF_6	7.41 ^a	---	---	----	----	----
Sb_2O_3	0.84	---	4.0 ^b	----	----	----

a. No corresponding value shown in references. M&H give cryolite (Na_3AlF_6) a factor of 7.4.

b. Calculated from M&H factor for Sb_2O_5 . No factor found for Sb_2O_3 .

B Factors derived in this investigation.

W&S Winkelmann and Schott.

M&H Mayer and Hayes.

E&T English and Turner (value for SiO_2 assumed).

F&P Fetterolf and Parmelee (value for SiO_2 assumed).

Hall Factors shown are three times the linear factors given in Hall's paper. The factor for SiO_2 is taken from his curve in which it varies from 1.5 for a composition containing 20% silica down to 0.15 for 100% silica.

DISCUSSION

DISCUSSION

Considering the data in Table 3, it will be observed that corresponding values of expansion for the same enamel usually check within 0.05 thousandth of an inch for those runs in which the total expansion difference does not exceed this figure. Only rarely do the differences exceed 0.10 thousandth of an inch. From this it would appear that the required check to within 0.05 thousandth of an inch was reasonably well chosen. In the case of Enamel F1 the first two runs seemed to check but after the readings were corrected to an initial reading of zero at 100° F, it was found that the two readings just preceding the final reading were more than 0.10 thousandth of an inch different and it was believed advisable to make a third run. Where such differences were found well removed from the significant first and final readings, with good checks on either side, repeat runs were deemed unnecessary. Admitting a possible error of 0.05 thousandth of an inch for the first and final readings of each run, it is observed that if these errors were in opposite directions there would be a plus or minus error of 0.10 thousandth of an inch, or approximately 0.35%. In calculating the volume coefficient of thermal expansion the same maximum error

of 0.35% may be obtained. However the formula for calculating oxide factors causes the error to become an additive numerical value which may be either positive or negative. It can be shown that this additive error has a maximum value of plus or minus 0.4×10^{-7} . It is evident that a much smaller error than this would account for the difference in the two oxide factors obtained for SiO_2 . In general the reasonably close agreement of the pairs of oxide factors indicate a much smaller and largely compensating error in most cases.

The difference in the oxide factors derived for PbO is greater than would occur even by the remote possibility of deriving the maximum error for each factor in opposite directions. A possible explanation lies in the fact that PbO has a relatively large influence on the softening point of enamel. It will be observed that in general those materials which tend to lower the softening point of the enamel show higher factors in the enamels which contain them in greater proportion. This effect may possibly reach a maximum in the case of PbO . In this connection it should be pointed out that Winkelmann and Schott and Mayer and Havas, using similar methods and compositions, obtained

quite different factors for PbO although generally in close agreement.

The derived oxide factors are in better general agreement with those of English and Turner than with the others shown in Table 5. The value of the factor for TiO_2 does not check with that of Mayer and Havas, the only one found in the literature, being considerably lower. The factor for Sb_2O_3 is also much lower than that calculated from the Mayer and Havas factor for Sb_2O_5 . Both of these oxides are probably amphoteric and it is quite conceivable that their effects on expansion would differ considerably with the composition of the glass or enamel in which they were used. The derived factor for B_2O_3 does not check with any of the others. In this connection, English and Turner found the effect of B_2O_3 on expansion did not follow the general additive rule. As the proportion of B_2O_3 in a glass was increased, its effect on expansion decreased to a minimum and then increased. The range of factors shown for this oxide would tend to confirm this finding.

Hall's results are probably explainable in the light of his having worked with glaze compositions varying considerably from those of enamels and glasses. His assignment of a variable factor to silica is

interesting, although not in agreement with the results reported here nor with those of other investigators.

As a matter of interest, and to give an example of how oxide factors are used, those derived in this investigation are used below to calculate the volume coefficient of thermal expansion of Enamel X.

SiO_2	40	x	0.17	x	10^{-7}	6.80	x	10^{-7}
TiO_2	6	x	1.57	"	"	9.42	"	"
B_2O_3	6	x	-0.53	"	"	-3.18	"	"
Na_2O	15	x	11.61	"	"	177.15	"	"
PbO	15	x	3.87	"	"	58.05	"	"
CaO	6	x	4.78	"	"	28.68	"	"
Na_2SiF_6	6	x	7.41	"	"	44.46	"	"
Sb_2O_3	6	x	0.84	"	"	<u>5.04</u>	"	"
					CTE	326.42		

The result of the calculated value differs from the measured value by a little less than four per cent. In considering this difference it must be remembered that the oxide factors were determined for comparatively small variations and there is reason to believe that they would not apply accurately to the whole amounts of each oxide.

Andrews and Howe calculated expansion coefficients of different enamels by three different methods. Significantly, in every case the result was lower than the measured value, the variation ranging from two to ten per cent.

These results confirm the opinion of previous investigators that oxide factors are additive only over narrow ranges of compositions. Nevertheless they do have definite value which is increased considerably if they have been derived within the composition range in which they are to be applied. The factors obtained in this investigation will permit the changing and substitution of raw materials within the acid resisting enamel range without exceeding the permissible variation of expansion coefficient. They will also be useful in formulating enamels of other types with due regard being given to the approximation of the results. The oxide factors for TiO_2 , B_2O_3 , and Sb_2O_3 are of particular interest since it is evident that even approximate factors for these oxides, in the range covered, have hitherto been lacking. As far as can be determined a factor for Na_2SiF_6 has not been available previously, probably due to the fact that acid resisting enamels in which its use is nearly universal, have been developed largely in recent years.

SUMMARY

SUMMARY

The Volume Coefficients of Thermal Expansion of enamels, calculated from dilatometric measurements, were obtained with a maximum error of less than one half of one per cent.

It was found that errors of expansion measurement become additive in calculating oxide factors, increasing the degree of approximation in respect to them.

Oxide Factors for SiO_2 , Na_2O , PbO , and CaO , derived in this investigation, were found to be in reasonably close agreement with factors derived previously by English and Turner. Oxide Factors for TiO_2 , B_2O_3 , and Sb_2O_3 differed considerably from those of previous investigators, and are believed to be more accurate for use in connection with acid resisting enamels.

The opinion of other investigators that Oxide Factors can be considered additive only through the range of compositions used in their derivation, was confirmed.

Evidence was found that a set of oxide factors which are suitable for calculating the effect of small changes in composition upon the expansion of a certain type of enamel, may not give accurate results if used to calculate the coefficient of expansion of the complete enamel.

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BIBLIOGRAPHY

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