Lead Free Decorating Alternatives for The Container Industry

Frits formulated for ceramic enamels need to have a number of properties; among them a firing temperature low enough so that glassware does not slump during heating, chemical durability to alkaline and acidic media, and a thermal expansion that leads to zero or compressive stress in the enamel.

Lead oxide has been widely employed in the formulation of borosilicate frits used in ceramic enamels. The unique property of the lead ion is that it is highly deformable. Lead lowers the melting temperature of frit and yields glossy ceramic enamels with firing temperatures suitable for use on soda lime silicate glass. The high deformability of lead also allows oxides of zirconium, titanium, and aluminum to be dissolved in the frit thus imparting chemical durability to the frit. Lastly lead in combination with boron produces frits that have suitable thermal expansions for commonly used soda lime silica glass substrates.

Due to the toxicity of lead a number of state and federal regulations are in place to control its use. The FDA has guidelines on the use of lead in the top 20 mm of decoration (lip and rim), Massachusetts regulates lead release to 2 ppm or less for tumblers completely immersed in acetic acid, and California's Prop 65 lists lead as chemical known to cause cancer or reproductive toxicity.

One commonly used alternative to lead oxide in frits is bismuth oxide. Bismuth is similar to lead in that its ion is highly deformable, and frits made with bismuth oxide have similar characteristics to leaded frits. One drawback to using bismuth is that cadmium based pigments; which provide popular colors like reds, oranges, and yellows, are not stable in bismuth frits.

Another familiar alternative to leaded frits are frits based on zinc oxide. Although the deformability of zinc is not the same as lead, frits can still be formulated with properties similar to lead, and the zinc-based frits are capable of developing colors based on cadmium pigments.

A comparison of a typical leaded frit (frit A) versus a zinc based lead free frit (frit B is shown in figure 1. The expansion of both frits in the 25 to 325 ^{o}C range is around 87 x 10^{-7} $^{o}C^{-1}$.

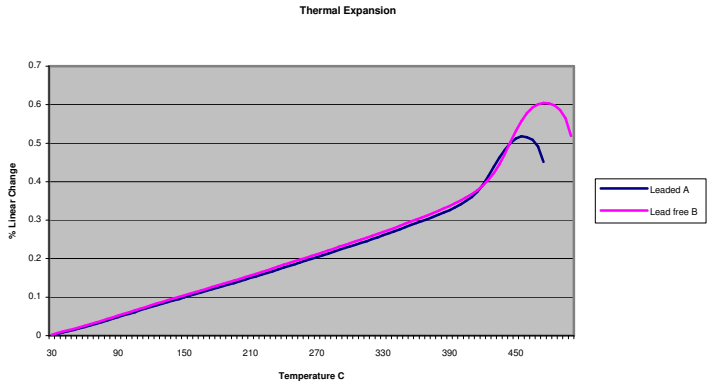

Figure 1. Thermal expansion comparison of leaded versus lead free frit.

Figure 2 shows a differential scanning calorimetry plot of the same two frits and indicates that the lead free frit B has a glass transition temperature (first exothermic deflection) around 10-20 ^{o}C higher than the leaded frit A, indicating that the lead free frit is harder to fire. Despite this difference the lead free frits can be fired and achieve satisfactory gloss on soda lime silica substrates.

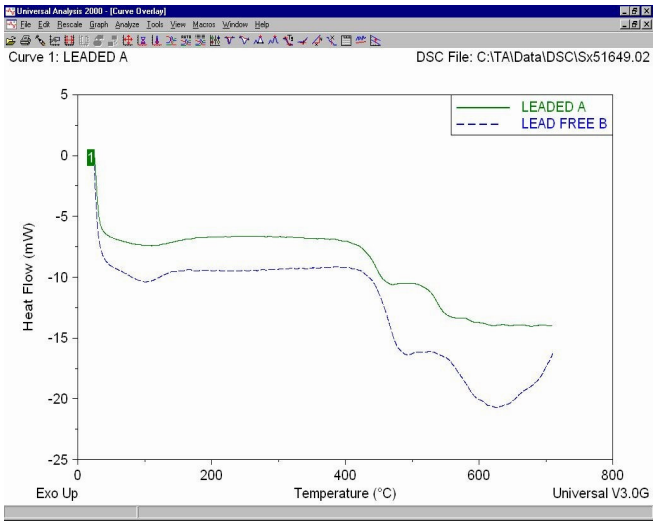

Figure 2. Differential scanning calorimetry curve of leaded versus lead free frit.

Table I lists a comparison of the leaded A versus lead free B for a number of properties. For chemical durability tests a scale of 1 (best) to 7 (worst) was used to

grade the degree of attack (1 representing no attack, 7 indicates complete removal). The table indicates that the lead free frit has comparable chemical durability to the leaded frit to both acidic and basic media.

Property	**Test**	**Leaded A**	**Lead Free B**
Thermal expansion	ASTM C732	87 x 10^{-7} $^{o}C^{-1}$	88 x 10^{-7} $^{o}C^{-1}$
Residual Stress	ASTM C937	0 psi	0 psi
Firing Temp	Side by side trial	616 ^{0}C (1140 ^{o}F)	627 ^{0}C (1160 ^{o}F)
Alkali resistance	ASTM C675	5	5
Detergent resistance	0.3 wt. %	4-5	5
HCl	ASTM C735	2	3
Citric	ASTM C735	3	4

Table I. Comparison of properties of leaded versus lead free frit.

In summary lead free frit B compares favorably to lead frit A in all properties measured. Also a wide range of colors is available using lead free frit B, including reds, oranges, and yellows.

Joe Ryan