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CONSISTENCY OF EIGHT TYPES OF VITREOUS ENAMEL FRITS AT AND NEAR FIRING TEMPERATURES

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ABSTRACT

The consistency of eight vitreous enamel frits, representing eight commercial types, was studied at and near the firing temperatures by means of a small rotation viscometer. The results are expressed in terms of viscosity for the frits which behaved as simple viscous liquids and apparent viscosity for those not behaving as viscous liquids. Comparisons are made at constant torque in the apparatus, and the effect of variations in temperature and variations in type of frit are reported. Also, for individual enamel frits, the effect of varying the speed of rotation at different constant temperatures is shown graphically.

CONTENTS

I. INTRODUCTION

The investigation reported in this paper represents the first work on a somewhat extensive program of research on vitreous enamels. This program was planned with the cooperation of an advisory committee of men active in the industrial and educational aspects of enameling.[1] The first item on this program was the determination of the important properties of eight vitreous enamel frits, which were selected with some care as representative of eight commercial types. This paper reports the results of a study conducted at this Bureau on the consistency of the eight frits at and near their firing temperatures. No additions of clay, opacifiers, or other materials were made to these frits. Such additions to the frits would undoubtedly change their properties, but a study of these effects was considered outside the scope of the present investigation.

[1] For a report of the advisory committee meeting and the names of the members, see Technical News Bulletin of the National Bureau of Standards 213 (Jan. 1935).

The members of the advisory committee having industrial connections assisted greatly in the work by supplying materials and preparing the frits in lots of several hundred pounds, so that these will be available throughout the entire series of studies still to be made. The authors acknowledge the invaluable help which these men and the other members of the advisory committee are contributing to this work.

The importance of knowing the consistency of enamels at or near firing temperatures is attested by the fact that a number of empirical tests are in use, often performed on the frits without mill additions, which are intended to indicate the flow characteristics of enamels during firing. Results obtained by several of these methods were compared in a previous paper.[2] In the present investigation, data were obtained which permitted the expression of results in terms of viscosity, or for enamels which do not behave as viscous liquids, in terms of apparent viscosity.

II. APPARATUS, PROCEDURE, AND DESCRIPTION OF ENAMEL FRITS

1. DESCRIPTION OF APPARATUS

A deflection-type rotation viscometer was chosen as the most suitable instrument. The viscometer was designed to contain only about 3 ml of material in order to facilitate bringing the entire sample to a steady temperature, with minimum temperature gradient, in a short time. Thus any change in composition and consistency of the sample through the necessity of long standing at firing temperatures was materially reduced.

A diagram of the apparatus is shown in figure 1. The cup and spindle are made of platinum containing 5 percent of iridium. The cup is 2 mm thick, 13 mm inside diameter, and 30 mm inside height. The hollow spindle, 6 mm outside diameter and 1.5 mm thick, was immersed during test to 5 mm from the bottom of the cup. The cup is suspended from above instead of being supported from below, so that the thermal expansion of the respective supporting elements, which are Nichrome in the case of both the cup and the spindle, will act in the same direction and tend to avoid a change in the depth of immersion of the spindle with temperature. The Nichrome cylinder supporting the cup is set in ball bearings and is revolved by means of a small, variable-speed electric motor with worm gear and pulley (not shown in fig. 1) acting through belts and a double set of multiple pulley wheels. The variation in motor speed and in the reduction ratio of the pulley system permitted a wide range of speeds of rotation for the cup during the tests.

The inner cylinder assembly is suspended by a piece of tungsten wire, selected because of the low elastic hysteresis of this material. During a test this wire is twisted by the torque transmitted from the revolving cup to the spindle by the test material. The amount of twist is measured by means of a mirror and scale. The scale and reading telescope are not shown in figure 1.

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

The temperature of the specimen during the test is measured with a platinum to platinum-rhodium thermocouple, with its junction in the spindle at the center of the sample and its lead wires emerging from the

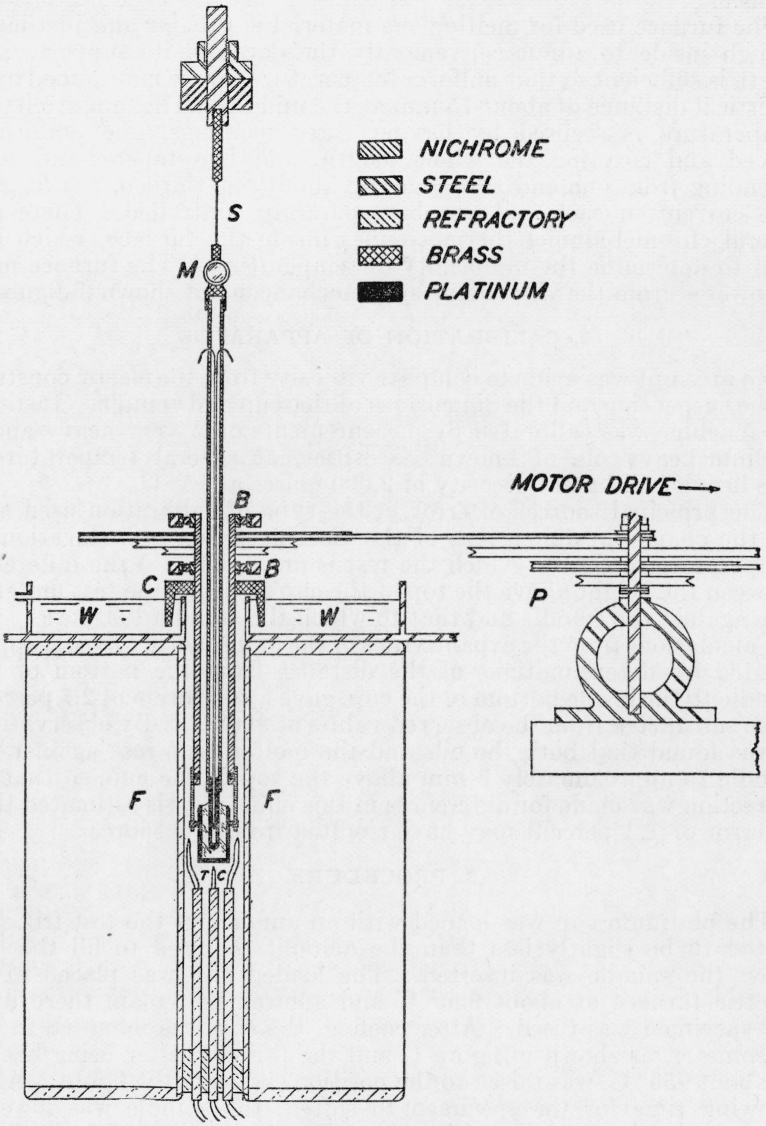

FIGURE 1.—*Schematic diagram of the viscometer.*

S, suspension wire (tungsten).
M, mirror.
B, ball bearings.
W, water.
C, cooling flange.
F, furnace.
TC, thermocouples.
P, pulleys.

supporting cylinder near the mirror. The temperature of the cold junction was maintained at 0° C and the electromotive force was read to ±0.01 mv. The rising of heat toward the torque wire during test is retarded by a flat metal dish containing water, which is in contact with the top of the furnace. A brass flange, attached to the outer Nichrome cylinder, conducts heat from it into the water, which is cooled by evaporation. The entire viscometer is mounted independently of the furnace.

The furnace used for melting the material is tubular and just large enough inside to admit conveniently the cup and its support. Its length is sufficient so that uniform temperature can be maintained over a vertical distance of about 75 mm at the middle. This uniformity of temperature is secured by having three windings, one uniformly spaced and covering the whole length, and two tapered-end coils extending from one end and covering about one-third of the length. The current in each coil can be separately controlled. There are several chromel-alumel thermocouples inside the furnace, which are used to determine the uniformity of temperature. The furnace may be lowered from the viscometer by a mechanism not shown in figure 1.

2. CALIBRATION OF APPARATUS

No attempt was made to compute viscosity from the elastic constant of the suspension and the dimensions of the cup and spindle. Instead, the machine was calibrated by measurements on a very heavy and a medium heavy oil, of known viscosities, at several temperatures.[3] The heavier oil had a viscosity of 2,090 poises at 15° C.

The principal sources of error in the type of calibration used are: (*a*) the change in dimensions of the viscometer with its elevation in temperature to that at which the test is made, and (*b*) the difference between the height above the top of the cup to which the test material rose against the spindle and that to which the standard oil rose.

Calculations from the expansivities of the materials involved, supplemented by determinations of the distance from the bottom of the spindle to the inside bottom of the cup, gave a correction of 2.7 percent to be subtracted from the observed values at 800° C. By observation, it was found that both the oils and the molten frits rose against the spindle to approximately 3 mm above the top of the cup, so that no correction was made for differences in this effect. It is estimated that an error of ±1 percent may have resulted from this source.[4]

3. PROCEDURE

The platinum cup was loaded with an amount of the test frit estimated to be slightly less than the amount required to fill the cup when the spindle was inserted. The loaded cup was placed in an electric furnace at about 950° C and allowed to remain there until the specimen was fused. After cooling, the cup was mounted in the viscometer, as shown in figure 1, and the furnace, after being heated to about 950° C, was raised to the position shown in the figure. After allowing time for the specimen to soften, the spindle was lowered into position by a screw mechanism. The furnace was then lowered,

[3] The viscosity of the standard oils was determined by R. C. Hardy, of the lubrication and liquid fuels section of the National Bureau of Standards.

[4] The ratios of surface tension to density for the oils and enamel frits would indicate that, at equilibrium conditions in a large enough container, the molten frits would rise against the spindle to a level considerably higher than the oils. Under the conditions of test, however, no substantial difference was observed.

and a sufficient number of grains of frit added to bring the outer rim of the molten material level with the top of the cup, the meniscus sloping upward to the spindle. With the furnace again in position and the sample at a steady temperature, the thermocouple within the spindle was disconnected where the leads emerged from the small supporting cylinder, so that the connections would not influence the amount of mirror deflection.

The lowest viscometer speed was used first. When the deflection had attained a steady value, the time interval for a convenient number of revolutions was measured (usually about 2 minutes), and the deflection was read every 10 seconds during this time. The average of the observed deflections was taken as the deflection corresponding to the average speed of the motor during the interval. The temperature was observed before and after each such set of readings. The speed was then increased and the procedure repeated. About eight speeds were used at each temperature, the maximum for each specimen being approximately 0.07 to 0.08 rps, or about 4.5 rpm. A given point on the inside of the cup therefore traveled, at maximum speed, about 20 cm in a minute, which was considered a sufficient maximum speed to cover practical firing conditions. The lowest speed used for any frit was 0.0005 rps, or 0.03 rpm. In this case, a point on the inside of the cup moved about 0.13 cm in 1 minute.

After completing the test at one temperature, the furnace was allowed to cool about 50° C, a reduced current was then applied, the temperature allowed to come to a steady value, and another test made. Tests were made on each frit at five or more temperatures, the range covered being roughly from 100° C above to 100° C (180° F) below the estimated firing temperature of the frit.

4. DESCRIPTION OF ENAMEL FRITS

The batch compositions of the frits studied are given in table 1, and the calculated chemical compositions of the frits are given in table 2. Each composition is supposed to be representative of its type. "Soft" ground-coat frit 1 and "hard" ground-coat frit 11 are of the types frequently mixed to form a two-frit ground coat, the soft composition usually constituting 20 to 40 percent of the mixture. These frits are for use on sheet iron or steel. Three types of cover coat for the same base were also studied: an "ordinary" white coat (25), a very opaque cover coat (35), and an acid-resisting frit (6). Three types of cover-coat enamel frits for cast iron were studied: a high-lead wet-process frit (72), a lead-bearing dry-process frit (85), and a dry-process leadless frit (65).

In enamel frits at room temperature, it can usually be seen with the microscope that ground coats of the type studied have very little suspended matter, whereas opaque cover coats have variable but substantial amounts of suspended particles. It is to be expected that a similar difference exists, at least to some degree, in the range of firing temperatures. Those frits containing considerable amounts of suspended matter at the temperatures of test would not be expected to behave as simple viscous liquids.

TABLE 1.—*Batch composition of enamel frits*

Ingredients	Soft ground coat	Hard ground coat	Ordinary white	Very opaque white	Acid-resisting white	Cast iron wet process (lead) [1]	Cast iron dry process (lead)	Cast iron dry process (leadless)
	Frit 1	Frit 11	Frit 25	Frit 35	Frit 6	Frit 72	Frit 85	Frit 65
Feldspar	31.00	31.00	22.80	17.60	9.50	18.72	32.44	31.56
Flint	11.40	18.00	21.13	23.47	39.00	9.13	------	------
Borax	37.10	37.10	23.07	22.88	18.00	18.82	25.27	27.87
Soda ash	5.90	5.90	6.34	6.70	10.00	------	2.70	1.72
Soda nitre	3.80	3.80	2.96	2.93	3.00	3.35	2.95	2.87
Fluorspar	9.00	3.00	3.38	2.51	1.50	5.10	8.42	8.19
Cryolite	------	------	10.14	8.38	------	3.00	------	------
Zinc oxide	------	------	3.38	2.93	------	------	6.74	7.78
Sodium antimonate	------	------	6.76	12.58	9.50	------	9.26	9.42
Sodium silicofluoride	------	------	------	------	5.00	------	------	------
Lead oxide	------	------	------	------	------	36.10	8.42	------
Bone ash	------	------	------	------	1.50	3.78	------	------
Titanium oxide	------	------	------	------	3.00	------	------	------
Barium carbonate	------	------	------	------	------	2.00	3.79	10.57
Cobalt oxide	0.50	0.50	------	------	------	------	------	------
Nickel oxide	.40	.60	------	------	------	------	------	------
Manganese oxide	.90	1.10	------	------	------	------	------	------
Total	100.00	101.00	99.96	99.98	100.00	100.00	99.99	99.98

[1] Not opaque—for use with color stain in mill batch.

TABLE 2.—*Chemical composition of enamel frits, as calculated from batch weight*

[Feldspar analysis known. All other batch materials considered as pure]

Ingredients	Soft ground coat	Hard ground coat	Ordinary white	Very opaque white	Acid-resisting white	Cast iron wet process (lead)	Cast iron dry process (lead)	Cast iron dry process (leadless)
	Frit 1	Frit 11	Frit 25	Frit 35	Frit 6	Frit 72	Frit 85	Frit 65
SiO_2	40.9	49.2	42.1	45.4	55.1	24.2	25.6	25.3
TiO_2	------	------	------	------	3.5	------	------	------
Al_2O_3	7.7	7.7	8.0	6.4	2.2	4.9	7.6	7.5
Fe_2O_3	tr	tr	tr	tr	tr	tr	tr	tr
B_2O_3	17.5	17.4	9.8	9.7	7.7	7.8	11.1	12.5
CaO	8.4	2.9	2.9	2.2	2.3	6.5	7.4	7.3
BaO	------	------	------	------	------	1.7	3.5	10.0
NiO	0.5	0.7	------	------	------	------	------	------
CoO	.6	.6	------	------	------	------	------	------
MnO_2	1.2	1.4	------	------	------	------	------	------
ZnO	------	------	3.9	3.4	------	------	8.1	9.5
PbO	------	------	------	------	------	40.7	10.1	------
K_2O	4.5	4.5	3.0	2.3	2.1	2.4	4.4	4.4
Na_2O	15.3	15.2	17.3	17.5	15.7	7.0	9.9	11.1
F_2 [a]	3.5	0.4	6.4	0.8	2.2	2.8	3.0	2.9
Sb_2O_5	------	------	6.6	12.4	8.4	------	9.3	9.6
P_2O_5	------	------	------	------	0.8	2.0	------	------
Total	100.1	100.0	100.0	100.1	100.0	100.0	100.0	100.1

[a] The percentage of F_2 which was lost in smelting was computed from data forwarded by Robert B. Schaal, then of Roberts and Mander Stove Co.

III. RESULTS AND DISCUSSION

From the data obtained on each frit a graph was made showing the relation of viscometer deflection to speed of rotation for each temperature at which the frit was tested. In these graphs, the actual viscometer deflections are of course of little significance since they depend on the dimensions of the apparatus and are therefore treated as arbitrary units. The property which is of fundamental significance is the viscosity (and to a lesser extent the apparent viscosity). This quantity is given on the speed-deflection charts, the unit being the poise.

1. FRITS OF SIMPLE VISCOUS CONSISTENCY

Frits 1 and 11, the graphs for which are shown in figures 2 and 3, respectively, behaved as viscous liquids, the speed-deflection curves being straight lines passing through the origin. Each such curve is

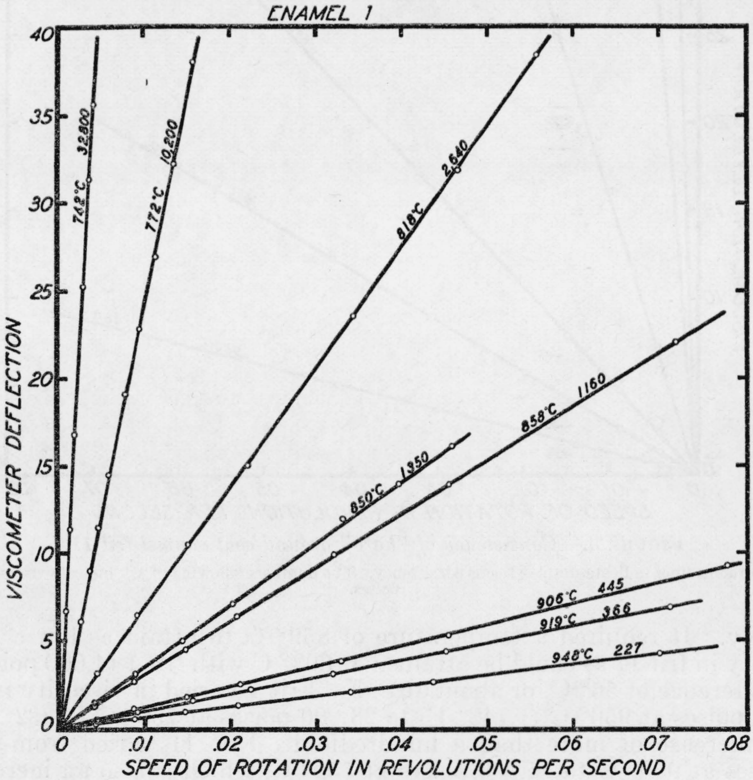

FIGURE 2.—*Consistency of "soft" ground-coat enamel frit 1.*

Linear relation between viscometer deflection and speed of rotation indicates simple viscous consistency. The numbers following "° C" indicate viscosity in poises.

labeled in these figures with the temperature and the viscosity in poises. At temperatures between the indicated limits the viscosities which are not shown can be read by interpolation on the graphs, along any straight line parallel to an ordinate.

In figure 4 the logarithms of the viscosities (in poises) are plotted against temperature for several enamel frits, including 1 and 11. Although the curves for these ground coats are roughly parallel, it is seen that frit 1 increased in viscosity with lowering temperature more rapidly than frit 11. At 850° C frit 11 was over 3.5 times as viscous as frit 1, the viscosities being 5,000 poises and 1,430 poises, respectively. It required a temperature of 859° C to attain as low a viscosity in frit 11 as could be attained at 803° C with frit 1 (4,000 poises) a difference of 56° C, or about 101° F. Frit 1 varied in viscosity from 216 poises at 950° C (1,742° F) to 23,000 poises at 750° C (1,382° F), an increase of more than a hundredfold. Frit 11 varied from 725 poises at 950° C to 75,000 poises at 750° C, which is also an increase of over a hundredfold.

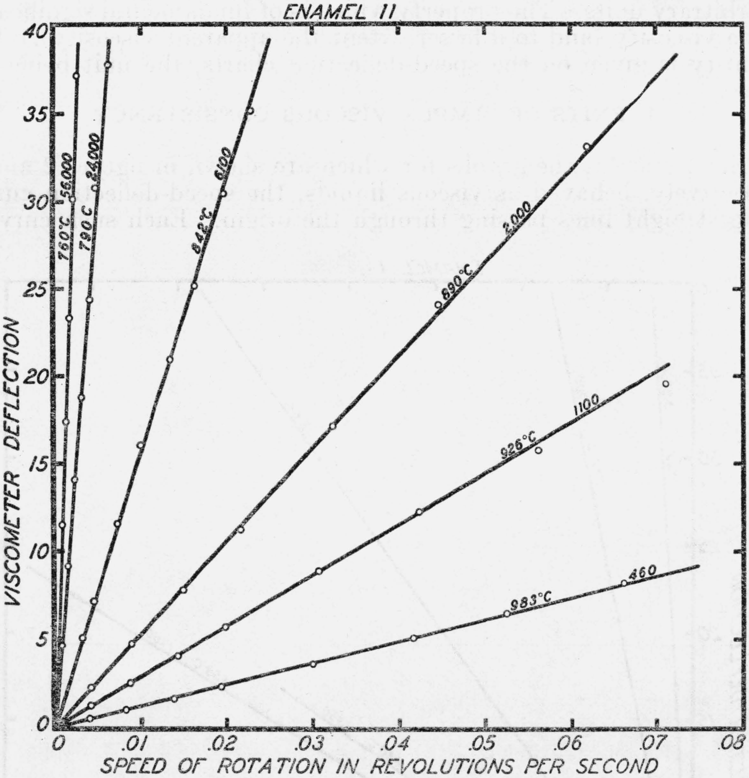

FIGURE 3.—*Consistency of "hard" ground-coat enamel frit 11.*

The straight lines indicate simple viscous consistency. The numbers following "° C" indicate viscosity in poises.

2. FRITS OF COMPLEX CONSISTENCY

The speed-deflection curves for acid-resisting cover-coat frit 6, shown in figure 5, are so nearly straight at several temperatures that no curvature could be detected with certainty. However, in the results obtained at 893° C, and to a greater extent in those obtained at 934° C, a definite curvature is apparent, indicating that the material is not a simple viscous liquid. Inasmuch as there is no evidence that any of these curves fail to pass through the origin, it may be said that at these temperatures frit 6 behaved as a complex liquid, sometimes called a non-Newtonian liquid.[5] Each curve in figure 5 has been labeled with a number indicating the average apparent viscosity.

Figure 6 shows the data for ordinary sheet-iron cover coat 25. All of the speed-deflection lines in this graph are definitely curved except that obtained at 750° C, and the nature of the entire chart suggests

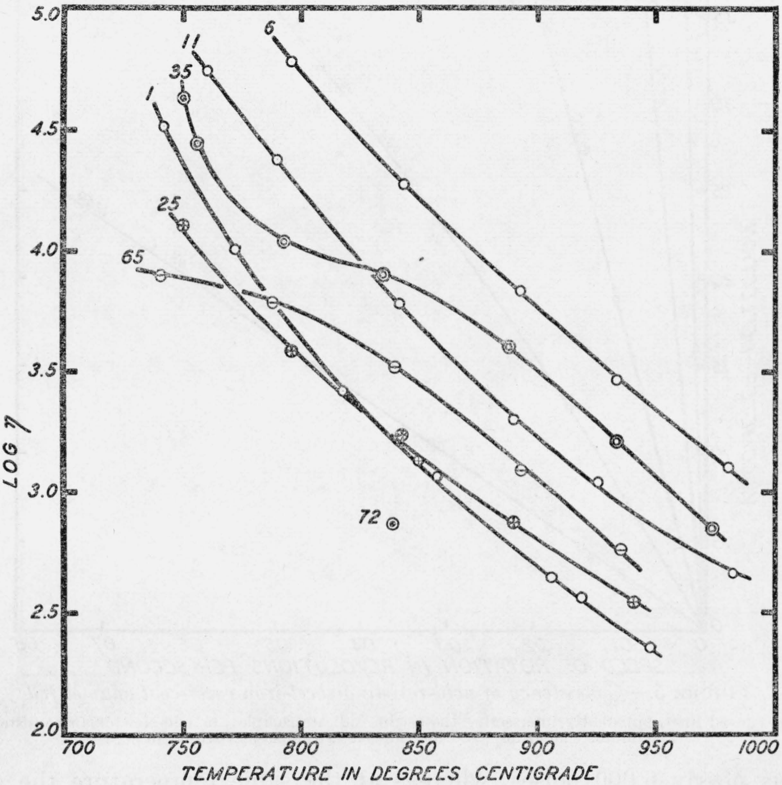

FIGURE 4.—*Log viscosity and apparent viscosity of six enamel frits at constant torque in the apparatus plotted against temperature.*

A single value at 839° C for enamel frit 72 is shown.

that curvature would be apparent at this temperature, too, if rates of shear as great as those reached at higher temperatures had been attained. In figure 6 and all succeeding figures, straight dashed lines have been superimposed on the charts. These dashed lines show the positions on the graphs corresponding to various viscosities. Wherever the curves cross these lines, the apparent viscosity of the sample at the indicated temperature and speed of rotation was equal to that indicated by the dashed line. The apparent viscosity for any point

[5] For pertinent definitions, see Proc. Am. Soc. Testing Materials, part 1, **34,** 1245 (1934). With the method of plotting adopted, a straight speed-deflection line passing through the origin denotes a simple viscous liquid, while a curved line, also passing through the origin, denotes a complex or non-Newtonian liquid.

on any data curve can be read by simple interpolation between two dashed lines, in a direction parallel to the ordinate.

Very opaque frit 35, the results for which are shown in figure 7, displayed a marked departure from simple viscous consistency. For example, at 887° C the apparent viscosity at a speed of 0.0028 rps

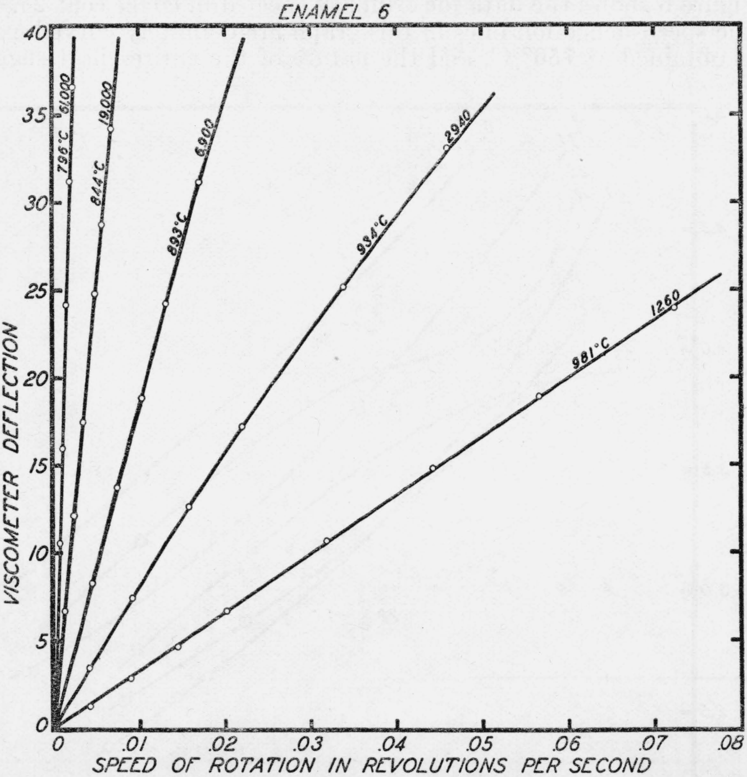

FIGURE 5.—*Consistency of acid-resisting sheet-iron cover-coat enamel frit.*

The curved lines, apparently intersecting the origin, indicate complex, or non-Newtonian consistency. The numbers following "°C" indicate average apparent viscosity in poises.

was nearly 6,000 poises, whereas at the same temperature the apparent viscosity at 0.060 rps was less than 2,000 poises.

Dry-process leadless frit 65, data for which are shown in figure 8, gave speed-deflection lines of even greater curvature than those of frit 35. At 936° C, for example the apparent viscosity at a speed of 0.0042 rps was 2,600 poises, whereas at 0.0696 rps it was only 536 poises, or approximately one-fifth as much. Nevertheless, the results were quite systematic, and gave no indication that any of the curves failed to pass through the origin.

Comparison of the apparent viscosities of frits 6, 25, 35, and 65 at stated temperatures must be made either at constant speed of rotation or at constant torque. Since, in practice, the force tending to make the enamel flow during firing would presumably be more nearly constant than the rate of flow, comparisons at constant torque were considered preferable. In figure 4 the apparent viscosities of these frits, at a viscometer deflection of 10 units, is plotted against temperature together with the viscosities of ground coats 1 and 11.

Figure 4 shows that acid-resisting sheet-iron frit 6 had the highest resistance to flow of all the frits shown. Its curve for log viscosity against temperature is almost parallel to that for ground-coat frit 11. At equal temperatures frit 6 was, however, about 3 times as resistant to flow as ground coat 11, and about 10 times as resistant as ground coat 1.

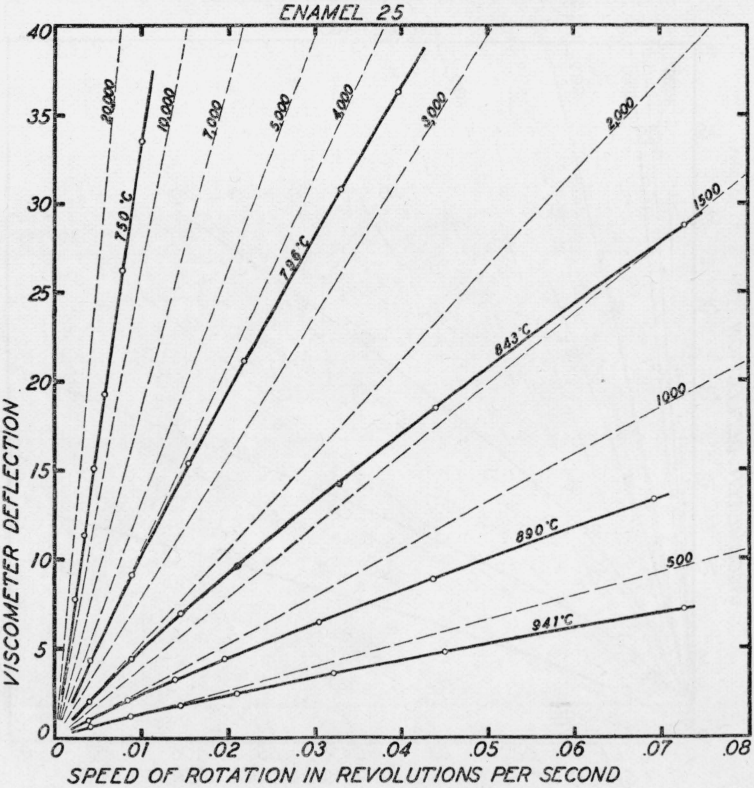

FIGURE 6.—*Consistency of "ordinary" sheet-iron cover-coat enamel frit.*

The shape of the speed-deflection curves indicates a complex consistency. The dashed lines show the positions on the graph corresponding to the viscosities, in poises, indicated by the adjacent numbers.

The ordinary sheet-iron cover coat 25 was about as resistant to flow between 800 and 850° C as ground coat 1, but below this temperature range it was more fluid, and above, less fluid than the ground coat.

The consistency of the very opaque sheet-iron cover coat 35 was so complex that a graph of apparent viscosity, at any selected torque, against temperature has questionable significance. Figure 4 does show, however, that the apparent viscosity of this frit is within the range found for other enamel frits, and is in the high-viscosity part of this range, between the temperatures of 850 and 950° C, within which zone it probably would be fired.

The significance of the curve relating log apparent viscosity of enamel frit 65 to temperature, at constant torque, is also questionable. However, this curve indicates that the apparent viscosity was in the lower part of the range covered by the entire series of frits, and appears similar in trend to the curve for frit 35, but shows equal apparent viscosity at about 60° C (108° F) lower than frit 35. There are no data to show whether the curve for frit 65 would curve upward at temperatures below 740° C, thus carrying through its parallelism to the curve for frit 35. This temperature was considered safely below the probable firing temperature of actual practice.

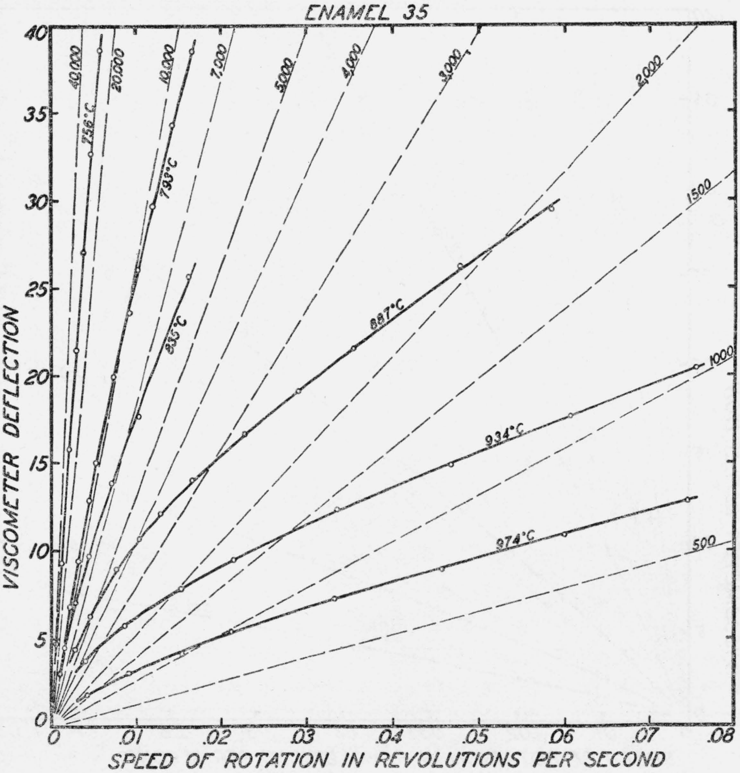

Figure 7.—*Consistency of a very opaque enamel frit for sheet iron.*

The marked curvature of the speed-deflection curves, which appear to pass through the origin, indicates a complex consistency. The dashed lines show the positions on the graph corresponding to the viscosities, in poises, indicated by the adjacent numbers.

3. FRITS OF ERRATIC CONSISTENCY

Frit 72, a high-lead composition for use with added stains to produce various colors in the wet-process enameling of cast iron, and number 85, a lead-bearing dry-process frit, were found to have consistencies which can well be described as erratic. These are the only lead-bearing frits studied. The data are shown in figures 9 and 10, respectively. It may be seen in figure 9 that frit 72, at 780° C, decreased gradually in apparent viscosity with increased speed of rotation up to 0.0046 rps. Further increase of speed up to 0.0058 rps gave no increase in deflection. Additional increase in speed gave a more rapid decrease in apparent viscosity than occurred at lower speeds, followed by still more rapid decrease with higher speeds. Although not exactly reproduced, the general shape of this curve was established by several tests at approximately this temperature. The kink in the curve, which occurred at speeds around 0.005 rps, did not appear to be caused by experimental error. The first data in figure 9 were taken at 927° C and the last at 930° C. It is seen that the latter curve is smoother and is more definitely pointed toward the origin.

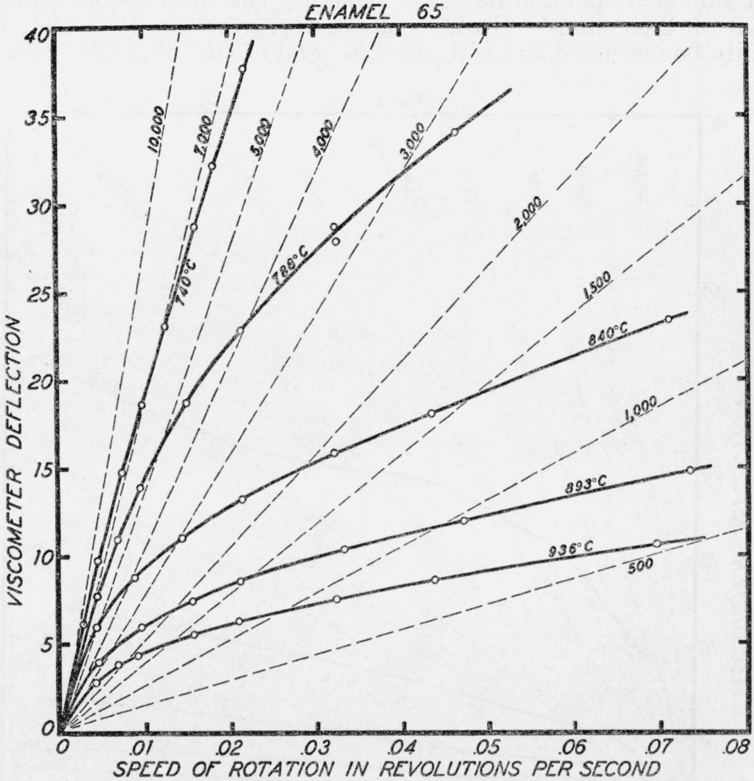

FIGURE 8.—*Consistency of a leadless dry-process enamel frit.*

The sharply curved speed-deflection lines indicate distinctly complex consistency. The dashed lines show positions on the graph corresponding to the viscosities, in poises, indicated by the adjacent numbers.

Figure 10 shows not only the erratic nature of the relation between temperature, speed of rotation, and apparent viscosity of frit 85, but also its instability under the conditions of test. The data were taken in order of decreasing temperature except that after the test at 736° C a second test at 835° C was made. The second test at this temperature showed lower apparent viscosities and a speed-deflection curve much more typical of other frits than that obtained in the first test at 835° C. This was the only frit for which curves obtained at substantially different temperatures actually crossed.

The data obtained on these two frits are not suitable, on the whole, for representation in figure 4. Nevertheless, one point from figure 9, namely, the apparent viscosity of frit 72 at 839° C and at a deflection of 10 units on the viscometer, has been placed in figure 4. The apparent viscosity of this composition, under the indicated conditions, is less than half that of frits 1 and 25, which are next higher. The average of the two curves for frit 85 at 835° C and 10 units of viscometer deflection corresponds to an apparent viscosity somewhat greater than that of frit 65 under the same conditions.

4. DISCUSSION

It should be pointed out that while the two ground-coat frits, because of their simple viscous consistency, gave results which may readily be discussed and compared, several of the other frits gave the

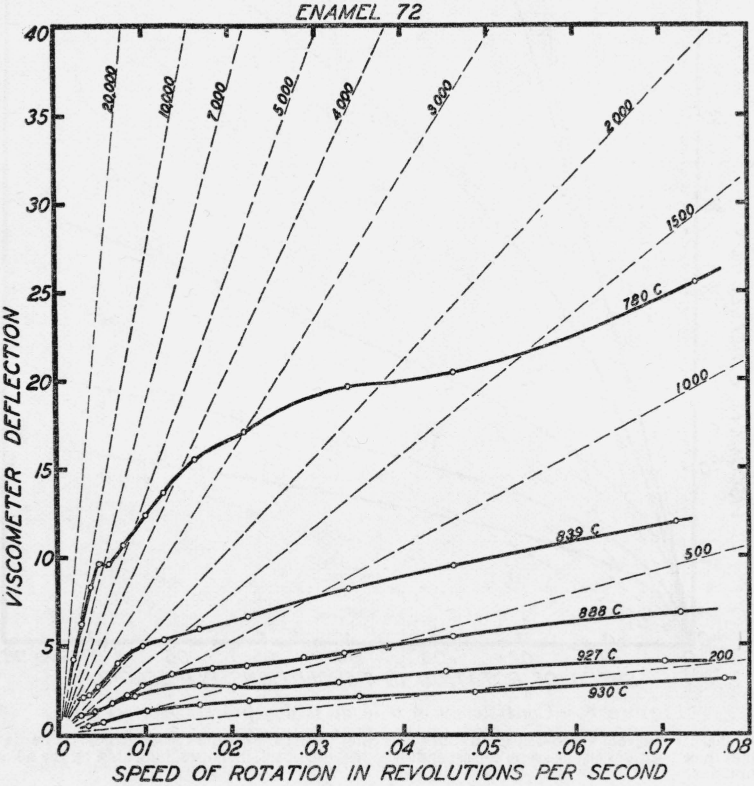

FIGURE 9.—*Consistency of a high-lead wet-process cast-iron enamel frit.*

The curves show marked deviation from simple viscous consistency, and the one for 780° C shows also an erratic shape near 7,000 poises, apparent viscosity. The dashed lines show positions on the graph corresponding to the viscosities, in poises, indicated by the adjacent numbers.

reported results only when they were tested in the particular manner described. Thus, frit 35 gave the results shown in figure 7 when the viscometer speeds were successively increased at given temperatures, but when returned to a given speed of rotation following a test at a higher speed, this frit gave first a smaller and later a greater deflection than the original apparent equilibrium value. This phenomenon may be a manifestation of thixotropy.[6] Frits 6, 25, 65, 72, and 85 behaved, in part, like frit 35, that is, when retested at a given speed of rotation

[6] Thixotropy may be defined as the tendency of a material to form a relatively stiff structure when not disturbed, which breaks down and gives place to a more fluid consistency under agitation. See E. L. McMillen, Effect of thixotropy on plastic measurements, J. Rheology 3, 185 (1932).

after a test at a higher speed, they gave different deflections than originally. It was thought that the procedure used, namely, to obtain values at successively increased speeds for any one temperature, was the one likely to yield values for consistency which would prevail in practice during the firing process.

Frit 85 appeared distinctly unstable, and some instability was also noticed in frits 35 and 72. In spite of these peculiarities of behavior

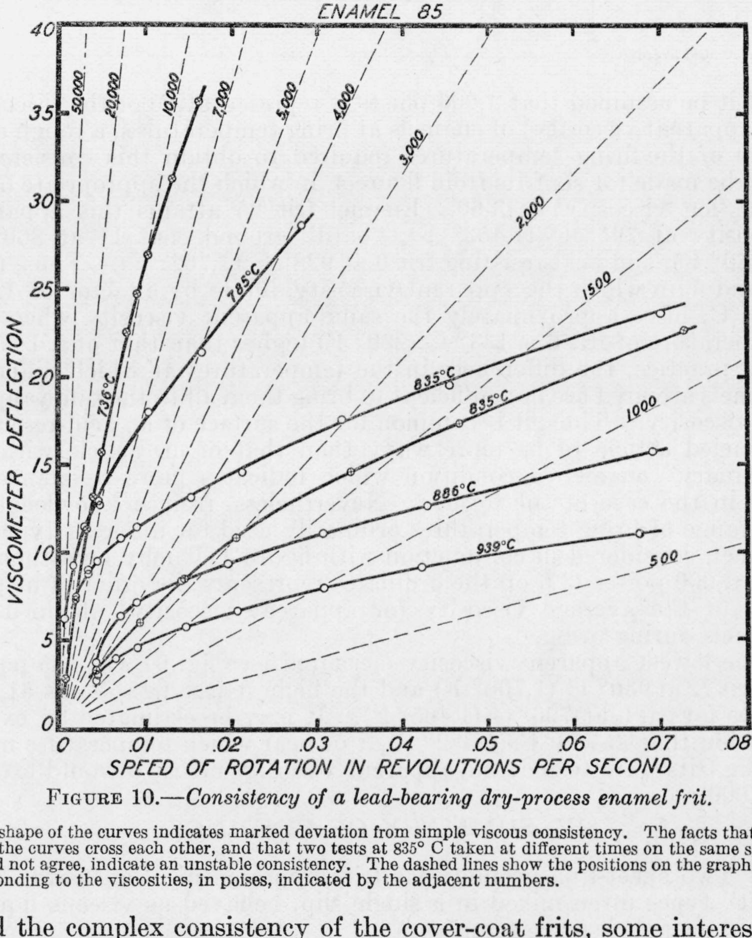

FIGURE 10.—*Consistency of a lead-bearing dry-process enamel frit.*

The shape of the curves indicates marked deviation from simple viscous consistency. The facts that some of the curves cross each other, and that two tests at 835° C taken at different times on the same sample did not agree, indicate an unstable consistency. The dashed lines show the positions on the graph corresponding to the viscosities, in poises, indicated by the adjacent numbers.

and the complex consistency of the cover-coat frits, some interesting comparisons may be made.

It so happens that the temperature 839° C (1,542° F) (which is the only temperature given for frit 72 in fig. 4), is within the usual range of firing temperatures of enamels, and a comparison of the different frits, under constant torque, at this temperature, is of interest. The figures are given in table 3.

It is seen in table 3 that under the indicated conditions the resistance to flow of acid-resisting frit 6 is over 28 times as great as that of frit 72 and over 12 times that of frit 25.

TABLE 3.—*Apparent viscosities of eight enamel frits under a chosen torque at 839° C (1,542° F)*

Frit	Apparent viscosity	Frit	Apparent viscosity
	Poises		*Poises*
72	750	85	[a] 4,140
1	1,660	11	6,460
25	1,740	35	7,760
65	3,390	6	21,380

[a] Estimated average.

If it be assumed that 4,000 poises is representative of the viscosity (or apparent viscosity) of enamels at firing temperatures, a rough estimate of the firing temperatures required to obtain this consistency may be made for six frits from figure 4, in which the appropriate ordinate (log viscosity) is 3.60. Enamel frit 25 attains this apparent viscosity at 795° C (1,463° F), "hard" ground coat 11 at 860° C (1,580° F), and acid-resisting frit 6 at 928° C (1,702° F). Thus, frits 25 and 6, in which the apparent viscosity differs by a factor of 12 at 839° C, have approximately the same apparent viscosity when the temperature of frit 6 is 133° C (239° F) higher than that of frit 25.

In practice, the differences in the temperatures at which different enamels are fired are not sufficient to bring them all to the same apparent viscosity. Thus, it is common for the surface of an acid-resisting enameled article to be more wavy than that of an article with an "ordinary" enamel, a condition which indicates more resistance to flow in the case of the former. Nevertheless, from a knowledge of the range of firing temperatures ordinarily used for different types of enamel, considered in conjunction with figure 4, it may be estimated that 4,000 poises (3.6 on the ordinate) represents the order of magnitude of the average viscosity (or apparent viscosity) attained by enamels during firing.

The lowest apparent viscosity measured (see fig. 9) was 155 poises for frit 72 at 930° C (1,706° F) and the highest (see fig. 5) was 61,000 poises for frit 6 at 796° C (1,465° F). It may be estimated by extrapolation that at 750° C (1,382° F), at or near which temperature most of the frits were tested, the apparent viscosity of frit 6 would exceed 200,000 poises.

IV. SUMMARY OF FINDINGS

1. Two sheet-iron ground-coat frits, representing the "hard" and "soft" types often mixed in a single slip, behaved as viscous liquids at and near their firing temperatures.

2. Four types of cover-coat frits behaved, not as viscous liquids, but as complex or non-Newtonian liquids at and near their firing temperatures. The data for these compositions were quite systematic. The types represented in this group were: an "ordinary" cover coat, a very opaque, and an acid-resisting cover coat for sheet iron, and a leadless dry-process frit for cast iron.

3. The two frits containing lead, namely, a dry-process frit with about 10 percent of lead oxide and a wet-process frit for cast iron, containing about 40 percent of lead oxide, did not behave as viscous liquids at the temperatures studied, but as complex liquids exhibiting

erratic behavior, possibly associated with instability and thixotropy. After heating for several hours in the range of firing temperatures, these frits gave speed-deflection curves more in conformity with those of the other compositions studied.

4. For all the frits studied, the change in viscosity or apparent viscosity with temperature was very large, a decrease in temperature from 950 to 750° C (1,742 to 1,382° F) causing as much as a hundredfold increase in the viscosity of some specimens.

5. Because of the apparent thixotropy and instability of some of the cover coats, and also because the apparent viscosities of the cover coats changed both with temperature and with speed of rotation, it is difficult to make simple comparisons of the frits studied. Most of them may be compared, however, on the basis of apparent viscosity at constant torque in the apparatus.

6. At a selected temperature and torque, the apparent viscosity of the acid-resisting frit for sheet iron was 28 times greater than that of the high-lead wet-process frit for cast iron and 12 times that of the "ordinary" sheet-iron cover coat. The other frits had apparent viscosities between the latter two.

7. The two sheet-iron frits mentioned in the preceding paragraph were brought to equal apparent viscosities by a temperature difference of 125° C (225° F).

8. The highest apparent viscosity measured was nearly 400 times as high as the lowest, the values being 61,000 and 155 poises, respectively.

9. On the average, the viscosity or apparent viscosity of enamels under firing conditions is estimated to be on the order of 4,000 poises.

WASHINGTON, November 12, 1937.