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Interfacial effects in the flow-bead test for vitreous enamels

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Evidence is presented that the rate of flow of a liquid enamel bead down a vertical plate depends on the nature of the plate surface. Two surfaces were compared. One was an enamel surface of the same composition as the bead, and therefore molten during the test; the other was a porous refractory coat that was solid at the test temperature. The rate of flow was greater over the refractory surface. Measurement of contact angles for the flowing beads and for sessile drops led to the conclusion that the surface tension forces per unit width were similar for the drops on the two surfaces. However, the gravitational force per unit width was higher for the drop on the refractory surface. This is responsible for the higher rate of flow over the refractory surface, and arises from the lower rate of lateral spreading of the bead caused by viscous resistance to the flow of the enamel through microchannels in the rough surface.

1. Introduction

The flow-bead test [1–4] is widely used for the production quality control of glass frit for vitreous enamelling. It is a comparative test. The flow of a molten bead of a sample of production material is directly compared with that of an approved standard. The production batch is accepted if the difference of flow lengths is less than a prescribed distance, for example 5 mm.

It is implied that the flow length of the bead is related to the viscosity of the enamel at the test temperature and, indeed, attempts have been made, notably by Dekker [5], to deduce viscosity–temperature relations for enamels from flow-bead data. In principle, however, interfacial effects will have an influence on the forces on the bead and therefore on the rate of flow. The object of the work now described was to assess the magnitude of this influence.

2. Theory for liquid drop on an inclined surface

A liquid drop on a homogeneous horizontal surface has a constant contact angle around its periphery. When the plate is tilted the lower three-phase contact line tends to advance down the plate and the upper contact line recedes. In these circumstances the contact angles differ, that for the advancing edge θ_A exceeding that for the receding edge θ_R, where θ is measured through the liquid. This asymmetry of the advancing and receding contact angles is referred to as hysteresis [6]. It can arise from various causes, for example from surface roughness, from surface inhomogeneity, or from the fact that the surface free energy of an unwetted surface, over which the drop is advancing, is different from that of a recently wetted surface from which the drop is receding.

If $\theta_A > \theta_R$ there will be a resultant surface-tension force on the drop acting up the inclined plane and opposing the gravitational force acting down the plane. So, in the case of a viscous drop, the effect of surface-tension forces will be to reduce the resultant force on the drop and thereby reduce the rate of flow down the plane. Indeed, if the drop is small enough surface-tension forces can equal the gravitational force and flow is prevented.

Imagine (Fig. 1) a liquid drop on a surface inclined at angle α to the horizontal. Consider a thin lamina of that drop with its plane perpendicular to the inclined solid surface and lying along the plane of symmetry of the drop. There can be no shear forces across a plane of symmetry, so the shear forces over the faces of the thin lamina parallel to the plane of symmetry will be small. The motion of the lamina can therefore be analysed by assuming that it is detached from the rest of the drop. So it follows that the behaviour of the drop can be deduced by analysing the forces on the lamina. This conclusion implies that the viscous forces on the lamina arise exclusively from viscous shear over planes whose normals lie in the plane of the lamina.

If the thickness of the lamina is Δx then the resultant force ΔF on the lamina down the plane will be

$$\Delta F = \Delta W g \sin\alpha - \gamma_{LA}(\cos\theta_R - \cos\theta_A)\Delta x$$

where ΔW is the mass of the lamina, g the acceleration due to gravity and γ_{LA} the surface tension of the liquid–air interface.

Now $\Delta W = A\varrho\Delta x$, where ϱ is the density of the liquid and A is the area of cross-section of the lamina, so

$$\Delta F = [A\varrho g \sin\alpha - \gamma_{LA}(\cos\theta_R - \cos\theta_A)]\Delta x$$

and the force per unit width is

$$F = \frac{\Delta F}{\Delta x} = A\varrho g \sin\alpha - \gamma_{LA}(\cos\theta_R - \cos\theta_A) \quad (1)$$

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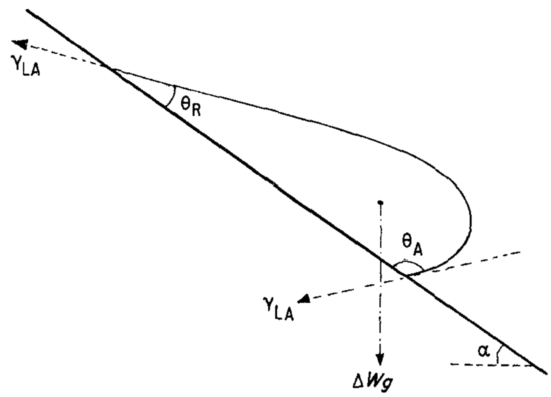

Figure 1 Diagram of the cross-section of a drop on an inclined surface.

We assess the effect of surface tension by comparing the second term in this expression, which is the surface-tension force per unit width of the lamina, with the first term which is the gravitational force per unit width.

3. Experimental procedure

A comparison was made of the rate of flow of beads of a proprietary lithia-bearing alkali borosilicate glass for vitreous enamelling of steel (designated 3350) over two surfaces:

1. A refractory enamel coat used for self-cleaning oven surfaces. It is solid at the temperature of the experiments now described (820° C) and has a porous structure. The material has a high iron content and is partly crystalline.
2. An enamel coating of the same material as the flow bead and therefore liquid at the flow temperature. The use of a plate coating identical to the flow bead material is recommended in some test specifications.

Hot-rolled steel plates 150 mm × 100 mm × 2 mm thick were coated, half with the refractory coating and half with the enamel. Two cylinders of compacted powdered frit were prepared, each weighing 2.5 gm and of diameter 12.7 mm and height about 12 mm. The particle size of the frit was less than 250 μm. Each cylinder was formed by mixing the frit with five drops of distilled water and compacting in a die under a load of 2000 lb (8960 N) and then drying in an oven at 100° C for 20 min.

The cylinders were placed about 60 mm apart on a coated plate, one on the refractory coat surface and the other on the enamel. The plate was supported horizontally on a jig and placed in a furnace at 820° C. After the cylinders had begun to fuse, the plate was tipped into a vertical position and the beads flowed downwards. The plate was removed after a prescribed period and returned to the horizontal position. Flow immediately ceased. The total length of each flowed bead was then measured.

4. Results and discussion

A series of tests was conducted with different times of flow, giving different flow lengths. The accumulated data are listed in Table I. A photograph of a typical plate appears in Fig. 2.

TABLE I Flow lengths of beads of 3350 frit on refractory-coated and enamel-coated surfaces at 820° C

Flow lengths (mm)		Difference (refractory − enamel) (mm)
Refractory coat	Enamel coat	
37.9	36.2	1.7
50.8	45.1	5.7
64.6	53.2	11.4
71.1	55.2	15.9

The difference of flow length increases with time of flow, and the flow rate is evidently faster over the refractory coat surface.

The flow at short times arises from viscous bending of the cylinders. Not until the flow length is about 30 mm is the bead completely fluid and sliding down the plate as an elongated drop. Flow lengths less than 30 mm have therefore not been investigated. The waisted appearance of the bead on the refractory surface (Fig. 2), and the fact that its width is less than the diameter of the compacted cylinder of frit, are expained by the viscous bending of the cylinder in the early stages of flow and the low rate of lateral spread of the bead.

In order to be satisfied that the differences of flow rate were not due to temperature differences between the cylinders, a test was carried out on a plate with the positions of the enamel coated area and the refractory coated area transposed. The flow lengths were:

Refractory coat	Enamel coat	Difference
51.3 mm	46.4 mm	4.9 mm

Having regard to the sensitivity of flow rate to temperature this represents good agreement with the second observation in Table I, and supports the assertion that the differences recorded in that table arise from the different surface over which the beads flow, and not from a temperature difference between the beads.

4.1. Assessment of surface tension forces

Two beads were examined, one on the enamel surface and the other on the refractory coat surface, to estimate the surface tension forces.

The profile of each bead was photographed in a direction perpendicular to the plane of symmetry at a

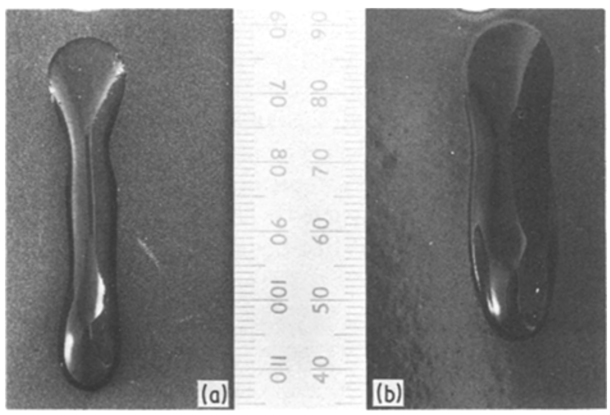

Figure 2 Typical photograph of flowed enamel beads on (a) the refractory and (b) the enamel coat surfaces. The scale is in mm.

TABLE II Values of contact angles and sectional area of bead in the plane of symmetry

Surface	θ_A (deg)	θ_R (deg)	Section area (mm^2)
Refractory coat	145.5	17	167.5
Enamel coat	133	9.5	129.9

TABLE IV Comparison of bead dimensions

Coating	Average width $\bar{w}$ (mm)	Length l (mm)	Ratio $\bar{w}/l$
Enamel	11.52	46.4	0.24_8
Refractory coat	7.88	51.3	0.15_3

magnification of $\times 3$. The lighting conditions were adjusted to give maximum contrast at the bead–substrate interface. The advancing and receding contact angles were measured. The area of cross-section of the bead in the plane of symmetry was measured by cutting round the image on a photographic print and weighing the piece. This weight was compared with that of a known area of the same piece of photographic paper cut from an adjacent region. Table II gives the results.

Both contact angles are greater for the bead on the refractory coat surface, and in both cases there is considerable hysteresis between the advancing contact angle θ_A and the receding angle θ_R. The sectional area of the bead on the enamel coat is the smaller because of more extensive lateral spread.

An indication of the magnitude of surface tension forces was sought by comparing the gravitational and the surface tension forces per unit width on the lamina lying in the axial plane of symmetry of the drop, given by Equation 1.

For this comparison we need values for the density of the bead and for the surface tension of the liquid enamel–air interface. The surface tension was derived from tabular data prepared by Appin and quoted by Vargin [7]. This gives surface tension factors $\bar{\gamma}_i$ for each major oxide constituent of the glass from which the surface tension γ of a mixture can be calculated using

$$\gamma = \sum_i \bar{\gamma}_i \alpha_i$$

where α_i is the mole fraction of the i^{th} constituent.

The data are quoted for a temperature of 1300° C. An approximate temperature correction is suggested: the surface tension values should be increased by 1.5% for each 100° fall in temperature. These data predict a surface tension of $305\,mJ\,m^{-2}$ for the 3050 frit. In view of the approximate nature of the prediction a value of $300\,mJ\,m^{-2}$ was used for the purpose now described.

The estimate of the gravitational force on the drop must take account of the fact that the bead has a distribution of gas bubbles. There is usually one large bubble near the advancing head of the drop. Its area of cross-section (about $15\,mm^2$) has been subtracted from the total projected area of section of the bead to give the nett area values listed in Table II. The bubble comprises part of the volume of air between the particles of frit in the compacted cylinder; the air is trapped when the surface layers fuse and seal off the core whilst it is still solid. The volume of the interparticle space is typically about $500\,mm^3$, which is about 35% of the total volume of the cylinder. Much of this gas escapes. There persists, in addition to the single large bubble, a finely distributed bubble structure. This was taken into account by measuring the density of detached beads by weighing in air and in water. The average density, excluding the large bubble, was $2.55\,g\,cm^{-3}$ for both beads. The density of the bubble-free glass was $2.63\,g\,cm^{-3}$.

Using these data we calculate the gravitational and the surface tension forces per unit width on a lamina of a drop along its plane of symmetry. The results are collected in Table III.

4.2. Discussion of surface tension forces

It is evident that the resultant force per unit width on the central lamina of the bead on the enamel surface is about three-quarters of that for the bead on the refractory surface, which accords with the observation that the bead on the refractory surface flows more rapidly. In reaching this conclusion we imply that the viscosity of both beads will be similar so, for example, we imply that no composition differences have been generated by interaction between the bead and the surface over which each flows.

The surface tension forces are almost the same for the two beads. Although both contact angles are higher for the refractory surface the hysteresis is similar for the two surfaces. The parameter that defines the resultant force is seen to be the area of cross-section A of the bead. This is significantly less for the bead on the enamel surface, because this bead has the greater lateral spread as it flows down the plate. The difference in spread was quantified by measuring the average width of two typical beads of comparable length, one of which flowed over the enamel surface and the other over the refractory coat, with the results given in Table IV.

The average width $\bar{w}$ was measured by photographing the bead, cutting the image out of the print and weighing it. This gave the area of the bead which was divided by the length l to give $\bar{w}$.

Table IV quantifies the greater lateral spread of the bead on the enamel surface. In both cases, the average width is less than the diameter of the compacted cylinder of frit (12.7 mm). In the initial phase of flow the cylinder bends viscously and the cylindrical surface touches the plate. This narrows the width of contact.

TABLE III Calculated forces per unit width on a lamina of a drop along its plane of symmetry

Surface	Gravitational force $A\varrho g$ ($N\,m^{-1}$)	Surface tension force $\gamma_{LA}(\cos\theta_R - \cos\theta_A)$ ($N\,m^{-1}$)	Resultant force ($N\,m^{-1}$)
Refractory coat	4.190	0.534	3.656
Enamel coat	3.250	0.500	2.750

TABLE V Variation of contact angle with time

Plate coating	Time molten (min)	Contact angle (deg)	Bead diameter (mm)
Refractory coat	2	76	20.7
Refractory coat	58	15	36.5
Enamel	2	40	25.5

In the case of the enamel surface, lateral flow of the enamel brings the width back almost to the cylinder diameter but the lower rate of spreading over the refractory surface limits the width to a lower value.

4.3. A comment on the contact angles

The differences in the lateral spread of the glass beads on the two different surfaces turns out to be related to differences in the rate of attainment of the equilibrium contact angle.

Evidence that the contact angle varies with time was secured by placing a 2.5 g cylinder of frit on a horizontal plate in a furnace at 820° C. The contact angle of the liquid drop and the diameter of the drop were measured. The diameter of the cylinder was 12.7 mm. The results are given in Table V.

The volume of a hemisphere with a base of diameter 12.7 mm is 536 mm^3. The volume of 2.5 g of the enamel is 960 mm^3. So, if the base of the drop is temporarily restricted by viscous forces to a diameter of 12.7 mm the contact angle will be greater than 90°. This is observed, but the drop on the enamel surface rapidly spreads and, as is evident from Table V, the contact angle has fallen to 40° in two minutes. The drop on the refractory coat spreads more slowly and the contact angle has fallen to only 76° over the same period but falls to 15° after an hour. The equilibrium angle for the enamel coating will be 0° and that for the refractory coating will be less than 15° because after one hour of contact the angle is still falling.

The refractory coat surface comprises a porous, partly crystalline high-iron glass which is solid at 820° C. The surface topography is revealed in the scanning electron micrograph of Fig. 3. The microstructure of the interfacial region between the liquid enamel and the plate coating near the advancing head of the flow bead, that is at a location where the enamel

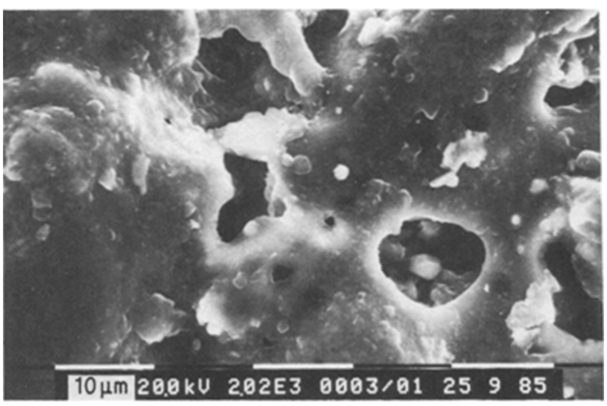

Figure 3 Scanning electron micrograph of the refractory coat surface showing the porous character of the coating.

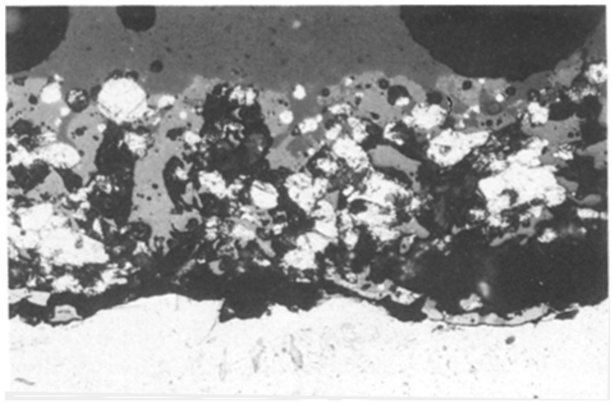

Figure 4 Photomicrograph of the interfacial region between the enamel and the refractory surface coating (× 171).

has been in contact with the surface for about half a minute, reveals that the glass readily wets the surface and penetrates the cavities that are open to the surface (Fig. 4). Now if a drop of liquid of surface tension γ_{LA} is in equilibrium on the plane surface of a solid of surface tension γ_{SA} and the interfacial tension at the solid–liquid interface is γ_{SL}, then the equilibrium contact angle θ is given by

$$(\gamma_{\mathrm{SA}} - \gamma_{\mathrm{SL}}) = \gamma_{\mathrm{LA}} \cos \theta$$

If the surface is rough such that for unit projected area the actual surface area is r ($r > 1$) then the equilibrium angle becomes θ' given by [8]

$$r(\gamma_{\mathrm{SA}} - \gamma_{\mathrm{SL}}) = \gamma_{\mathrm{LA}} \cos \theta'$$

Evidently $\cos \theta' = r \cos \theta$, so, if $\theta < 90°$, which is the case for the surface that is our concern, $\theta' < \theta$. So the effect of roughening a surface which the liquid wets is to enhance wetting and decrease the contact angle. The low value of the equilibrium contact angle for the refractory surface is consistent with this conclusion.

So the high advancing contact angles of the flowing beads are a dynamic effect. The high shear-strain rates close to the solid surface produce viscous forces which cause the overlying fluid to roll over this interfacial region. The fact that the contact angle falls with time less rapidly for a sessile drop on the porous refractory surface than on the enamel surface is likely to arise from the higher viscous resistance to the flow of the molten glass through the narrow channels of the porous surface. It is this effect that also causes the smaller lateral spread of the flowing bead on the refractory surface.

So we conclude that the higher rate of flow of the enamel bead down the refractory coat surface is explained by the lower lateral spread of the bead, caused in turn by the viscous resistance to flow of the enamel through the microchannels in the coating surface. The gravitational force per unit width of drop is therefore higher than is the case for flow over the smooth enamel surface where lateral spread is greater. The difference of surface tension force per unit is quite small – less than 0.04 $\mathrm{N\,m^{-1}}$ compared with a resultant force of 3 to 4 $\mathrm{N\,m^{-1}}$ – and will have only a trivial effect on the relative flow rate.

4.4. Implications for production flow-bead testing

The work now described leads to the conclusion that the surface tension forces acting on the flow-bead are about 15% of the gravitational force. In production testing, where the standard bead and the tested sample flow over the same surface, interfacial tension forces will show only a trivial difference. The surface tension of the liquid is not affected by change of composition nearly so sensitively as is viscosity. So a difference of composition that would change the flow distance of a bead by say 12%, which is a typical upper limit of acceptance in flow-bead testing, would be associated with only a small difference of surface tension. The contribution of this to the difference of flow length would therefore be secondary.

However, any attempt to relate flow distances to absolute values of coefficient of viscosity must take account of surface tension forces. Dekker [5], for example, appears to have ignored surface tension forces in his attempt to extract values of the coefficient of viscosity from flow-bead data.

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