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SURFACE TENSION OF VITREOUS ENAMEL FRITS AT AND NEAR FIRING TEMPERATURES

By William N. Harrison and Dwight G. Moore

ABSTRACT

A method is described for measuring at high temperatures the surface tension of liquids with viscosities as high as 10,000 poises. It consists in weighing the portion of the liquid supported by the meniscus adhering to a platinum cylinder, the bottom edge of which is at the level of the undisturbed surface of the liquid. The method insures a zero angle of contact and eliminates the necessity of determining the specific gravity of the sample at the temperature of test. Results were in good agreement with those obtained by the bubble-pressure method on molten sodium chloride and also on a molten "soft" ground-coat frit at a viscosity of 400 poises. The results obtained on eight typical commercial vitreous enamel frits at 850° C showed, with one exception, maximum differences of less than 10 percent. The mean value for seven of the frits was approximately 250 dynes/cm, while that for a high lead composition was about 200 dynes/cm. The surface tension in all cases increased with decreasing temperature between 925° and 775° C, the maximum increase being less than 10 percent. Mill additions had very little effect on the surface tension.

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I. INTRODUCTION

As the second part of an extensive investigation of the properties of vitreous enamels, a method has been developed for measuring the surface tension of highly viscous liquids against air at elevated temperatures. Measurements have been made of the surface tension at firing temperatures of eight vitreous-enamel frits chosen as representative of the field of enamels in commercial use. The consistencies of these enamels have been reported in an earlier paper [1].¹

The results of the present work are of interest because differences in the degree to which various enamels are subject to surface irregularities have, from time to time, been attributed wholly or partly to differences in their surface tension.

II. METHOD OF TEST

Several investigations have been reported on the surface tension of molten glasses at elevated temperatures, but none on vitreous enamels. In the present investigation, the pull on a hollow vertical cylinder, touching the liquid at its lower end, was measured with a torsion balance. Following Hall [2], the lower end of the cylinder was kept at the level of the undisturbed surface of the test liquid and buoyancy effects were thereby eliminated. The surface tension is given by the relation:

$$T = \frac{Kg\alpha}{2L \cos \theta}$$

in which

T = surface tension in dynes per centimeter.

K = calibration constant for torsion balance in grams per degree of twist.

g = gravitational acceleration, 980.1 cm/sec/sec.

α = twist of torsion wire, in degrees, required to balance pull of the meniscus.

L = average of outside and inside circumference of cylinder, in centimeters, at the temperature of test.

θ = angle between cylinder wall and tangent to the meniscus curve at the point of contact with the cylinder.

The angle of contact, θ , was made equal to zero as described later, and therefore:

$$T = \frac{Kg\alpha}{2L}$$

The apparatus is shown in figure 1. The platinum-5-percent-iridium cylinder, C , which is 2.5 cm in diameter and whose walls are 0.01 cm thick, is suspended from a pulley on the torsion wire by a chain of 22-gage Alumel wire, the tare, B , nearly balancing the assembly. The tare permits the use of a sensitive torsion wire and the pulley provides a constant lever arm for different levels of the cylinder. The telescope and curved scale at the right in figure 1, in conjunction with a small mirror attached to the pulley on the torsion wire, serve to determine displacements of the bottom of the cylinder from the plane of the undisturbed liquid surface. The test liquid is contained in the

¹ Figures in brackets indicate the literature references at the end of this paper.

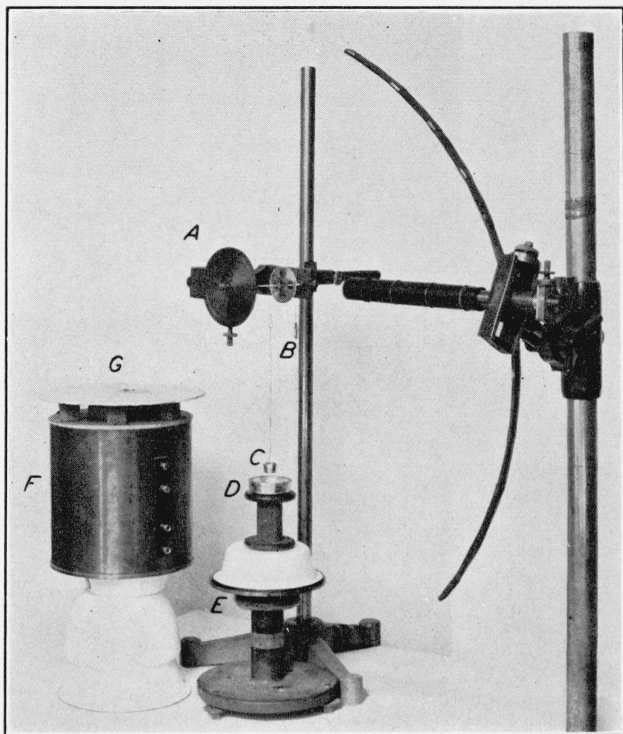


FIGURE 1.—Surface tension apparatus with furnace displaced to left to show essential parts.

A, torsion-wire balance; *B*, counterweight; *C*, platinum-5 percent of iridium hollow cylinder; *D*, platinum-5 percent of iridium dish; *E*, adjustable supporting stand for furnace; *F*, Nichrome-wound furnace; and *G*, asbestos radiation shield.

platinum-5-percent iridium dish, *D* (7.5 cm diameter by 2 cm deep) and can be raised by the adjustable stand, *E*, until contact is established with the bottom edge of the cylinder.

The furnace, *F*, displaced to the left in figure 1 from its normal position on the stand, *E*, is 8 cm inside diameter and 25 cm tall, and has a main winding and bottom heater, both of Nichrome. A thermocouple of platinum to platinum-rhodium is inserted through the furnace top and is placed, during test, just above the surface of the specimen. The asbestos shield, *G*, at the top of the furnace is supported on insulating blocks and prevents excessive rise of the temperature of the torsion balance. In practice, this temperature did not exceed 30° C.

III. CALIBRATION OF APPARATUS

1. CALIBRATION WITH WEIGHTS

The balance was calibrated by replacing the cylinder with a weight pan and establishing the conversion factor between known applied weights and the number of degrees of twist in the torsion wire required to maintain the original level of the pan. With an 0.014-inch-diameter spring-steel wire at 30° C, the calibration constant was 0.0617 g per degree of twist, and the angle of twist could be read with certainty to 0.1 degree, equivalent to a surface-tension increment of 0.38 dyne/cm.

2. CALIBRATION WITH KNOWN LIQUIDS

Table 1 shows the values of surface tension obtained with this apparatus for water, benzene, and a viscous oil (viscosity, 780 poises at 25° C), as compared with values obtained by the capillary rise method. Table 2 gives the values obtained on molten sodium chloride as compared with those of other investigators. In these tables the method used in this study is referred to as the "pull-on-cylinder" method.

TABLE 1.—*Determinations of surface tension by method used in this study, compared with determinations by capillary rise method*

Liquid	Temperature	Surface tension	
		Pull-on-cylinder method ¹	Capillary rise method ²
	° C	Dynes/cm	Dynes/cm
Water	20	72.8	72.75
Do.....	21	72.5	72.59
Do.....	23	72.5	72.28
Do.....	25	71.8	71.97
Do.....	26	71.4	71.82
Benzene.....	22	29.1	28.60
Do.....	24	29.1	28.35
Do.....	26	28.6	28.09
Viscous oil.....	24	31.9	31.2

¹ Determinations made with 0.012-inch-diameter wire in balance, having a sensitivity of 0.2 dyne/cm. A larger wire was found necessary in the test on molten enamel frits because of the greater stresses encountered.

² Values for water and benzene from International Critical Tables; value for the viscous oil determined for this comparison.

TABLE 2.—*Surface tension of sodium chloride*

Investigators	Method	Surface tension	
		857° C	945° C
Washburn and Libman.....	Dipping cylinder.....	<i>Dynes/cm</i> 115.2	<i>Dynes/cm</i> 107.4
Jaeger.....	Bubble pressure.....	109.9	103.6
National Bureau of Standards ¹	Pull on cylinder.....	109.6	103.7

¹ Values obtained from determined surface tension-temperature curve with 0.014-inch-diameter wire in balance.

3. CORRECTIONS APPLIED

(a) CHANGE IN LEVEL OF LIQUID

Small changes in the level of the surface of the specimen with respect to the cylinder after the initial contact are potential sources of error. The magnitude of such errors will be small since the cylinder walls were thin and the volume of liquid displaced or lifted through such changes in relative level is, therefore, small. The sources of such changes were evaluated as follows:

1. Lowering of the liquid level through the loss of material into the volume of liquid supported by the meniscus on the cylinder, and through thermal contraction of the molten frit when cooled for test at a lower temperature, was calculated to the required accuracy from available data on surface tension, density, and thermal expansion.

2. The sag in the torsion wire caused by pull of the meniscus was evaluated by observing, with a cathetometer, the sag caused by a series of weights.

3. The effect of dimensional changes in the apparatus during the series of tests at different temperatures was evaluated by means of the calibrated screw and an electric circuit with which the making and breaking of contact could be detected. No permanent "creep" or elongation of the Alumel wire suspending the cylinder was apparent.

The maximum change in level from all three sources was 0.5 mm (equivalent to 0.5 dyne/cm). During test, changes in level were compensated by adjustment of the calibrated screw supporting the stand.

(b) DIAMETER OF DISH

In the type of test used, appreciable error may be introduced unless the dish is large enough in diameter to provide an area of flat surface on the test liquid beyond the outside of the meniscus around the cylinder [3]. To determine experimentally whether the 7.5-cm-diameter dish was sufficiently large, a platinum strip 30 cm long by 1 cm wide was shaped into a cylinder of adjustable diameter and placed in the platinum-iridium dish so as to decrease the effective diameter of the latter. The results, as given in table 3, indicate that the 7.5-cm dish is sufficiently large to prevent significant error from this source.

TABLE 3.—Surface tension of enamel frit 1 at 925° C, tested in dish of varying effective diameter

Effective diameter of dish	Surface tension
<i>Cm</i>	<i>Dynes/cm</i>
7.5	245.0
7.5	245.7
6.0	245.7
5.0	246.1
5.0	245.7

(c) OXIDATION OF SUSPENSION CHAIN

To determine whether oxidation of the Alumel suspension chain during test would increase its weight enough to introduce significant error, the cylinder was suspended free in the furnace for 2 hours at 900° C and for an additional 1½ hours between 700° and 900° C. At the end of this period the reading of the torsion balance had not changed, indicating that any increase in weight due to oxidation was less than the sensitivity of the balance.

(d) CONTACT ANGLE

It was recognized that the determination of the surface tension of materials as viscous as enamel frits at firing temperatures requires a technique somewhat different from that required for even the most viscous of the liquids used in calibration. In the first tests with molten enamel frit, the bottom of the cylinder was not allowed to sink appreciably below the surface of the specimens at any time, but was held at the surface level by continuously increasing the torque to balance the weight of the material which slowly climbed onto the cylinder walls. Though gradual at all times, the rate of increase in weight of the meniscus was relatively rapid at first, after which it was progressively slower. Several hours were necessary with this procedure before an apparently steady condition was reached, and even after an apparent equilibrium had been attained there was no assurance of a zero angle of contact. A more rapid procedure was desirable to minimize any possible change in composition of the specimen during test, through selective volatilization. One method of hastening the establishment of equilibrium is to adjust the procedure so that the force of gravity accelerates the attainment of equilibrium instead of retarding it as with the procedure in which the cylinder was held at the surface.

This can be done by allowing the cylinder to sink and become wetted to a height equal to or exceeding the equilibrium height of the meniscus, then withdrawing it to its initial level and allowing the meniscus to drain to its equilibrium position.

Figure 2 shows graphically the results of a study of the effect of initial depth of immersion on the apparent surface tension of frit 1 at 900° C. The two lower curves show the apparent surface tension gradually increasing with time, indicating that the cylinder had not been dipped a distance as great as the normal height of the meniscus, so that at the end of the tests the molten frit was still climbing on the cylinder toward the equilibrium position. In the two upper curves the cylinder had been dipped a greater distance than the equilibrium

height of the meniscus and the decrease in apparent surface tension with time was caused by the continued draining of the liquid from the cylinder walls. The center curve indicates that a condition of equilibrium at 246.6 dynes/cm was reached within 7 minutes after the cylinder had been returned to the surface level.

In all five tests the cylinder was carefully examined after its removal from the furnace. In the tests represented by the two upper curves a film of enamel about 0.04 mm thick remained on the cylinder walls above the meniscus proper. Under these conditions there exists in effect a dipping cylinder made of the same material as the specimen, its rigidity resulting from the platinum core. This is an ideal way of securing perfect wetting, which insures a zero angle of contact. To obtain correct results, however, the weight of the film above the equilibrium height of the meniscus must be considered. It was found difficult to make corrections for this film as it was impossible

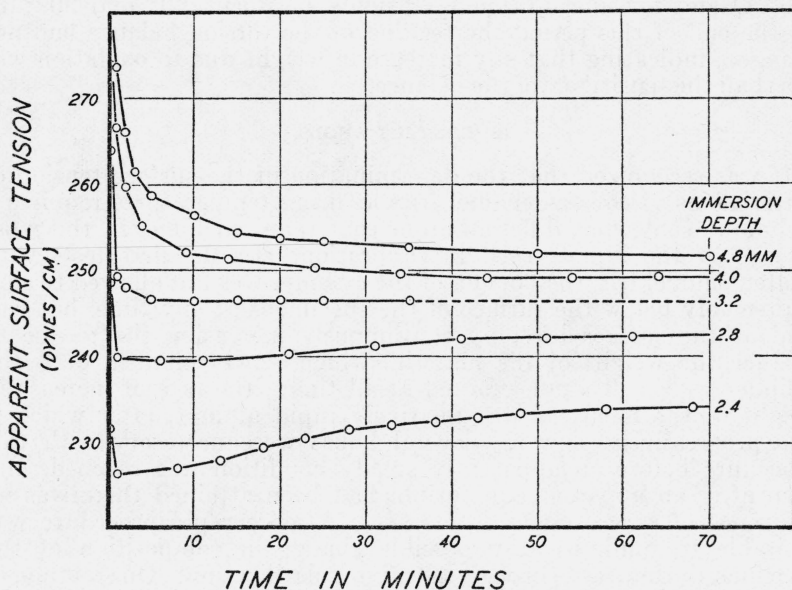


FIGURE 2.—Apparent surface tension plotted against time for frit 1 at 900° C, showing effect of initial immersion depth of the cylinder.

to determine accurately the point at which the meniscus merged into the vertical-walled film adhering to the cylinder above the meniscus. A condition was, therefore, sought in which the depth of immersion would be such a small amount greater than the equilibrium height of the meniscus that the weight of the vertical-walled film would be negligible, although its presence would insure the full benefits of the method. It is thought that the center curve in figure 2, representing an immersion to a depth of 3.2 mm, closely represents this condition.

In view of these tests with the soft ground-coat frit 1, it was decided to allow the cylinder to dip to a depth of 3.2 mm in each of the tests with the other frits, and to plot the results as in figure 2. If the resulting curve was of the same general shape as the center curve in figure 2, indicating that equilibrium had been reached quickly, it was concluded that the cylinder had been dipped to the desired depth.

IV. TESTS WITH ENAMEL FRITS

1. DESCRIPTION OF FRITS

The compositions and methods of selection of the eight representative commercial enamel frits used in this study have been reported in a previous paper [1]. The types represented are as follows:

Frit 1, a "soft" sheet-iron ground-coat frit, to be mixed with a harder frit before use.

Frit 11, a "hard" sheet-iron ground-coat frit, used with admixture of a softer frit.

Frit 6, an acid-resisting type of white cover-coat frit for sheet iron.

Frit 25, an "ordinary" white cover-coat frit for sheet iron.

Frit 35, a very opaque white cover-coat frit for sheet iron.

Frit 65, a leadless dry-process frit for cast iron.

Frit 72, a high-lead (40 percent of PbO) wet-process frit for cast iron.

Frit 85, a lead-bearing (10 percent of PbO) dry-process frit for a cast iron.

It is thought that this variety of types is sufficiently representative of the field of commercial enamels that the conclusions drawn from them should be generally applicable.

2. MEASURED SURFACE TENSIONS

(a) TEST PROCEDURE

In each test the furnace was heated to 925° C in 2 hours and the temperature held constant for 30 minutes before making initial contact.

Since the resistance to flow of the molten frits increases greatly with decrease in temperature, it was thought desirable to make the initial determination for each frit at the highest temperature of test (925° C), and then lower the temperature without disturbing the specimen for determinations at lower temperatures. As a check on values obtained at the lower temperatures by this method, independent determinations at 850° and 775° C were made on frit 1. The results obtained at 850° C by the two procedures were the same (247 dynes/cm), while the result after making contact at 775° C was 1.1 percent (2.7 dynes/cm) lower than when contact was made at 925° C. This was considered a satisfactory agreement.

(b) REPRODUCIBILITY

To determine the reproducibility of determinations by the described method, six determinations were made on frit 1 at 925° C. These results, given in table 4, all fell between 245.0 and 246.1 dynes/cm, the extreme variation being 0.28 percent from the average.

TABLE 4.—Results of six determinations of the surface tension of frit 1 at 925° C

Test	Surface Tension
	<i>Dynes/cm</i>
1.....	245.7
2.....	245.0
3.....	245.7
4.....	245.7
5.....	246.1
6.....	245.7
Average....	245.7

(c) RESULTS ON FRITS

The determined values for surface tension of the eight frits are given in table 5. It will be noted that values for frits 11 and 6 at 775° C remain undetermined. Their viscosities at that temperature, about 36,000 and 160,000 poises, respectively, are too high to permit satisfactory surface-tension measurements by this method. Some satisfactory determinations were, however, made on specimens having viscosities (or apparent viscosities) as high as about 10,000 poises. The table shows that seven of the eight frits gave values within a narrow range around 250 dynes/cm, and the other one approximately 200 dynes/cm. The exception was the wet-process cast-iron frit 72 containing about 40 percent of lead oxide.

TABLE 5.—*Surface tensions of eight frits at three temperatures*

Enamel type	Enamel frit number	Time for equilibrium at 925° C	Surface tension at—		
			925° C	850° C	775° C
		<i>Minutes</i>	<i>Dynes/cm</i>	<i>Dynes/cm</i>	<i>Dynes/cm</i>
Soft ground coat ¹	1	7	246	247	249
Hard ground coat ²	11	9	243	245	-----
Ordinary white ³	25	-----	233	240	248
Very opaque white	35	10	242	250	259
Acid-resisting white ²	6	14	249	256	-----
Cast iron-leadless	65	6	248	258	270
Cast iron-high lead ⁴	72	23	187	196	206
Cast iron-low lead	85	5	244	251	260

¹ The value reported for frit 1 at 925° C is the average for 6 closely agreeing determinations (see table 4), and that for frit 1 at 850° C was obtained in 2 independent determinations (see text). The values for each of the other frits comprise a single determination at each temperature.

² Too viscous for measurement at 775° C.

³ Readings on frit 25 at 925° C, unlike those on other frits, increased noticeably after remaining nearly constant for 25 minutes. Values at 850° and 775° C were obtained by making initial contact at 850° C. The 925° C value was a minimum reading obtained before the apparent surface tension began increasing.

⁴ First determination indicated a large increase in surface tension from 850° to 775° C. Later tests allowing 16 hours for equilibrium gave the 775° C value as listed. The stiff consistency of the enamel at low-rates of flow was responsible for the original error.

From the values given in table 5, it is apparent that at any one temperature, the surface tensions of the frits, with the exception of frit 72, vary less than 10 percent. The change in surface tension of any given enamel throughout the temperature range of 150° C is likewise less than 10 percent.

3. COMPARISON WITH BUBBLE-PRESSURE METHOD

A sample of frit 1 was kindly tested by Badger, Parmelee, and Williams [4] at 925° C by the bubble-pressure method. They reported a surface tension of 244 dynes/cm, which was only 0.7 percent lower than that obtained in this study. Frit 1 at 925° C had a viscosity of 400 poises.[1]

4. EFFECT OF MILL ADDITIONS

To determine the extent to which mill additions affect the surface tension of enamels, experiments were made on frit 1 at 925° C with additions of borax, clay, and tin oxide. The results are given in table 6, and indicate that mill additions up to 12 percent have little effect on the surface tension.

TABLE 6.—Effect of mill additions on surface tension of frit 1

Additions per 100 parts frit	Surface tension
<i>Parts</i>	<i>Dynes/cm</i>
None.....	246
Clay 6.0, borax 0.1.....	247
Tin oxide, 6.0.....	247
Tin oxide, 12.0.....	250

V. CONCLUSION

The method of determining surface tension which was used in this study is believed to be satisfactory for measurements at high temperatures on materials of viscosities up to the order of 10,000 poises. A zero angle being assured, the necessity for measuring the contact angle is eliminated. Further, because there is no buoyancy effect resulting from immersion of the cylinder in the liquid specimen, the difficulty of determining the specific gravity of the specimen at the temperature of test is avoided. Surface tension can be computed from an observed angular deflection, merely by using a conversion factor.

The enamel frits studied cover a wide range of commercial types. With one exception they differed only slightly in surface tension from a central value approximating 250 dynes/cm.

Temperature variations in the vicinity of firing temperatures affected the surface tension of the different frits to various degrees, but the maximum change was only about 10 percent for a 150° C change in temperature.

Mill additions of clay, and tin oxide up to 6 percent had almost no effect on the surface tension of a frit. Twelve percent of tin oxide caused a slight increase in surface tension.

The exceptional frit was a cover-coat used in wet-process enameling on cast iron, which contains about 40 percent of lead oxide and had a surface tension of approximately 200 dynes/cm. The ease with which this type of enamel flows out to form a smooth surface in firing is well known. A knowledge of the physical properties of this type of frit has diminished importance, however, because of the fact that such high-lead enamels are becoming obsolete. A dry-process frit containing about 10 percent of lead oxide was found to have a surface tension nearly equal to the average for frits containing no lead.

In estimating the possible importance of the observed differences in surface tension of the enamel frits, it is necessary to consider the forces of gravity and surface tension, which usually tend to produce flow in the enamel during firing, and viscosity or internal friction resisting flow.

The effect of gravity must ordinarily be negligible, since a successful enamel may be fired in any position and the resulting coating is apparently the same. Hence, the only force consistently operating against internal friction to smooth the irregular surfaces of continuous enamel coatings during the firing must be surface tension. But since variations in the surface tension of enamels with composition are small, while variations in viscosity are often very large [1], the latter factor would seem a more important source of any differences in the ease with which the several enamels flow out to form a smooth surface when fired.

It is true that a decrease in the surface tension of a cover coat, other things being equal, would increase its tendency to spread on the ground coat and hence facilitate the healing of any discontinuities which might occur during the firing process, such as from "curling" of the dried coating prior to fusion. In this respect, the low surface tension of the high-lead enamel must contribute to its recognized tendency to form a smooth surface when fired. But since ordinarily an enamel coating is well spread before fusion, whether applied by the wet or the dry process, variations in its tendency to spread on the underlying material are of restricted importance. That the effect of surface tension on spreading tendency is not the controlling factor in obtaining satisfactory coatings of enamel is indicated by the fact that frit 35, having a higher surface tension than ground-coat frits 1 and 11, and frit 25, having a lower surface tension, are both suitable for application over a ground coat made up of frits 1 and 11.

In summary, it would appear that the high surface tension of enamels under firing conditions is an important factor in overcoming their high viscosity, or internal friction, to flatten wavy surfaces, but that variations in surface tension with composition are far less effective in this respect than the accompanying changes in consistency.

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