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 frit 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 molten 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 (T_g) at which the solid glass becomes a highly viscous supercooled liquid. As the temperature is increased above T_g, 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-Tamman (VFT) equation[1]:

$$\log (n) = A + B/(T-T_0)$$

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.

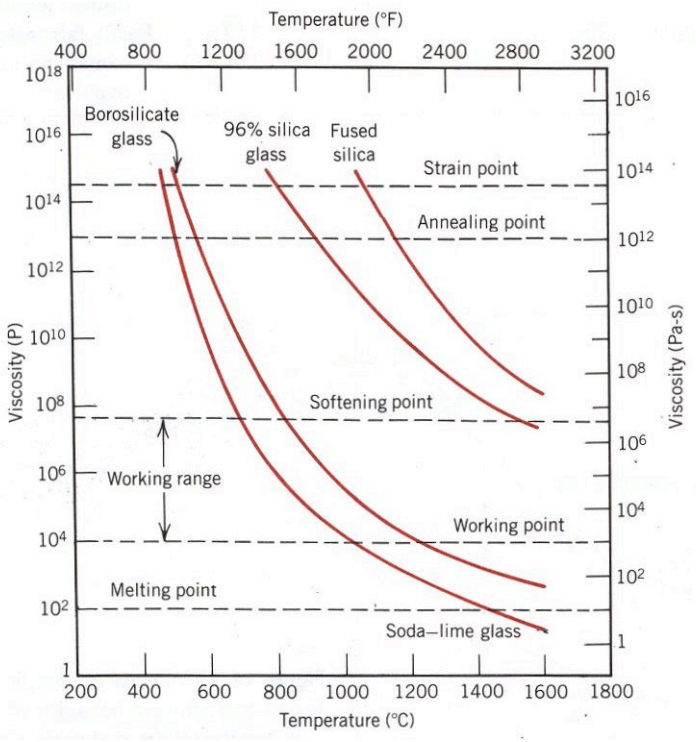

Figure 1. Glass viscosity versus temperature[2]

Firing Enamels

It is most straightforward to consider the processes, which occur during firing of a ground coated part. First, the dried enamel and steel expand according to the respective thermal expansion (α) of each. As such, the value of α, T_g, and dilatometric softening point (T_s) of three ground coats was measured with an Orton 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 (621°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 T_s.

The thermal expansion curves are shown in Figure 2. The theoretical linear curve for enameling steel based on $\alpha = 12.1 \times 10^{-6}$/°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.

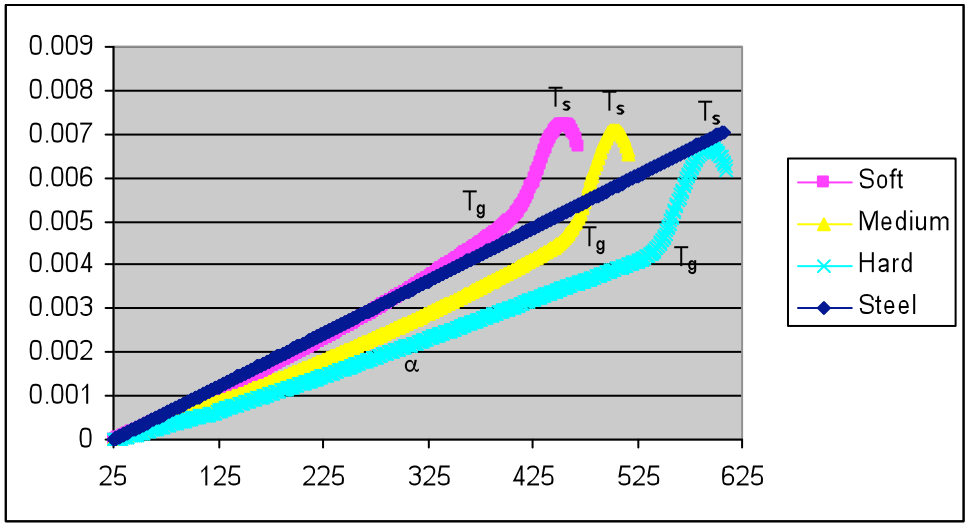

Figure 2. Measured thermal expansion of the three ground coat frits

While a number of sophisticated tests exist to measure glass viscosity versus temperature,[3] 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 frit powder were pressed into a pellet, which was placed along a line on the top edge of a ground coated bent 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:

$$f = x_{sample} - x_{ref}$$

where x_{sample} is the distance from a line parallel to the top edge of the panel that the test sample flowed, and x_{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 α, T_g, and T_s.

Glass	α (x 10^{-6}/°C)	T_g (°C)	T_s (°C)	Fusion Flow (816°C)
Soft	13.1	407	457	+170
Medium	10.0	456	504	-6
Hard	8.1	536	594	-25

Table 1. Thermal expansion and viscosity results

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 (l) on surface (s) under a vapor (v) is schematically shown in Figure 3.

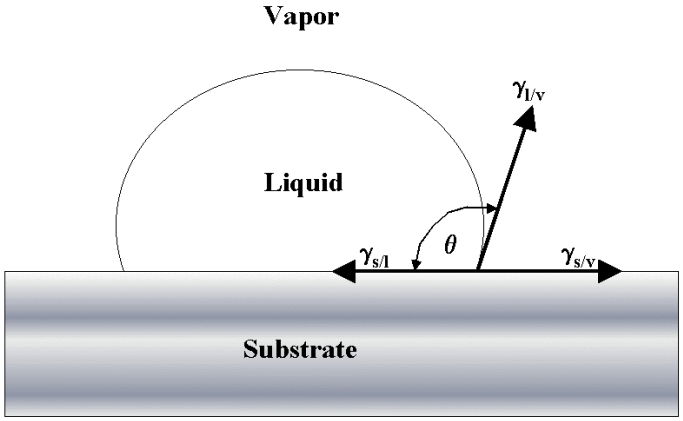

Figure 3. Liquid droplet on a solid surface[4]

Young's equation describes the balance of forces:

$$\gamma_{s/v} = \gamma_{s/l} + \gamma_{l/v} \cos\theta$$

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

With typical enamel firing temperature between 1400 to 1600°F (760 to 871°F), the reactivity of the steel affects the wetting, and high-temperature reactive wetting remains relatively poorly understood.[5] In fact, the liquid enamel is not in contact steel, but actually with iron oxide that forms after firing begins. K. Sarrazy showed this by firing an enamel (with α = 11.5 x 10^{-6}/°C, T_g = 475°C (887°F), and T_s = 545°C (1013°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, $\gamma_{s/v} < \gamma_{s/l}$, the enamel could not wet the steel, and adhesion would not be possible.

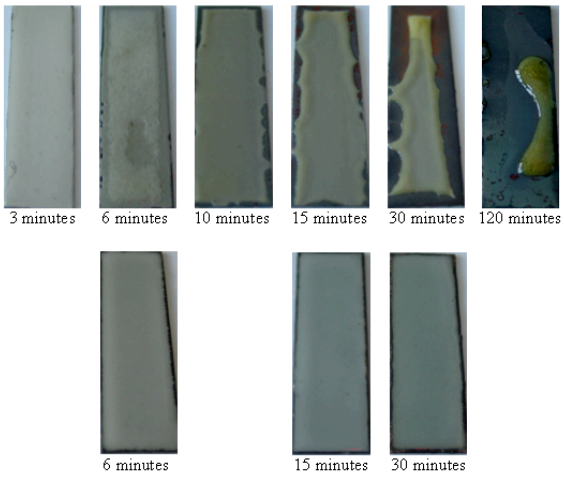

Figure 4. Clear enamel after firing at 1472°F (800°C) under argon (top) and air (bottom)[6]

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.

Frit	Surface Tension (Dynes/cm)
Soft	2.74
Medium	2.46
Hard	2.32

Table 2. Estimated surface tension

Figure 5 shows the viscosity is a more important factor than the surface tension. The fusion flow 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.

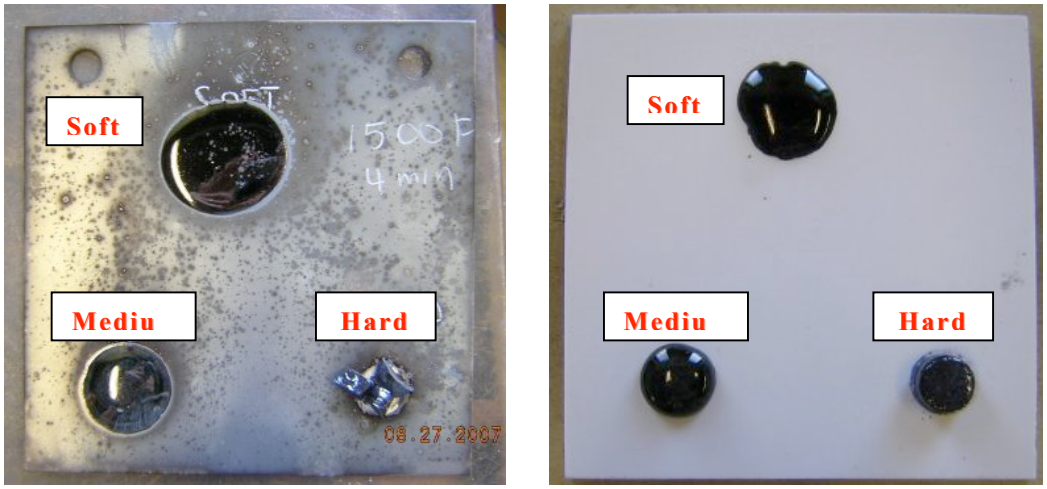

Figure 5. Button flow results on sheet steel (left) and alumina tile (right)

Enamel/Steel Reactions

The bisque enamel permits the transport of O_2 from the surrounding air to the enamel/steel interface, resulting in the formation of an iron oxide (FeO) scale on the surface of the steel starting at about 600°F (316°C). According to Dietzel[7] and also King[8], 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 molten 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 anchors itself into the holes. The required galvanic reactions are:

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

On optical micrographs, the iron-rich layer is visible as a brown haze layer at the enamel/steel interface. Some evidence of the reaction reaching the enamel surface as copperheads is visible in the puddle of soft frit in Figure 5. A cross-section of the reaction layer from Sarrazy's study is shown on a scanning electron microscope (SEM) micrograph in Figure 6.

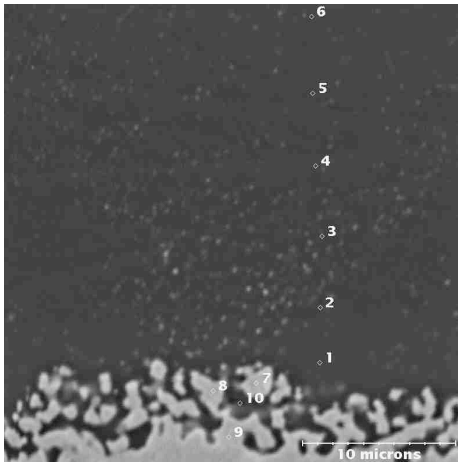

Figure 6. SEM micrograph of the enamel/steel interface[9]

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.

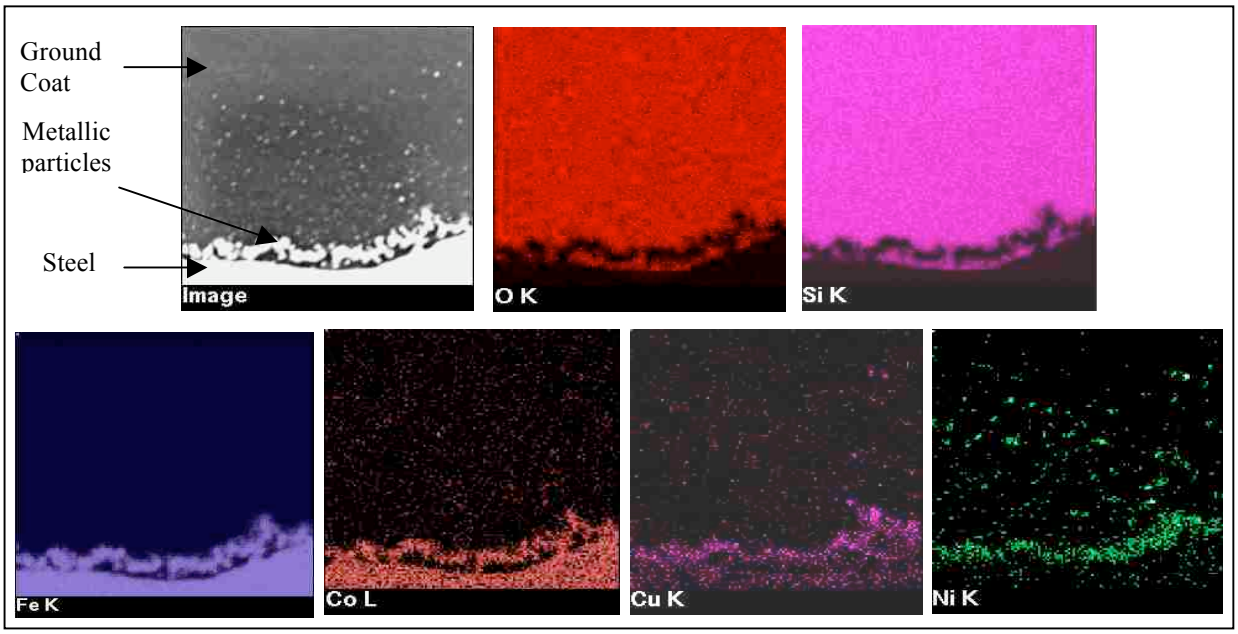

Figure 7. SEM EDS maps of the ground coat/steel interface[10]

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 clays 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 starting below 1200°F (649°C). Excessive bubble can result if the moisture level in the furnace is too high. Excess trapped hydrogen from the steel can cause the spontaneous fracturing phenomena called fishscale.

Andrews observed the evolution of the enamel microstructure during firing.[11] First, the bisque enamel surface cracked, presumably from the expansion of the steel. With increasing temperature, a wavy appearance was observed as the T_g was passed and the enamel became a decreasingly viscous liquid. Then, the enamel smoothed out, and bubbling, which could be violent, began. 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:

$$\Delta\varepsilon_0 = \int_T^{T_0} (\alpha_2 - \alpha_1) dT$$

where α_1 and α_2 are the respective coefficients of thermal expansion for the enamel and steel and dT is the amount of cooling. As seen on Figure 2, above T_g, the enamel is in tension because its expansion is greater than the steel. Below T_g, 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_g and the linear thermal expansion below T_g. 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.

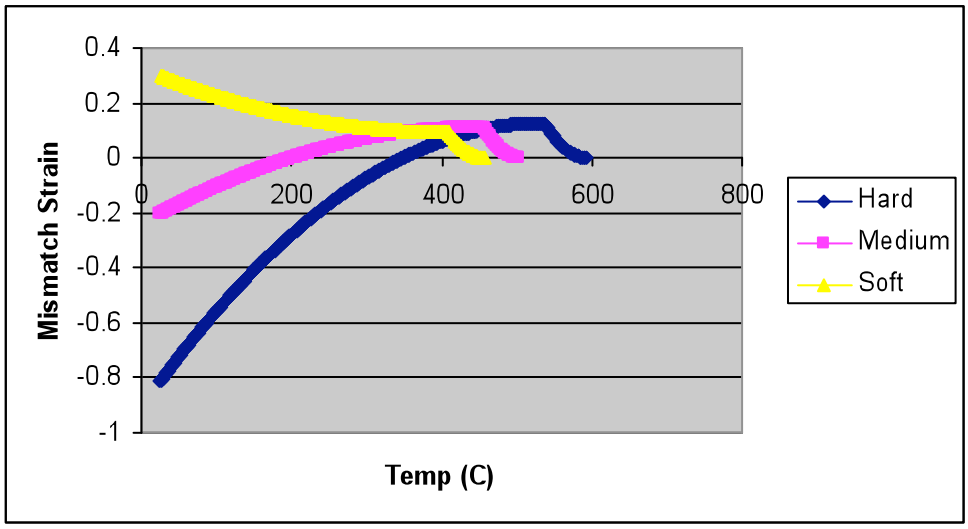

Figure 8. Mismatch strain in the three glasses

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.

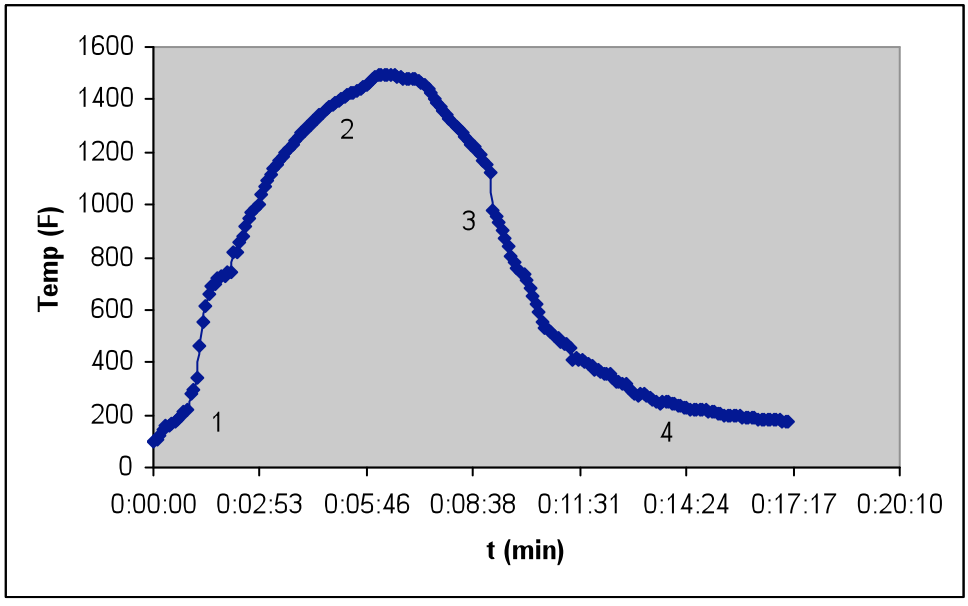

Figure 9. Enamel firing profile

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_g, 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 value of glass viscosity at one temperature compared to a reference standard. Dilatometry provides values for α, T_g, and T_s. 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.

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