SURFACE TENSION AND FUSION PROPERTIES OF PORCELAIN ENAMELS

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ABSTRACT

High-temperature viscosity of glasses is an important key to understanding the phenomena that occur when firing porcelain enamels.

PORCELAIN ENAMELS

Porcelain enamel is a glass coating fused to metal. While there are similarities between the spray application of enamels and paints, there are important differences because of the vitreous nature of porcelain.

Porcelain enamel glass list is typically alkali borosilicate where the alkalis are lithium, sodium, or potassium. Alkaline-earth ions such as calcium, strontium, or barium are also often present as fluxes. For adhesion, cobalt, nickel, iron, and copper are added to the glass.

During smelting, the melt glass is quenched, which results in an amorphous molecular structure. Glass does not have a distinct melting point, which is a sudden transition from a solid to liquid phase, but instead has a glass temperature (Tg) at which the solid glass becomes a highly viscous supercooled liquid. As the temperature is increased above Tg, the viscosity drops.

GLASS VISCOSITY

Viscosity is resistance of a fluid to deformation. For a glass, the viscosity varies with temperature according to the Vogel-Fulcher-Tammann (VFT) equation:

$$\log(\eta) = A + B(1-T/T_g)$$

This is equivalent to the Williams-Landel-Ferry (WLF) model for viscosity of a polymer above its glass temperature, but neither model is used in the enameling industry. Typically, the enamel industry has interpreted glass viscosity according to the type of generalized diagram in Figure 1. On the chart, the borosilicate and soda-lime glass pass through the various points on the viscosity scale at lower temperatures than the nearly pure silica glasses. The curve for porcelain enamel alkali borosilicate glasses would be expected to be lower and to the left of the one for borosilicate glass.
FIRING ENAMELS

It is most straightforward to consider the processes, which occur during firing of a ground coated parts. First, the dried enamel and steel expand according to the respective thermal expansion (ε) of each. As such, the value of α, Tf, and dilatometric softening point (F1) of three ground coats was measured with an Otton Model 1000R dilatometer.

Samples bars for thermal expansion measurements were prepared by placing 8 g of glass frit powder into a carbon mold. The mold was fired at 1550°F (843°C) for 12 min. Next, the glass bar was placed into a 1000°F (538°C) furnace, which was switched off and allowed to cool overnight. Then, the bar was cut to a length of 2 ± 0.2 inches (50.8 ± 5 mm), and the edges were rounded on a grinding wheel.

The sample was placed in a quartz tube in contact with a ceramic pushrod. As the temperature was increased from room temperature, a linear voltage displacement transducer (LVDT) measured the expansion of the bar. When the temperature was reached that the bar viscosity was low enough to start contracting under the force of the pushrod, the dilatometer automatically shut off shortly after a preset amount of contraction. That temperature is the F1.

The thermal expansion curves are shown in Figure 2. The theoretical linear curve for enameling steel based on α = 12.1 x 10⁻⁶/°C is included for reference. The value of α was determined by calculating the slope of the linear portion of the curve below 662°F (350°C) and is marked accordingly.
While a number of sophisticated tests exist to measure glass viscosity versus temperature, the fusion flow test is used by the enamel industry to determine relative glass viscosity at a fixed temperature. Two grams of -10+30 M fin powder were pressed into a pellet, which was placed along a line on the top edge of a ground coated butt panel. The panel was put into a furnace at 1500°F (816°C) for 1.5 min and then tilted up. The fusion flow, f, is:

\[ f = \frac{x_{\text{sample}} - x_{\text{ref}}}{x_{\text{ref}}} \]

where \( x_{\text{sample}} \) is the distance from a line parallel to the top edge of the panel that the test sample flowed, and \( x_{\text{ref}} \) is the distance run by the reference standard. The fusion flow is negative if the test sample runs a shorter distance than the standard. The results are given in Table 1 with the values of \( \alpha \), \( T_g \), and \( T_s \).

<table>
<thead>
<tr>
<th>Glass</th>
<th>( \alpha \times 10^8{^\circ}C )</th>
<th>( T_g , {^\circ}C )</th>
<th>( T_s , {^\circ}C )</th>
<th>Fusion Flow (816°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soft</td>
<td>13.1</td>
<td>407</td>
<td>437</td>
<td>1.70</td>
</tr>
<tr>
<td>Medium</td>
<td>10.0</td>
<td>456</td>
<td>504</td>
<td>-6</td>
</tr>
<tr>
<td>Hard</td>
<td>8.1</td>
<td>533</td>
<td>593</td>
<td>-25</td>
</tr>
</tbody>
</table>

**ENAMEL WETTING ON OXIDIZED STEEL**

As the metal temperature increases during firing, the reactions occur that create adhesion of the enamel to the steel. Additionally, good spreading of the liquid enamel on the steel is a basic requirement for adhesion. The balance of forces arising from a drop of liquid enamel (I) on surface (S) under a vapor (V) is schematically shown in Figure 3.
Figure 3. Liquid droplet on a solid surface

Young's equation describes the balance of forces:

$$\gamma_{lv} = \gamma_{li} + \gamma_{si} \cos \theta$$

where $\gamma$ is the energy per unit area of the appropriate interface and $\theta$ is the contact angle between the liquid and the substrate. If $\gamma_{s} > \gamma_{l}$, the surface will be wetted to decrease the area of the higher energy air interface; this is the preferred situation. If $\gamma_{s} < \gamma_{l}$, beading up of the liquid will occur to reduce the area of the higher energy air interface.

With typical enamel firing temperatures between 1400 to 1800°F (760 to 870°C), the reactivity of the steel affects the wetting, and high-temperature reactive wetting remains relatively poorly understood. In fact, the liquid enamel is not in contact steel, but actually with iron oxide that forms after firing begins. K. Surzycki showed this by firing an enamel (with $\alpha = 11.5 \times 10^{-6}$) $T_s = 475°C$ (887°F), and $T_a = 545°C$ (1003°F) on steel under argon and air as part of a study of adhesion. The appearance of the panels is shown in Figure 4. Since the iron oxide did not form under argon, $\gamma_{s} < \gamma_{l}$ the enamel could not wet the steel, and adhesion would not be possible.

Figure 4. Clear enamel after firing at 1472°F (800°C) under argon (top) and air (bottom)
The surface tension of the soft, medium, and hard frits was estimated by calculating a weighted average of the oxide components, and is shown in Table 2. It suggests that the soft frit will actually wet the substrate the least, and this was observed on the fusion test. The flow on the soft frit was narrower and at a greater contact angle than the medium frit.

Table 2. Estimated surface tension

<table>
<thead>
<tr>
<th>Frit</th>
<th>Surface Tension (Dynes/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soft</td>
<td>2.74</td>
</tr>
<tr>
<td>Medium</td>
<td>2.46</td>
</tr>
<tr>
<td>Hard</td>
<td>2.32</td>
</tr>
</tbody>
</table>

Figure 5 shows the viscosity is a more important factor than the surface tension. The frit melt buttons were melted on a steel plate and a high-density aluminum oxide tile at 1500°F (816°C). The tile was used as a non-reactive substrate. The soft frit wetted the steel and tile much more than the other two frits. Therefore, the glass viscosity at the firing temperature is a more important factor than the surface tension. On the steel panel, it should be noted that the hard frit shattered, presumably from tensile stresses that arose on cooling.

Figure 5. Button flow results on sheet steel (left) and alumina tile (right)
ENAMEL-STEEL REACTIONS

The bisque enamel permits the transport of O₂ from the surrounding air to the enamel-steel interface, resulting in the formation of an iron oxide (Fe₂O₃) scale on the surface of the steel starting at about 600°C (1112°F). According to Dietzel¹ and also King², cobalt or nickel precipitated from the ground coat glass in contact with the iron-containing substrate forms a short-circuited local cell in which iron is the anode. The current flows from the iron through the mullite enamel to the cobalt and back to the iron. These local cells are not exhausted during firing because there is an abundance of anodic iron (in the steel), and diffusing atmospheric oxygen has a depolarizing action on the cathode side (the cobalt and nickel). The result is that the iron goes continuously into solution, the surface becomes roughened, and the glass throws itself into the holes. The required galvanic reactions are:

1) \( Fe^{2+} + CoO \rightarrow FeO \text{ (wustite)} + Co^{3+} \)
2) \( 2Co^{3+} + O_2 \rightarrow 2Co^{2+} + 2O^2^- \)
3) \( Co^{2+} + 2e^- \rightarrow Co^{0} \)
4) \( Fe^{2+} + 2e^- \rightarrow Fe^{0} \)

On optical micrographs, the iron-rich layer is visible as a brown layer at the enamel-steel interface. Some evidence of the reaction reaching the enamel surface as copperheads is visible in the middle of soft iron.

Figure 5. A cross-section of the reaction layer from Sarnoff’s study is shown on a scanning electron microscope (SEM) micrograph in Figure 6.

Figure 6. SEM micrograph of the enamel-steel interface³

With SEM, characteristic X-rays emitted by interaction of the electron beam and the sample identify the elements present using electron energy dispersive spectroscopy (EDS). The EDS images of Figure 6 are shown in Figure 7. These confirm the formation of metallic Fe, Co, Cu, and Ni at the enamel-steel interface.
The microstructure of enamels contains a bubble structure. In wet-spray enamels, the gases that form the bubbles originate from the thermal degradation of organic material contained in the clay used to suspend the frit particles in water. Otherwise, the bubbles are from gases such as hydrogen, water vapor, carbon monoxide, carbon dioxide, and nitrogen emitted by the steel heating below 1200°F (649°C). Excessive bubble formation can result if the moisture level in the furnace is too high. Excessive trapped hydrogen from the steel can cause the spontaneous fracturing phenomena called flakelage.

Andrews observed the evolution of the enamel microstructure during firing. First, the bisque enamel surface cracked, presumably from the expansion of the steel. With increasing temperature, a wavy appearance was observed as the Tg was passed and the enamel became a decreasingly viscous liquid. Then, the enamel smoothed out, and bubbling, which could be violent begun. Finally, large bubbles were eliminated, leaving a fine distribution of smaller ones.

**THERMAL EXPANSION**

Porcelain enamels develop compressive strength on cooling from the mismatch between the expansion of the substrate and the enamel. The thermal strains that would occur are:

\[ \Delta \alpha = \int (\alpha_e - \alpha_s) dT \]

where \( \alpha_e \) and \( \alpha_s \) are the respective coefficients of thermal expansion for the enamel and steel and \( dT \) is the amount of cooling. As seen in **Figure 2**, above Tg, the enamel is in tension because its expansion is greater than the steel. Below Tg, the frit expansion decreases to the value in the linear range, and the tension is relieved by increasing compression.
Figure 8 shows the total mismatch strain from the contribution of the tensile strain above \( T_f \) and the linear thermal expansion below \( T_f \). The hard ground coat frit will have the highest residual compressive stress while the soft frit, while potentially good for creating bond, would be at risk from spontaneous delamination from the steel through spalling. Actual results depend on the strength of adhesion, which is determined by the amount of wetting and the amount of cobalt and nickel present in the glass.

![Figure 8. Mismatch strain in the three glasses](image)

**SUMMARY**

Data was drawn from the literature and laboratory work to illustrate the phenomena that occur while firing a ground coat on steel. Figure 9 shows a typical industrial furnace profile of steel temperature versus time to summarize the points discussed.
Surface Tension and Fusion Properties of Porcelain Enamels

Figure 9. Enamel firing profile

Before firing, the enamel is a dry compact of frit and additive particles. At about point 1 on Figure 9, if clay is present, it begins to dehydrate, and the organic components degrade. This contributes to the formation of the bubble structure. The steel oxidizes, and, as the temperature passes \( T_a \), the enamel becomes a decreasingly viscous supercooled liquid. At point 2, the galvanic reaction, during which the enamel reduces the iron oxide to create adhesion, occurs. While the surface tension of the enamel is a consideration, the viscosity at the firing temperature more strongly determines if the enamel will wet the oxidized steel. After reaching a peak temperature, the part begins to leave the hot zone of the furnace. The enamel cools, becomes more viscous, and contracts faster than the steel. At point 3, the enamel becomes rigid, and the tensile stresses are relieved. If the linear thermal expansion of the enamel is less than the steel, residual compressive stresses begin to build that strengthen at point 4.

Considerable lab work goes into predicting and understanding enamel behavior in service. The fusion flow test gives values of glass viscosity at one temperature compared to a reference standard. Dilatometry provides values for \( T_a \), \( T_g \), and \( T_r \). These determine if an enamel might spall, how well it might adhere, and when it will soften and begin to “fire out.” Lastly, work continues to better understand the high-temperature reactions between enamels and steel that result in bond.
REFERENCES


