SOME FUSION PROPERTIES OF GROUND COAT ENAMELS AS INFLUENCED BY COMPOSITION

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ABSTRACT

The compositions of nine vitreous ground coat enamels for sheet iron were varied within a region approximating commercial practice by substituting silica (added as flint) for feldspar, and by substituting boric oxide for sodium oxide, and vice versa. In two other enamels the above named fluxes were varied as a unit against the refractories as a unit. The fusion properties of the enamels were studied through determinations of (1) temperature of maximum heat absorption, (2) softening temperature as observed with the interferometer, (3) cone deformation temperature, (4) "button" deformation behavior, and (5) fusion block deformation behavior. The conclusions were: (a) Increasing silica at the expense of feldspar increased the refractoriness moderately and approximately uniformly. (b) Increasing boric oxide at the expense of sodium oxide caused an increase in refractoriness which varied with the percentages of these constituents. It was quite marked when the boric oxide content was near its minimum and the sodium oxide content near its maximum, but diminished progressively as the opposite limits of composition were approached. (c) The extent of this variation was different for different tests, and diminished as the amount of flow required to complete the respective tests increased. This effect was probably due to the fact that differences in viscosity of the enamels had more opportunity to influence the results of those tests which involved a greater flow of the specimens. (d) The mean end temperatures of the various tests increased as the amount of flow required to complete the tests increased. (e) More systematic comparisons of enamels could be made by measuring the heat treatment necessary to produce a given effect than by submitting all samples to the same treatment and distinguishing between them by the varying effect produced. (f) Application of the enamels to test pieces under varying conditions indicated that all of the tests placed them in approximately the correct order of fusibility.

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I. INTRODUCTION

The general subject of the relation between composition and properties is a familiar one to enamel technologists. The broad purpose of investigations in this field is to enable the enameler to predict the important properties of an enamel from its composition, or conversely to estimate with sufficient accuracy the composition which will be required to produce an enamel of given properties lying within attainable limits.

While substantial progress has been made in the investigation of this general subject, still greater steps remain to be taken. The magnitude of the task is better appreciated when it is borne in mind that results in the literature taken as a whole give no assurance that relations exist which hold good without modification for enamels, glazes, and glasses alike, nor indeed for wide variations in composition within these classes.¹ Hence to secure results of the greatest practical usefulness it is desirable to work with specimens representing a range of compositions which are typical of actual commercial practice and which extend beyond such limits only for special reasons.

In accordance with this conception the investigation reported here concerns a group of enamels with a restricted range of compositions embracing typical commercial ground coats for sheet iron. Further, it concerns in the main only one type of the characteristics of these enamels, namely, fusion behavior.² This report forms the first in a series, of which later units will deal with other specific properties of the same enamels.

II. COMPOSITIONS OF ENAMELS STUDIED

The plan was to vary the compositions in such manner and proportions as would be fairly typical of commercial practice.³ No attempt was made to include the extreme limits of compositions which have been used commercially, nor to include all ingredients which have been successfully used in commercial ground-coat enamels. The scheme of variations in composition is given in Table 1, which also includes the results of various tests discussed later in this paper. The first nine enamels (A to I, inclusive) all contained 30 per cent sodium oxide plus boric oxide, 60 per cent silica (added as flint) plus feldspar, and 10 per cent fluorspar plus the oxides of manganese and cobalt. The percentages of the ingredients constituting the 10 per cent portion were kept constant throughout the series, substitutions being made only between sodium and boric oxides and between flint and feldspar. Feldspar, although it contains more than two elements, was varied as a unit in this investigation because that is the usual commercial practice. Enamels J and K do not fit into the system of variation governing the first nine compositions, but are

¹ In this connection special attention is called to International Critical Tables, vol. 2 pp. 87 to 106 (first edition), and to the work of F. P. Hall, "The Influence of Chemical Composition on the Physical Properties of Glazes"; *J. Am. Cer. Soc.*, vol. 13, no. 3, p. 182, March, 1930.

² Although the use of the word "melt" to describe the action of enamels and similar materials when subjected to high temperatures may be of questionable accuracy, the use of "fuse" would seem entirely proper if only for its secondary meaning of "unite" or "coalesce," which would apply to the action of the enamel grains when the material is powdered before heating, as it is in the application of enamels to metal. All tests reported in this paper except those made with the interferometer were performed on samples which had been powdered prior to testing.

³ Use was made of an opinion obtained from R. R. Danielson as to the most prevalent commercial practice in this respect.

included in order to study the effect of altering the described scheme of variation by raising the content of silica and feldspar simultaneously at the expense of both sodium and boric oxides, and conversely of raising the total of the latter two at the expense of the former.

TABLE 1.—Scheme of variation in composition, and results of tests ¹

Enamel designation	Variable constituents ²				Temperature of maximum heat absorption ³		Softening temperature by interferometer method ⁴		Cone deformation temperature ⁵		"Button-test" end temperature ⁶		Fusion block test			
	Feldspar	Flint	Sodium oxide	Boric oxide									"Start" temperature ³		"Finish" temperature ³	
	Per cent	Per cent	Per cent	Per cent	° C.	° F.	° C.	° F.	° C.	° F.	° C.	° F.	° C.	° F.	° C.	° F.
A.....	35	25	17	13	488	910	513	955	644	1,191	697	1,287	705	1,301	737	1,359
B.....	35	25	14	16	520	968	550	1,022	675	1,247	726	1,339	733	1,351	770	1,458
C.....	35	25	11	19	531	988	558	1,037	693	1,279	750	1,382	757	1,395	799	1,470
D.....	30	30	17	13	493	919	518	964	654	1,209	705	1,301	706	1,303	742	1,368
E.....	30	30	14	16	525	977	555	1,031	680	1,256	734	1,353	735	1,355	776	1,429
F.....	30	30	11	19	536	997	562	1,044	701	1,294	759	1,398	761	1,402	805	1,481
G.....	25	35	17	13	499	930	522	971	661	1,222	712	1,314	717	1,323	752	1,386
H.....	25	35	14	16	531	988	560	1,040	685	1,265	742	1,368	750	1,382	785	1,445
I.....	25	35	11	19	542	1,008	569	1,056	705	1,301	765	1,409	775	1,427	814	1,497
J.....	27	27	17	19	501	934	521	969	641	1,186	706	1,303	709	1,308	740	1,364
K.....	33	33	11	13	540	1,004	565	1,049	722	1,332	771	1,420	784	1,443	827	1,521

¹ The temperatures in this table are reported to 1°, not because the absolute values are necessarily correct within 1°, but because the differences in temperature with variations in composition can be more accurately determined from exact than from rounded figures, in view of the fact that each reported value is based on from 3 to 24 determinations.

² Each enamel contained, in addition to the above constituents, 7.7 per cent of fluorspar, 1.7 per cent of manganese oxide, and 0.6 per cent of cobalt oxide.

³ Means of 6 values from duplicate determinations on each of 3 samples.

⁴ Means of 3 determinations on 3 different samples.

⁵ Means of 24 determinations, 8 on each of 3 batches.

⁶ Each value based on 6 to 9 determinations.

The compositions of the batches were calculated from the results of chemical analyses of the raw materials, and are given in Table 2. The calculated melted compositions are given in Table 3, together with the results of analyses of the enamel frits.

TABLE 2.—Compositions of raw batches calculated to give 100 parts of enamel

Enamel designation	Ingredients (parts by weight)								Total
	Borax	Feldspar	Quartz	Soda ash	Soda niter	Fluorspar	Cobalt oxide	Manganese oxide	
A.....	34.90	35.38	24.75	16.53	5.00	8.06	0.60	1.94	127.16
B.....	43.00	35.38	24.75	8.92	5.00	8.06	.60	1.94	127.65
C.....	51.00	35.38	24.75	1.30	5.00	8.06	.60	1.94	128.03
D.....	34.90	30.30	29.76	16.53	5.00	8.06	.60	1.94	127.09
E.....	43.00	30.30	29.76	8.92	5.00	8.06	.60	1.94	127.58
F.....	51.00	30.30	29.76	1.30	5.00	8.06	.60	1.94	127.96
G.....	34.90	25.26	34.76	16.53	5.00	8.06	.60	1.94	127.05
H.....	43.00	25.26	34.76	8.92	5.00	8.06	.60	1.94	127.54
I.....	51.00	25.26	34.76	1.30	5.00	8.06	.60	1.94	127.92
J.....	51.00	27.28	26.75	11.83	5.00	8.06	.60	1.94	132.46
K.....	34.90	33.35	32.76	6.00	5.00	8.06	.60	1.94	127.11

TABLE 3.—Chemical compositions of finished enamels, as calculated from Table 2, and as indicated by the results of chemical analysis ¹

Enamel	Constituents ²						
	B ₂ O ₃	Na ₂ O	K ₂ O	SiO ₂	Al ₂ O ₃	Ca	F ₂
	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>
A-----	{ 13.0	17.7	4.4	48.6	6.4	4.0	3.7
	{ 13.1	16.9	4.6	48.9	6.8	4.1	3.4
B-----	{ 16.0	14.7	4.4	48.6	6.4	4.0	3.7
	{ 15.9	14.2	4.6	50.3	6.7	4.1	3.1
C-----	{ 19.0	11.7	4.4	48.6	6.4	4.0	3.7
	{ 18.8	11.1	4.4	49.8	6.8	4.1	3.1
D-----	{ 13.0	17.6	3.8	50.3	5.5	4.0	3.7
	{ 13.1	17.0	3.9	50.9	5.8	4.0	3.2
E-----	{ 16.0	14.6	3.8	50.3	5.5	4.0	3.7
	{ 16.3	14.0	3.9	51.1	5.7	4.0	3.1
F-----	{ 19.0	11.6	3.8	50.3	5.5	4.0	3.7
	{ 19.0	11.1	3.8	50.6	6.1	4.0	3.0
G-----	{ 13.0	17.5	3.1	51.9	4.6	4.0	3.7
	{ 13.3	16.7	3.3	51.8	4.9	4.1	3.1
H-----	{ 16.0	14.5	3.1	51.9	4.6	4.0	3.7
	{ 16.6	13.8	3.3	51.8	5.0	4.1	2.8
I-----	{ 19.0	11.5	3.1	51.9	4.6	4.0	3.7
	{ 19.3	10.9	3.2	51.9	5.0	4.1	2.9
J-----	{ 19.0	17.6	3.4	45.3	4.9	4.0	3.7
	{ 19.4	16.7	3.6	45.0	5.3	4.0	3.1
K-----	{ 13.0	11.7	4.1	55.3	6.0	4.0	3.7
	{ 13.2	11.4	4.3	55.3	6.5	4.0	3.0

¹ Values in roman type were calculated, and those in italics were obtained by chemical analysis. The analyses were made by J. F. Klekotka and F. W. Glaze, of the Bureau of Standards.

² Only a part of the enamels were analyzed for cobalt and manganese oxides, but the indication was that all may be considered as having the theoretical content of 0.6 per cent cobalt, reported as Co₂O₄, and 1.7 per cent of manganese oxide reported as MnO₂. The values reported from analytical results are averages from analysis of two of the triplicate batches, except for enamels G and H, and all fluorine values, each of which is based on analysis of only one enamel batch.

III. PREPARATION OF ENAMELS

Each individual raw material was thoroughly mixed in a pebble mill and placed in sealed containers to prevent contamination or change in moisture content before use. The batches were made up in quantities sufficient to give 1 kg, melted weight, of each enamel. A second set of batches was made to duplicate the first. Each of these raw batches was divided into halves. Three of the four resulting lots were used, and were smelted in 75 ml platinum crucibles to avoid contamination by partial solution of fire-clay crucibles. Each half batch made four such crucible batches, which were combined after smelting, so that finally each enamel was available for test in triplicate. The enamels were identified by the first 11 letters of the alphabet, and the triplicate batches distinguished numerically. Two of the three sets (one from each of the two original raw batches) were analyzed to obtain the results given in Table 3.

The furnace used for smelting was similar to one described by F. H. Norton and C. L. Norton, jr.⁴

The heating arrangement was modified to permit better temperature control and to insure oxidizing conditions. This change was effected by using a burner which, although of essentially the same type, had

⁴ Norton, F. H., and Norton, C. L., jr., A Small, Gas-fired Laboratory Furnace, J. Am. Cer. Soc., vol. 13 (3), p. 161, 1930.

additional facilities for a forced air supply. Both gas pressure and air pressure were controlled, and the temperatures could be held constant within about $\pm 5^{\circ}$ C. (9° F.). The enamels were all smelted at approximately $1,250^{\circ}$ C. ($2,280^{\circ}$ F.) for one hour and stirred during smelting at 10-minute intervals with a small nickel rod. After smelting they were fritted in cold water, dried, and pulverized in a mortar to pass a No. 150 sieve.

IV. DESCRIPTION OF TESTS AND ANALYSIS OF RESULTS

Various methods of testing the fusibility or refractoriness of enamels are in use. To what extent the results obtained by these methods may be correlated, and whether or not it is practicable to convert values expressed in terms of one test into equivalent values in terms of another, are among the questions which it is hoped the present study will clarify. Further, the various tests on fusibility were carried out with the object of investigating the effect of the specified variations in composition upon the fusion behavior of the enamels. Stated briefly, the dual object was to compare the tests and to compare the enamels.

1. TEMPERATURES OF MAXIMUM HEAT ABSORPTION

Determinations of the temperatures of maximum rate of heat absorption were included because there is evidence to support the view that an enamel when heated to a sufficiently high temperature undergoes a readjustment, as indicated by the absorption of heat. Above this temperature the material deforms at a rate which increases with the temperature. Such a conception ranks the temperature of maximum heat absorption as a closer approximation to a true "fusion" temperature than any of the other tests described in this paper. Thus these determinations supply something which at least approaches a constant of the material, and with which the other tests, more adaptable to shop and industrial laboratory use, may be compared. They may serve a further useful purpose in certain fields of composition by virtue of their close reproducibility because, on comparison of enamels intended to have the same composition, any considerable difference in the temperatures of maximum heat absorption indicates a departure from the desired composition. Another reason why these determinations are desirable is because they indicate an annealing temperature of the enamels, falling as they do about midway in the annealing range. Thus the readjustment takes place within a range of temperature between the lower and upper critical temperatures; that is, between the temperature at which the rate of thermal dilatation per degree rise in temperature suddenly increases, and the temperature at which vertical elongation becomes negative due to softening of the specimen.⁵

The exact temperature at which the rate of readjustment, and hence the rate of heat absorption, is most rapid depends to some extent on the thermal history of the specimen and the rate of increase of temperature during the test. Closely reproducible results may be obtained, however, if the specimens are heated before testing to a

⁵ Tool and Valasek, B. S. Sci. Paper No. 358, 1920; Tool and Eichlin, B. S. Jour. Research, Vol. 6 (RP292), p. 523, April, 1931; Peters and Cragoe, B. S. Sci. Paper No. 393, 1920.

temperature at which all strains are relieved, cooled at a suitable rate, and then tested at a reasonably constant rate of temperature elevation.⁶

(a) DESCRIPTION OF TEST

The test was made as follows: A 20 g portion of the powdered enamel was placed in a 25 ml platinum crucible, which was then placed approximately in the center of an electric muffle furnace having inside dimensions of 7 by 5 by 12 inches. The junction of a platinum, platinum-rhodium thermocouple was placed near the center of the sample. The cold junction of the thermocouple was kept at 0° C., and the emf was indicated by means of a type K potentiometer graduated to 0.0005 mv. The temperature of the

FIGURE 1.—Typical inverse rate heating curve (enamel I, specimen 9-12) as used to determine temperature of maximum rate of heat absorption

Curve A shows time interval (upper scale) required for 2.5° C. increase in temperature at the average temperature (emf) indicated by each point on curve. Curve B shows time interval (lower scale) required for 10.0° C. increase in temperature at the average temperature (emf) indicated by each point on curve.

sample was then raised to approximately 75° C. above its initial deformation temperature as determined with the interferometer and allowed to cool in the furnace, thus preparing it for the test. This treatment incidentally caused a sintering effect in the powdered enamel, and firmly fixed the thermocouple in place. The temperature of the sample was increased at a rate of 5° to 6° C. per minute in the temperature range of maximum heat absorption. A typical temperature schedule is shown in the inverse rate curves in Figure 1.⁷ From curve B it may be seen that the rate of temperature increase just before the heat absorption began (about 470° C.) was approximately 10° C. per minute, and at the end of the test was a little over

⁶ See second item, footnote 5.

⁷ See first item, footnote 5.

6° C. per minute. The dotted line indicates approximately the temperature schedule of the furnace itself between these temperatures.

After one set of observations had been completed, the sample was prepared for a second test by allowing the elevation in temperature to continue until it again reached 75° C. above the initial deformation temperature, so that its condition due to thermal history would be virtually the same as before the test. After cooling, a second determination was made on each sample.

(b) LOCATION OF END POINT

Curve *A*, in Figure 1, was plotted from the data as obtained. Exactly the same data were used to compute the points in curve *B*, and each point on the latter represents the sum of four points on the former. For example, the time-increment value of the bottom point of curve *B* is obtained by adding the time-increment values of the first four points of the original data (curve *A*). The next higher point is obtained from the second, third, fourth, and fifth original points, etc. By the use of this system a more accurate location of the point of maximum deflection could be accomplished, and better agreement between check determinations was obtained because mechanical and personal errors were largely compensated.

The point of maximum deflection was estimated from the computed curves to 0.005 mv (0.5° C.), and at least two determinations were made on each sample. The average deviation of the individual values from the mean of the two determinations was 0.6° C. (1.1° F.) and the maximum deviation was 1.5° C. (2.7° F.). The values obtained by the two determinations on a given sample were averaged with the corresponding values for the other two of the triplicate samples, and the final averages are given in Table 1. The average individual deviation from mean in this case was 0.9° C. (1.6° F.) and the maximum 2.3° C. (4.1° F.).

(c) ANALYSIS OF RESULTS

From the data in Table 1 it may be seen that the increase of silica from 25 to 30 per cent at the expense of feldspar caused an increase in the temperature of maximum heat absorption of 5° C. (9° F.). This conclusion is based upon the results of 36 determinations, since it involves six mean values (for enamels *A*, *B*, *C*, *D*, *E*, and *F*, respectively) each of which is obtained from six determinations. In a similar manner, the conclusion that the further increase of silica to 35 per cent at the expense of feldspar caused a 6° C. (11° F.) increase is also based upon 36 determinations. Disregarding the slight difference in magnitude of effect between the first and second substitutions, it may be stated that in every case the temperature of maximum heat absorption increased approximately 1.1° C. (2° F.) for each substitution of 1 part of silica for 1 part of feldspar.

No such generalization is applicable in describing the effect of increasing boric oxide at the expense of sodium oxide while the percentages of silica and feldspar remained constant. Enamels *A*, *B*, and *C* all have 25 per cent feldspar and 35 per cent silica, and in the order named boric oxide is increased from 13 to 19 per cent at the expense of sodium oxide, which is reduced from 17 to 11 per cent. The substitution of 3 parts of boric oxide for 3 parts of sodium oxide, as indicated in enamels *A* and *B*, caused an elevation in the determined

temperature of 32° C. (58° F.), but the further substitution of 3 more parts of boric oxide for 3 parts of sodium oxide, as indicated in enamels B and C caused a further elevation of only 11° C. (20° F.), or about one-third as much.

The parallel case of enamels D, E, and F, in which silica and feldspar are both maintained at 30 per cent while sodium oxide and boric oxide are varied as in the preceding group, shows exactly the same relation which prevails also in the third parallel case, comprising enamels G, H, and I.

Here again, the general conclusion that the first 3 per cent increase in boric oxide at the expense of sodium oxide caused a 32° C. (58° F.) rise in the determined temperature, is based upon 36 determinations, and the statement that the second 3 per cent substitution

FIGURE 2.—Variation in temperatures of maximum heat absorption with the compositions of the enamels

Key: SPAR=Feldspar (considered as a unit).
 SIL =Silica added as flint.
 BOR =Boric oxide.
 SOD =Sodium oxide.

causes an 11° C. (20° F.) rise is based upon a like number. The values for enamels J and K show that when boric and sodium oxides are decreased together from 19 and 17 per cent, respectively, to 13 and 11 per cent, respectively, with simultaneous increase of feldspar and silica from 27 per cent of each to 33 per cent of each, the temperature of maximum heat absorption is increased 39° C. (70° F.).

This system of relations may be visualized more readily with the aid of a suitable diagram. Accordingly a space model was constructed and projected in perspective as in Figure 2. In this figure silica increases at the expense of feldspar from left to right, and boric oxide increases at the expense of sodium oxide from front to rear. The letters at the base of the pillars designate the enamels having compositions corresponding to the positions of the pillars on the base

plane. These compositions are the ones given in Table 1, except that J and K are omitted. The vertical scale represents temperatures of maximum heat absorption. The base plane is arbitrarily set at the level of 470°C . (878°F .), and the determined value for any of the enamels can be closely approximated by adding to this temperature an amount determined by counting the alternate light and dark bands, or fraction thereof, on the pillar corresponding to the enamel in question. Each band has a length corresponding to a temperature interval of 10°C . (18°F .). Reference to these bands minimizes any error of parallax in reading the diagram.

This figure illustrates graphically the relations which were obtained from the data in Table 1. In addition, it has the advantage that it enables the observer to visualize simultaneously these several relations and their mutual interdependence. It is apparent from this figure that substituting silica for feldspar caused virtually a straight line increase in the temperature of maximum heat absorption and that this increase is the same for all three groups of enamels in which the percentages of boric and sodium oxide are fixed. It is also apparent that the substitution of boric oxide for sodium oxide caused an increase in the determined temperature which does not follow a straight line, inasmuch as the effect per unit of substitution decreases as the substitution progresses.

Although the compositions of enamels J and K are outside of the field shown in this diagram, the latter may be used with reference to these two enamels by comparing their determined temperatures as given in Table 1 with the observed points for other enamels which are given in the diagram. A comparison of this sort indicates that the high flux enamel J has about the same maximum heat absorption temperature as enamel G and the low flux enamel K has about the same maximum heat absorption temperature as enamel I. A comprehensive statement of this relation is as follows: The simultaneous decrease from 19 to 13 per cent B_2O_3 , and from 17 to 11 per cent Na_2O , accompanied by a corresponding increase from 27 to 33 per cent each of silica and feldspar, caused approximately the same increase in the temperature of maximum heat absorption as was caused by increasing boric oxide from 13 to 19 per cent with a simultaneous reduction of sodium oxide from 17 to 11 per cent.

The immediately preceding statement could have been expressed more conveniently in an abbreviated form by saying that the J-K change caused about the same increase in the determined temperature as the G-I change. From this point on, this abbreviated form of expression will be used.

2. INITIAL DEFORMATION TEMPERATURES BY INTERFEROMETER METHOD⁸

The specimens used for the interferometer tests were segments of rods which had been drawn from the molten frit. They were about 3 mm in diameter and 5 mm in height. The bottom end of each specimen was ground to form three short legs, and the top to form a cone of gently sloping sides and a slightly blunted point. When these

⁸ The interferometer, and method of using it, is described by G. E. Merritt, in B. S. Sci. Paper No. 485, 1924.

specimens were heated in the interferometer to temperatures approximating 25°C . (45°F .) above their respective temperatures of maximum heat absorption they softened sufficiently so that a slumping movement could be detected.⁹ The temperature at which this deformation occurred is referred to here as the initial deformation temperature.¹⁰ This temperature may vary somewhat with the heating rate, the weight of the upper quartz plate, and the shape of the specimens. All of these factors were therefore kept as constant as possible, the heating rate being 3°C . per minute.

The averages of three determinations on the three different batches of each of 11 enamels are given in Table 1 and bear quite a symmetrical relation one to another. The mean deviation from the average results reported was 3°C . (5.4°F .) and the maximum was 10°C . (18°F .) A graphical arrangement (not shown) of these data bears a striking similarity to Figure 2. The outstanding differences are that this phenomenon occurred at approximately 25°C . (45°F .) higher temperature, and that in the relation between the substitution of boric for sodium oxide and the elevation in the determined temperature, the deviation from a straight line is even more pronounced than in the case of Figure 2. Thus the mean elevation in softening temperature caused by the A-B, D-E, and G-H changes in composition is 37°C . (67°F .) and the mean for the B-C, E-F, and H-I changes is 8°C . (14°F .) Each of these mean values (37° and 8°C .) is based upon the results of 18 determinations. The ratio of the smaller temperature increase to the larger is about two-ninths, which compares with about three-ninths in Figure 2.

By interpolation it was estimated that a 1 per cent substitution of boric oxide for sodium oxide beginning with composition A, D, or G would elevate the softening temperature approximately ten times as much as a similar 1 per cent substitution, ending with composition, C, F, or I. This ratio of 10 to 1 corresponds with that of 6 to 1 in the case of the temperatures of maximum heat absorption.

The mean elevation in softening temperature caused by the A-G, B-H, and C-I changes in composition was virtually the same as in Figure 2, being 10°C . (18°F .) as against 11°C . (20°F .) Thus it appears that the substitution of silica for feldspar, within the limits studied, causes approximately a straight line increase in the initial deformation temperature of 1°C . (1.8°F .) for each 1 per cent substitution.¹¹

3. CONE DEFORMATION TEMPERATURES

(a) DESCRIPTION OF TEST

The cone deformation tests were modeled after the tentative standard method of the enamel division, American Ceramic Society.¹² Instead of the standard size cones, $2\frac{1}{2}$ inches high, cones $1\frac{1}{4}$ inches high were used, because the supply of each enamel was limited. In order to minimize breakage in handling, the dried cones were slightly

⁹ The data obtained in these tests relative to coefficient of expansion were reserved for a separate publication.

¹⁰ Some authors have called this temperature the initial softening temperature.

¹¹ The results reported here were obtained on first heatings of the specimens involved. Second heatings, carried out in connection with expansivity determinations, gave results generally a few degrees higher, but bearing the same relationship to one another.

¹² Bull. Am. Cer. Soc., p. 269, September, 1930.

sintered by heating for a few minutes to a temperature about 50° C. (90° F.) above the initial deformation temperatures.

Two cones of an arbitrarily chosen standard enamel were placed at diagonally opposite corners of a rectangle, and two of the test enamel at the remaining two corners.

The results obtained were less closely reproducible than those for any of the other tests, and to compensate for this fact a large number of determinations was made and statistical methods were used in analyzing the data. The averages of eight test cones (in no case less than seven) and of an equal number of standard cones were used in determining the cone-deformation temperature for any given batch of enamel. Since all enamels studied were made in triplicate batches, 48 cones were tested to obtain the reported value for any given enamel.

(b) ANALYSIS OF RESULTS

Use was made of the standard cones to reduce all determinations to a common basis in the following way: The deformation temperatures of 242 standard cones were arranged graphically according to their frequency distribution. This arrangement showed a symmetrical distribution in which the arithmetical mean, the median and the mode (the latter being determined graphically) all virtually coincided at 677.5° C. (1,252° F.). Each determination was then corrected by the formula:

$$T_c = T_t - T_s + T_s$$

in which:

T_c = corrected deformation temperature.

T_t = mean deformation temperature of the eight test cones under consideration.

T_s = mean for the eight corresponding standard cones.

T_s = mean deformation temperature of 242 standard cones.

By this method better agreement was obtained between separate determinations on a given enamel composition, and also between separate determinations of the variation in deformation temperature caused by the change from one composition to another.

The results of the cone-deformation test are shown in Table 1 and in Figure 3. The mean rise in cone-deformation temperature due to the A-D, B-E, and C-F changes in composition is 8° C. (14° F.). Since each point given in the figure represents a mean value based upon results obtained with 24 test cones, corrected by 24 standards, the mean temperature rise of 8° C. given above is based upon the results obtained with 288 cones, half of which were test cones and half standards. Each of the other mean values given in the following discussion which applies to Figure 3 is likewise based upon the data obtained with 288 cones. The mean elevation in cone-deformation temperature resulting from the D-G, E-H, and F-I changes in composition was 5° C. (9° F.). Thus the second substitution of 5 per cent silica for 5 per cent feldspar was somewhat less effective than the initial substitution in elevating cone-deformation temperatures, although this was not true in the case of temperatures of maximum heat absorption and initial softening points.

With reference to the substitution of boric oxide for sodium oxide, it is seen that the mean elevation in deformation temperature caused by the A-B, D-E, and G-H changes in composition was 27° C. (49° F.). The mean elevation caused by the B-C, E-F, and H-I

changes was 20° C. (36° F.). Thus while the initial substitution of 3 per cent boric oxide for 3 per cent sodium oxide has a distinctly greater effect upon the cone-deformation temperatures than the second similar substitution, the difference is not so pronounced as in the cases of the two previously described tests.

By interpolation it was estimated that a 1 per cent substitution of boric oxide for sodium oxide, beginning with composition A, D, or G, would have about twice as much effect upon the cone-deformation temperature as a similar 1 per cent substitution ending with composition C, F, or I.

FIGURE 3.—Variation in cone deformation temperatures with compositions of the enamels

Key: SPAR=Feldspar (considered as a unit).

SIL =Silica added as flint.

BOR =Boric oxide.

SOD =Sodium oxide.

4. BUTTON TESTS

A test of fusion behavior which has had considerable use in determining the fusibility of feldspar, but has had less application in work on enamels, is the "button" test. It consists in heating cylinders of the powdered material and observing the resulting deformation into button-like shapes. For this work, frit, which had been slightly moistened, was formed into cylinders three-fourths inch in diameter and three-fourths inch in length by hand tamping in brass molds.¹³ The cylinders were dried before testing. For control purposes cylinders made from the standard enamel were heated simultaneously with each test enamel. The same standard enamel was used as in the

¹³ The technique used in this test was based upon that worked out by B. A. Rice while a fellow at the Mellon Institute for the Standard Sanitary Manufacturing Co.

case of the cone-deformation tests. The similarity of procedure was carried further in that four cylinders, two of a test enamel and two of the standard, were placed in the furnace at one time. They were arranged with their centers at the four corners of a $1\frac{1}{2}$ -inch square on a piece of one-eighth inch cast iron, coated with TiO_2 powder to prevent sticking.

(a) VARIABLE-END-POINT PRINCIPLE

The manner of using this test, which has been followed heretofore, is to place a plaque bearing cylinders of two or more enamels which it is desired to compare into a furnace at a given temperature and allow it to remain a given time. The resulting "buttons" are then compared visually according to their relative stages of deformation. Hence in comparing different enamels the time-temperature conditions are constant and the end points vary for the different enamels. The underlying principle of this procedure will be referred to here

FIGURE 4.—*Illustrative diagram, showing approximately the relative deformation behavior of cylinders of different enamels when treated simultaneously in a furnace at constant temperature*

as the variable-end-point principle. The enamels were first tested according to that procedure, and for purposes of correlation the stage of deformation of each enamel was numerically evaluated by measuring the height and diameter of the buttons of that enamel after the specified heat treatment. When the results were plotted in a solid diagram, as in the case of Figures 2 and 3, the shape of the resulting surface varied, depending upon the time-temperature conditions which happened to be chosen for the comparison. By selection of the test conditions the shape of the figure could be made to vary from wholly convex (with gradual variation in the extent of convexity from one end to the other) through partly convex and partly concave to wholly concave (with gradual variation in the extent of concavity from one end to the other). The reason for these varying relationships may be seen from the diagram shown in Figure 4. The numbered curves in this figure correspond to enamels of different fusibilities, No. 1 being the most fusible. If the extent of deformation

of the respective enamels is compared at the time T_1 , the relation between enamels will be different than if compared at T_2 or T_3 , and the latter two comparisons will also differ from each other. This effect is produced by the fact that the deformation progresses first slowly, then rapidly, and then slowly again as the buttons flatten, giving a typical S curve. Hence one unit of change in shape at a given stage of the deformation is not comparable with one unit at a different stage of the deformation, and it is misleading to make correlations in which these irregularities are ignored.

While tests based on the variable-end-point principle are quickly and easily carried out, and may quite possibly give all the information which is usually desired from a shop test, it was concluded that such tests are unsuitable for the purpose of correlating properties quantitatively with systematic variations in composition.

(b) CONSTANT-END-POINT PRINCIPLE

The tests described in preceding sections of this paper, up to and including the cone test, were all made on the constant-end-point principle; that is, the temperature was raised on a definite schedule until a given end point was reached. This end point was the same for the different enamels, and the severity of the heat treatment required to attain it was used as a measure of the fusibility.¹⁴

In the three previously described tests, however, a definite end point could be readily detected, while in the button test it is not easy to estimate when the test piece in the furnace has reached a definite stage of deformation.

To avoid this difficulty two precautions were taken. One was to place on the plaque with the test cylinders a bar of a refractory material which would not deform, having a height corresponding to that desired for the buttons as an end point. The effort was made to remove some "buttons" of a given enamel from the furnace at a slightly greater height, some at the same height, and some at a slightly lower height than the guide. The height and diameter of these buttons were measured with a micrometer caliper, and the deformation expressed in terms of the ratio of height to diameter. The selected end point was a ratio of 0.6, and when the several ratios for the respective buttons of a given test enamel were plotted against the corresponding temperatures of removal from the furnace, it was possible to determine by interpolation the temperature required to attain the exact end point selected.

The buttons of the standard enamel were used to reduce all the tests to a common basis in the following ways: Since the test buttons were all brought to approximately the same stage of deformation by means of different degrees of heat treatment, the simultaneously tested buttons of the standard enamel reached various stages of deformation. The respective deformation values for all the buttons of the standard enamel were plotted against the corresponding temperatures of removal from the furnace. Then, in making the graphs for interpolation referred to above, instead of using the observed end temperatures, in each case corrected temperature values

¹⁴ The question logically arises as to what the effect may be of choosing different end points (for example, different degrees of deformation) upon which to base comparisons, any given comparison, however, being based on the constant-end-point principle. The effect of such a procedure is brought out in the discussion accompanying Figure. 7.

FIGURE 5.—*Two specimens tested by the fusion block method*

The one at the right (dry packed) reached the stage shown at approximately 15°C . (27°F .) lower than the specimen at the left (wet packed), although the enamel was the same in both cases. Note that in the case of the dry-packed block the enamel stream is wider and the receptacle has been left clean.

obtained from the standard enamel curve were used. To obtain these corrected values for the buttons of a given test enamel, the degree of deformation of the simultaneously tested buttons of standard enamel was measured, and the corresponding temperatures were read from the standard enamel curve. The corrected values sometimes differed slightly from the observed temperatures, and gave a more symmetrical relation with the enamel compositions.

The temperatures given in Table 1, when arranged in a space diagram gave a figure similar in appearance to Figure 3, falling approximately 50° C. (90° F.) higher on the temperature scale, and differing somewhat as to the detail of dimensions. The mean rise in end temperature due to the A-D, B-E, and C-F changes in composition was 8° C. (14° F.), and that due to the D-G, E-H, and F-I changes was 7° C. (13° F.). The mean effect of the A-B, D-E, and G-H changes in composition was to raise the determined temperature 29° C. (52° F.), and that of the B-C, E-F, and H-I changes was a further increase of 24° C. (43° F.). Each of these mean values is based upon tests of 36 buttons of the test enamel corrected by 36 of the standard. Here again, the substitution of silica for feldspar causes a moderate and approximately uniform increase in deformation temperature, while the substitution of boric oxide for sodium oxide causes a more rapid change, which diminishes somewhat for each percentage of substitution as the substitution progresses.

5. FUSION BLOCK TESTS

Another test designed initially for use on feldspars, but which has been applied also to the study of the fusion characteristics of enamels, involves the use of "fusion blocks" (see fig. 5), which are made of porcelain and are available commercially.

As in the case of the button tests, the usual practice has been to compare enamels on the variable-end-point principle, by placing two fusion blocks packed with the respective enamels together in a furnace at constant temperature and removing them for comparison when the more fusible one has flowed to the lowest graduation mark. Here again this practice was rejected in favor of the constant-end-point principle, in accordance with which the temperature was increased on a definite time schedule, and the end point taken as the temperature at which the test enamel flowed past a given graduation mark. Both the temperature at which the uppermost graduation mark was passed (the "start" temperature) and that at which the lowest graduation mark was passed (the "finish" temperature) were recorded in this case.

In analyzing the original set of data some discrepancies were observed which resulted in studying the manner of packing the enamel into the receptacles. It was observed that the greatest difference in results existed between specimens which had been moistened and packed very tightly and those which were dry packed. Before testing the dry-packed specimens, the loaded fusion block was placed horizontally in a furnace and the enamel sintered just sufficiently to hold it in place. When the enamel powder was moistened before packing it remained in place, even after drying, without the sintering treatment. When tested, the dry-packed specimens flowed at a lower temperature and in a broader stream than the wet-packed ones, leaving the receptacles free from enamel, as shown in Figure 5.

Thus to secure results which could be compared one with another it was necessary to pack the different specimens uniformly. It is thought that uniformity can be secured more easily by dry packing, but it was not considered necessary to repeat the tests on that basis. The more serious of the original discrepancies were avoided by eliminating a few specimens which by the peculiar character of the enamel streams indicated that the packing had not been consistent with that of the majority of the specimens. Such vacancies in the data were filled by the testing of additional specimens.

The results are shown in Table 1 and Figure 6. Each of the mean temperatures shown in Table 1 is based upon six individual deter-

FIGURE 6.—Variation in "start" and "finish" temperatures of fusion block determinations with the compositions of the enamels

The lower surface represents "start" and the upper surface "finish" temperatures. The lengths of the intervening pillars indicate the difference between these two temperatures for the respective enamels.

Key: SPAR = Feldspar (considered as a unit).

SIL = Silica added as flint.

BOR = Boric oxide.

SOD = Sodium oxide.

minations, two on each of the enamels made in triplicate. The individual determinations varied from the means by an average of 4° C. (7° F.), and a maximum of 11° C. (20° F.).

Figure 6 shows the relation between composition and (1) "start" temperature, (2) "finish" temperature, and (3) spread between "start" and "finish" temperatures. For the A, D, and G compositions the mean spread is 34.3° C.; for B, E, and H, 37.7° C.; and for C, F, and I, 41.0° C. Thus the mean increase in spread from enamels A, D, and G to B, E, and H is 3.4° C., and the mean further

increase to C, F, and I is 3.3°C . These latter two mean values are each based upon the results of 72 temperature determinations.

Since the temperature was increased in these tests according to a definite schedule, an increased temperature interval indicates also an increased time interval. Thus it is apparent that as boric oxide was substituted for sodium oxide, not only did the flow begin at a higher temperature, but once begun it proceeded at a slower rate in spite of the increased temperature. Hence the viscosity at corresponding stages of flow must have been greater. Also, since there is experimental evidence from other sources that the substitution of boric oxide for sodium oxide increases the firing range,¹⁵ it is not unreasonable to assume that the spread between "start" and "finish" temperatures in this test may be an indication of the firing ranges of the enamels under study.

The "finish" temperatures were in better agreement than the "start" temperatures. Considering the effect upon "finish" temperatures of substituting silica for feldspar, it is seen that the A-D, B-E, and C-F changes in composition caused a mean rise in "finish" temperatures of 5.7°C . (10°F .), while the D-G, E-H, and F-I changes caused a mean rise of 9.3°C . (17°F .).

The substitution of boric oxide for sodium oxide was, as in previously described tests, more effective than the feldspar-silica substitution in changing the property under study. The A-B, D-E, and G-H changes caused a mean elevation in "finish" temperature of 33.3°C . (60°F .), while the B-C, E-F, and H-I changes caused a mean elevation of 29.0°C . (52°F .). As may be seen in Figure 6, the "finish" temperatures have almost straight line relations with the enamel compositions. The data indicate, however, that the lines do actually deviate from straightness in approximately the same manner as, but to a lesser degree than, in the previously discussed cases. By interpolation it was estimated that an increase in boric oxide from 13 to 14 per cent, at the expense of sodium oxide decreasing from 17 to 16 per cent would cause an increase in the determined temperature of about 12°C . (22°F .) while a similar increase from 18 to 19 per cent at the expense of sodium oxide decreasing from 12 to 11 per cent would cause an elevation of 9°C . (16°F .).

V. CORRELATION OF FUSION TESTS WITH EACH OTHER AND WITH FIRING BEHAVIOR OF THE ENAMELS

There is a systematic relation between the results of the five tests which have been described. The increase of silica, at the expense of feldspar caused, according to all of these tests, a moderate increase in refractoriness, averaging around 1° to 1.5°C . (1.8° to 2.7°F .) for each 1 per cent substitution. The curves representing this relation deviate slightly from a straight line, but hardly enough to invalidate the preceding generalization.

The substitution of boric oxide for sodium oxide falls in a different category. The first substitution, embracing the A-B, D-E, and G-H changes in composition, caused in all tests a decided increase in the determined temperatures, approximating 30°C . (54°F .) for a 3 per cent substitution. The second substitution, embracing the

¹⁵ Danielson, R. R., and Sweely, B. T., Relation Between Composition and Properties of Enamels for Sheet Steel, *J. Am. Cer. Soc.*, vol. 6, No. 10, p. 1011, 1923.

B-C, E-F, and H-I changes caused a further increase which varied in magnitude with the temperatures involved. In general, for the tests having lower end temperatures, the rise caused by this second composition change was only about one-third that caused by the first, but this ratio increased with the end temperatures of the tests until, at the fusion block finish temperatures, the rise was about seven-

FIGURE 7.—Effect of temperature at which end point occurs upon change of end point with enamel composition

The "labels" of the curves indicate the respective types of test involved. Note that the curves become straighter with increasing temperature.

eighths of that caused by the first substitution. This relation is shown in Figure 7, in which there are six groups of three connected points. The three points in each case correspond to three different percentages of boric and sodium oxides, as shown on the abscissa. The ordinate shows for the respective tests the mean of the determined temperatures for all enamels having the indicated percentages of boric

and sodium oxide. Thus the points at the left are means for the A, D, and G compositions, those midway for the B, E, and H, and those at the right for the C, F, and I compositions. As indicated in the figure, each set of three points pertains to a different kind of test. The numbers in columns *a* and *b* indicate in °C. the temperature increases corresponding to the changes in composition shown on the abscissa. In column *c* are given the ratios of the *a* to the *b* increases, which will be referred to as the "*c* ratios." It is apparent that, in general, the higher the temperature at which the end point occurs, the higher the *c* ratio.¹⁶

It is not necessary to search far for a reasonable explanation of why there should be a systematic change in the *c* ratio with temperature. The bottom group of three points in Figure 7, relating to temperatures of maximum rates of heat absorption, represents determinations which involve no flow of the enamel whatever. The next higher group, relating to initial deformation points as indicated by the interferometer, represents determinations involving only an almost infinitesimal amount of flow, which may be disregarded. These two types of determinations, therefore, may be considered as involving fusibility, uninfluenced by viscosity. The remaining types of determinations involve not only fusibility, but also viscosity, and they are therefore influenced by the time required for the enamels to flow from one position to another.

If the rate of flow from the beginning of flow to the end point were uniform in any particular test for all the enamels studied, obviously whatever end points were chosen would bear the same relation to one another as the temperatures at which flow started, which are indicated by the interferometer test. But since the flow is slower for the compositions having higher ratios of boric oxide to sodium oxide, the end temperatures for those compositions are displaced upward on the temperature scale relative to the more rapidly flowing compositions. The greater the amount of flow involved the greater the displacement. This condition operates progressively to straighten the lines connecting the various groups of points as the amount of flow involved increases from virtually none at the initial deformation temperatures to a very considerable amount at the fusion block finish temperatures.¹⁷

The question naturally arises as to whether any or all of the tests which have been described indicate the relative behavior of the enamels when actually fused as coatings on sheet iron. It has been reported that in some instances enamels which appear in a certain order of "flowability" when tested at lower temperatures will reverse this order when tested at considerably higher temperatures.¹⁸ This observation is in harmony with the fact that the viscosities of different

¹⁶ Although the lines connecting the points in Figure 7 are drawn straight, there is no reason to assume that a sharp break in properties actually occurs. The true relation is thought to be better depicted in Figures 2, 3, and 6. The ratios obtained by interpolation from such figures (given earlier in the text) are in even greater contrast than those cited above, which are based upon the uninterpolated data.

¹⁷ The above explanation answers the question raised in footnote 14 as to the influence of the choice of end point upon the results obtained when using the constant-end-point principle. Each of the five tests was carried out on this principle, and each has a different end point. The results of any one test give a cross section showing the relation between enamels of the respective compositions at a given stage of the process of "fusion." A number of such cross sections are required, as in Figure 7, to complete the picture. These several cross sections constitute a framework upon which a three dimensional figure could be readily constructed, if desired, bringing the whole set of relations into representation by a single continuous surface, which could be used for interpolation between the established points.

¹⁸ C. J. Kinzie, *J. Am. Cer. Soc.*, vol. 15, No. 6, p. 357, 1932.

glasses do not always remain in the same relative order at different temperatures.¹⁹

Each of the enamels used in this study was fired on test pieces in the laboratory under a variety of conditions of temperature and time. Due to the fact that a workable enamel may be fired satisfactorily within a comparatively wide range of conditions, it was impracticable to establish optimum firing temperatures closely enough to determine whether the tests giving a lower "c ratio" or those giving a higher "c ratio" were more indicative of the firing behavior of the enamels. The establishment of such ratios requires the accurate location of the several temperatures involved, and it is probable that only an accumulation of observations under various plant conditions will determine which of these tests best gives the information desired in any particular case. The firing ranges of the respective enamels did, however, accord with the general pattern followed by all of these tests in which the substitution of feldspar for silica caused a moderate increase in fusibility, and the substitution of sodium oxide for boric oxide caused a considerably more marked increase in fusibility. It appears, therefore, that at least in so far as these particular enamels are concerned, the indications of the described tests are not subject to any general reversals when applied to actual working conditions.

VI. SUMMARY AND CONCLUSIONS

The compositions of nine ground coat enamels for sheet iron were varied within a region approximating commercial practice by substituting silica (added as flint) and feldspar one for another while the percentages of other ingredients remained constant, and by substituting boric oxide and sodium oxide one for another, while the percentages of other constituents remained constant. In two other enamels the above-named fluxes were varied as a unit against the two refractories as a unit. The fusion properties of the enamels were studied through five different tests, namely, (1) temperature of maximum heat absorption, (2) softening temperature as observed with the interferometer, (3) cone deformation temperature, (4) button deformation temperature, and (5) fusion block deformation behavior.

The following conclusions, applicable within the limits of composition studied, were drawn:

1. The increase of silica from 25 to 35 per cent with simultaneous reduction of feldspar from 35 to 25 per cent, caused a moderate increase in refractoriness. The full 10 per cent substitution raised the end temperatures of the different tests by 10° to 15° C. (18° to 27° F.), or an average of 1° to 1.5° C. (1.8° to 2.7° F.) for each percentage of change in composition.

2. The increase of boric oxide from 13 to 19 per cent with simultaneous reduction of sodium oxide from 17 to 11 per cent caused an increase in end temperatures of the various tests which was quite marked in the region near 13 per cent boric oxide, and which became less perceptible as the boric oxide content approached 19 per cent. This diminution in effectiveness was most conspicuous in the tests involving no flow of the specimens, and became less prominent as

¹⁹ G. S. Fulcher, *J. Am. Cer. Soc.*, vol. 8, No. 6, p. 339, 1925. E. W. Washburn, G. R. Shelton, and E. E. Libman, *U. of Ill. Bull.*, vol. 21, No. 33, 1924.

the amount of flow involved in the respective determinations increased. The maximum diminution of effect with successive substitutions occurred in the case of the initial deformation temperature determinations by the interferometer method, in which a 1 per cent increase in boric oxide from 13 to 14 per cent (with corresponding decrease in sodium oxide) caused an elevation in the end temperature estimated by interpolation to be approximately 15°C . (27°F .), while a similar increase from 18 to 19 per cent caused an elevation estimated to be about 1.5° to 2°C . (2.7° to 3.6°F .). The minimum diminution occurred in the case of the fusion block finish temperatures, in which these same two changes in composition caused elevations in the determined temperatures of 12°C . (22°F .) and 9°C . (16°F .), respectively.

3. The reason that the diminution in the effectiveness of successive substitutions of boric oxide for sodium oxide became less noticeable as the amount of flow involved in the respective determinations increased might be traced to the fact that variations in viscosity of the enamels had more opportunity to influence the results of those tests which involved a greater flow of the specimens.

4. Since the tests were conducted on definite time-temperature schedules, the end temperatures of the respective determinations increased with the amount of flow involved. This effect placed the determinations in the following order of increasing temperature: Maximum heat absorption temperature, initial deformation temperature as observed in the interferometer, cone deformation temperature, button deformation temperature, fusion block start temperature, and fusion block finish temperature. These determinations were spread over a range of approximately 300°C . (540°F .) from about 500°C . (900°F .) to about 800°C . ($1,470^{\circ}\text{F}$.).

5. In conducting tests for the purpose of correlating properties quantitatively with systematic variations in composition, it is desirable to avoid the "variable-end-point" principle, according to which all specimens are treated alike and the various degrees of effectiveness of the treatment in the respective cases noted. The use of this principle makes the apparent relationships irregular, variable, and dependent upon chance to a much greater extent than is the case when using the "constant-end-point" principle, according to which the extent or intensity of treatment required to produce a given effect is the basis of comparison.

6. While the results of this study do not warrant the statement that any one of the described tests gives a truer picture of the behavior of the enamels in practice than another, they do indicate that the general pattern covering the results of all the tests, as outlined in conclusions 1 and 2, is indicative of the relative behavior of the enamels in process of fusion on metal.

WASHINGTON, April 16, 1932.