Pressure Forming of Automotive Glass and Challenges for Glass-Ceramic Enamels

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Abstract

Automotive glass pressure forming parameters and glass-ceramic enamel performance requirements are reviewed. "Deep bend" forming processes require ever more demanding anti-stick behavior from the enamel. Experimental results are presented for the pressing of trials within and exceeding current time, temperature, and pressure manufacturing limits. Anti-stick release force measurements, developments, and advantages of new enamel technologies are discussed.

Introduction

Glass science is an important and increasingly challenged technology in today's automotive business. Each year manufacturers use more glass surface area with more complex shapes[1,2]. These automobile design trends are influenced by the need for better aerodynamics, styling, and improved visibility. Also, lighter vehicle weight requirements for improved fuel efficiencies are resulting in thinner glass. Glass-ceramic enamel coatings around the outer periphery of automotive glass provide UV protection to the underlying adhesive holding the glass to the vehicle frame. The black enamel coatings also provide a decorative function by hiding adhesive layer unevenness and by enhancing the appearance of the glass. Enamels are screen printed on cut sheets of soda-lime-silica float glass, dried, and sintered during the forming and heat strengthening of the substrate. For rear window glass (back lights), the dried enamel is typically overprinted with silver enamel heater bands and bus bars before sintering. Long term durability and ease of integration into glass forming processes make glass-ceramic enamels the functional material of choice.

Widely used industrial glass forming operations have used gravity-sag processes for more than 50 years[3]. Gravity-sag shaping uses steel jigs that support only the glass sheet edges. The jig is passed slowly through a long tunnel oven and brought to temperatures in the range of 500 °C. Localized heaters then raise the glass temperature above 600 °C so the actual bending occurs when the glass sheet sags under its own weight into the shape of the jig. Several disadvantages of such processing include rates, inability to form severe bends, and the fact that many different jigs must have exactly the same shape. Weight assisted sag forming operations can be used. Press bend or pressure forming technology innovation has resulted in significant change within the automotive glass manufacturing industry[4,5,6]. One part at a time is formed by the same mould, press ring, and annealing ring by combinations of pressure and vacuum forming. Advantages of such press bend forming operations include precise shape control, ability to form more severe or complex shapes, quick change tooling, and faster production rates. To prevent the mould from marking the hot glass, the mould contact surface is covered with a knitted cloth made of stainless steel or glass fibres. During the pressing operation, the enamel is in direct contact with the press mould cloth, and can be in the hot zone of the furnace, thus creating an even more challenging situation. Front windscreens require annealing and the formation of high edge compression to minimize breakage during installation, low differential expansion stresses from the enamel, and low residual stresses elsewhere. Two pieces of glass are laminated together with a layer of polyvinyl butyral (PVB) between them. Press bend formed side window glass (side lights) and rear window glass (back lights) are typically tempered. Enamel performance is critical on automotive glass forming production lines for yields, and is as important as the final fired film properties reviewed below.

Composition

Automotive enamels are comprised of fine powders of low melting glass frit fluxes (50–85 wt%), inorganic pigments (10-40 wt%), and other additive oxides, sulfides, or metals (0-20 wt%). Chemistries of the glass frit fluxes generally are within the $PbO\text{-}B_2O_3\text{-}SiO_2$, $ZnO\text{-}B_2O_3\text{-}SiO_2$, or $Bi_2O_3\text{-}B_2O_3\text{-}SiO_2$ systems. Other oxides typically present would include TiO_2, ZrO_2, Al_2O_3, Na_2O, K_2O, Li_2O, CaO, and the like. Fluorides may also be present in the frit composition. The glass flux forms the binder which holds together the glass-ceramic enamel and will control the melting properties and durability. The glass flux can also significantly affect the anti-stick properties of the enamel. Lead based glass systems are known to have a wider firing window due to the more gradual change in viscosity as a function of temperature[7]. Durability of lead systems is also very good. However, environmental legislation is limiting the use of lead based systems[8], and potentially could affect the use of zinc based systems.

Pigments used for black color development can be from the copper chromite spinel $CuCr_2O_4$, chrome iron nickel spinel $(Ni,Fe)(Cr,Fe)_2O_4$, iron cobalt chromite spinel $(Co,Fe)(Fe,Cr)_2O_4$, with modifiers of CuO, MnO or others. Additives to the enamel compositions are included to enhance antistick and silver bleed-through properties. Additives could include: aluminum, iron, silicon, zinc, zinc sulfide, zinc borate, zinc silicate, alumina, bismuth oxide, tin oxide, bismuth silicate, zirconium silicate, refractory mineral fillers, carbides, and nitrides.

The carrying vehicle, or medium, is selected based upon the application. It is important that the vehicle provide good particle suspension, good rheological properties for screen print registration, storage stability, adhesion/green strength after printing, and burn off completely upon firing of the enamel. Typical infrared (IR) heat curing vehicle compositions can be based upon pine oils, vegetable oils, mineral oils, low molecular weight petroleum fractions, tridecyl alcohol, and other modifiers. Ultraviolet (UV) radiation cure vehicles can be comprised of polymerizable monomers and oligomers containing such functional groups as acrylates or methacrylates, and photoinitiators and polymerization inhibitors. Special oxidative cure (IS) resin systems[9] are also used. Critical to the performance of the enamel can be processing steps which control mixing, milling, and dispersion of particles.

Fired Film Physical Properties

Opacity is a property that must be below 0.1% light transmission to provide the necessary function of UV protection. Pigment load, solids load, particle size distribution, dispersion, vehicle burnout, wet film thickness, and print drying can significantly affect opacity. Specially formulated high loading mediums can improve differences between a lead frit (density $3.5 \leq \rho \leq 4.5$ g/cm^3) and a lead-free frit ($2.5 \leq \rho \leq 3.5$ g/cm^3). *Scratch and abrasion resistance*s of the enamel are also important properties that must be controlled, and can be impacted by the above considerations. *Color* of the final fired film is important for uniform appearance of the vehicle for glass made on different processes and different lines. Customer specific quantitative specifications generally require low L value black color with light and dark scale limits, and minimum variation in color space. Grey color is occasionally specified.

Adhesive bond strength is also a critical property. Lap Shear test methods are performed under a variety of environmental test exposures to ensure that the enamel will maintain a bond to the frame adhesive/primer. The cataplasma test (14 days, 100% humidity, 70-80 ^{o}C) is a widely accepted method for adhesion and hydrolytic stability testing. Enamels with high zinc content are generally degraded by water and will leach. PVB adhesion is also tested on windscreen ceramic and silver enamels. Mulitvalent metal anti-stick additives potentially lead to loss of PVB adhesion[10]. Glass-ceramic enamels must also be compatible with pyrolytic, sol-gel, CVD, sputter, or any other type coatings present. *Chemical durability* of the glass-ceramic enamel is a related and extremely important property. Poor durability could also lead to loss of adhesion. A variety of ASTM and customer specific acetic acid, citric acid, hydrochloric acid, sulfuric acid, sodium hydroxide, water, humidity, salt, solvent, and other test methods and specifications exist. In the Japanese automotive market, the ability to pass sulfuric acid durability tests is a requirement. For lead free low fire glass-ceramic enamel systems, bismuth borosilicate frits will have superior chemical durability in comparison to zinc borosilicate frits.

Glass strength in combination with the fired enamel coating is also important as manufacturers move to thinner lighter weight glass. Thermal expansion (contraction) coefficient must be well controlled. In general low melting glass fluxes should have expansion coefficients between 70 to 85 x 10^{-7} /^{o}C over the range 25 to 325 ^{o}C for most major manufacturers substrate glass. Additions of pigments, metals, and other inorganic additives will influence expansion characteristics of the glass-ceramic enamel composition. Residual stress caused by significant differences in expansion between the enamel and soda lime glass can result in a decrease in substrate strength. It is desirable to have the enamel expansion coefficient less than the automotive glass substrate for improved strength. Substrate thermal history can also be affected by the different emissivity of the black band and print free edge stresses are important. If the expansion characteristics are not well controlled, breakage can occur during tempering or annealing. In addition, the chemistry of the glass frit can ion exchange with the soda lime glass and also result in weakening of the substrate. Smaller more mobile Li+ ions can migrate and exchange with larger Na+ ions in the substrate resulting in a tensile region of stress below the enamel. These processes, in addition to phase transformations and other chemical reactions, must be well understood and controlled. An improved strength glass-ceramic enamel test result is shown in Figure 1.

Figure 1- Weibull Plot of Enamel Coated Soda-Lime-Silica Glass Substrate

Silver bleed through resistance, as it is referred to in the automotive industry, is an important property for the glass-ceramic enamels which are overprinted with conductive silver enamels. Discoloration can occur when Ag^+ ions exchange with Na^+ ions in the glass. Migration of Ag^+ can occur through the enamel and into the soda lime glass substrate during firing. The tin contact surface of float glass is highly reducing and will cause reduction of Ag^+ to Ag^o metal. Color centers formed by submicroscopic crystals of silver metal produce a visible discoloration. Particles 10 to 20 nm produce a yellow color in transmitted light, and a blue color in reflected light. Silver staining is dependent upon the thermal history, the type of printing vehicles used, and the tin count of the substrate glass. Patented reducing metal additives to the enamel and glass chemistry solutions can help control silver staining. *Silver solder adhesion* is measured by pull strength methods and must also be maintained at a high value.

Manufacturing Performance

In addition to the properties discussed, the enamel performance during the glass forming process creates perhaps the most significant challenge for glass-ceramic enamels. Production heating times can be shorter than 3 minutes from room temperature to forming temperatures between 600 to 700 ^{o}C[5,6]. Typical glass forming production heating rates are shown in Figure 2.

Figure 2- Heating Curves of Laminated Glass (LG) and Tempered Glass (TG) for Commercial Automotive Glass Forming.

Important during the first stages of this heating process is the ability of the printing medium to burn-out cleanly before the frit particles begin to sinter. A weight loss curve for a high loading IR medium with a lead free enamel is shown in Figure 3. Continued weight loss after the glass begins to sinter can result in entrapped porosity, reductions in scratch resistance, abrasion resistance, opacity, durability, solder adhesion, and poor color development. The organic medium must burn out cleanly and the glass frit particles fuse together to form a coating without interconnected porosity within the application time-temperature limits to obtain the properties discussed. Process times only continue to decrease as manufacturing production rates continue to be increased.

Figure 3- Medium Burnout in a Highloading Lead Free Enamel System

A variety of enamels have been developed over the last 10 years which have performed satisfactorily in evolving bending processes. Metal powder additions such as iron and zinc have proven to be effective at high loadings. However, metal additives are strong reducing agents which helps to reduce silver migration, but can cause additional gas evolution during the firing process and reduced binder burn-out resulting in entrapped porosity[5,10]. Refractory mineral fillers such as zirconia, alumina, and the like, other fillers such as carbides, nitrides, and metal oxide powders have produced less than satisfactory results by raising the firing temperature and decreasing color development. Early reactive type systems have shown poor durability and inability to fuse properly at low temperatures. Newly developed reactive Cerdec enamels give low melting, high chemical durability, high substrate strength, and low stick force to the pressing pad in addition to all other required properties.

Understanding and advancing the technology[5] for automotive enamel systems necessitated the development of a method to reproduce the thermal history and press bend forming operation. An Anti-stick test machine was developed to accomplish this task. A pressing pad covered with the same fibre glass or stainless steel cloth used in commercial furnaces reproduces the manufacturing process as illustrated in Figure 4. No additional coating or powder is applied to the cloth.

Figure 4- Schematic Illustration of Glass Pressing

The screen printing process is reproduced on 4"x4" pieces of automotive glass. Samples at room temperature are loaded into a preheated high convection furnace, and temperature and time are controlled to duplicate the industrial firing cycles of interest as shown in Figure 5.

Figure 5- Typical Slow and Fast Laboratory Heating Rates

Pressing pressures and contact times can be adjusted to duplicate the forming process. Typical industrial forming pressures will be in the approximate range of $1.5 < P < 2.0$ psi. The stick pressure, or force required to pull away the pad from the hot enamel is reproduced and recorded several times at each temperature and time of interest. Results of anti-stick tests performed on the soda-lime-silica substrate are shown in Figure 6. At temperatures above 690 ^{o}C, the float glass substrate with no enamel is very sticky, and enamel data above this temperature are shown as a trend line indicator.

Figure 6- Soda-Lime-Silica Glass Substrate Stick Response Curve at 2.2 psi Pressing Pressure

Tests performed at 3.2 pressing pressure for a lead based and lead free systems are shown in Figure 7. Data are shown with error bars, and presented beginning at enamel maturity, i.e. when interconnected porosity no longer exists throughout the coating. Results of peak stick release pressure as a function of pressing pressure are presented in Figure 8.

Figure 7- Lead and Lead-free Stick Response Curves at 3.2 psi Pressing Pressure

Figure 8- Lead and Lead-free Peak Stick Release Pressure as a Function of Pressing Pressure

New lead free reactive systems recently developed exhibit superior anti-stick properties. Industrial cycle time requirements impose restrictions on the kinetics. Results are presented in Figure 9 as a function of heating times for a lead free system.

Figure 9-Lead-free Reactive System Stick Response Curve at 2.2 psi Pressing Pressure as a Function of Heating Cycle Times.

Comparisons of reactive and non-reactive homogeneously melting systems can be seen in Differrential Scanning Calorimetry (DSC) curves shown in Figure 10.

Figure 10-DSC Curves for a Lead-free Reactive System and a Non-Reactive System.

Partial crystallization controls melting properties, stress development, and anti-stick properties. Surface morphology of different glass enamel systems has been shown to be different and to play an important role in the wetting and sticking phenomenon[5]. Sticking can result in enamel defects, the glass substrate becoming distorted or out-of-bend, excessive wear of the press cloth, and even complete shut down of the line if the substrate does not release from the mould. Because of short cycle times, enamel performance must be optimum.

Conclusions

Automotive glass press bend forming processes are becoming more severe. Glass-ceramic enamel anti-stick performance is critical to the performance of these deep bend processes. Other enamel properties such as opacity, durability, adhesion, scratch resistance, stress, expansion, color, silver bleed through resistance, and substrate strength are essential to the protective and aesthetic functions of the enamels. In addition, environmental legislation will continue to shape the industry. As the leader in automotive glass decoration technology, Cerdec is committed to meeting and exceeding the challenges facing our industry for fired film properties, customer manufacturing process performance, and environmental initiatives.

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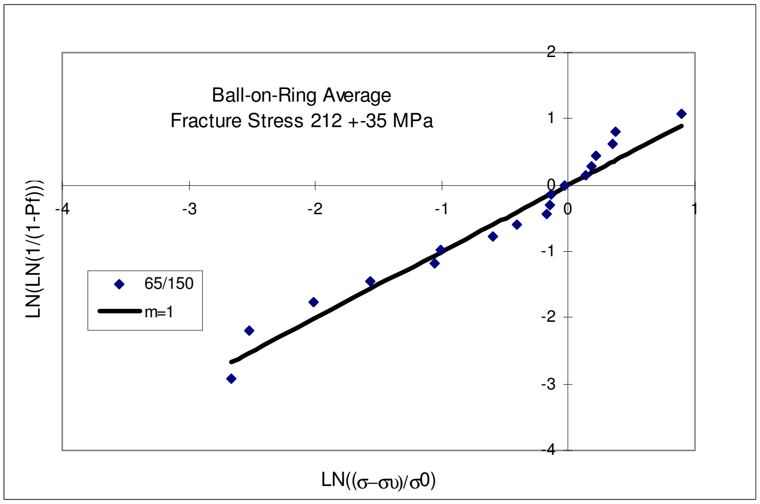
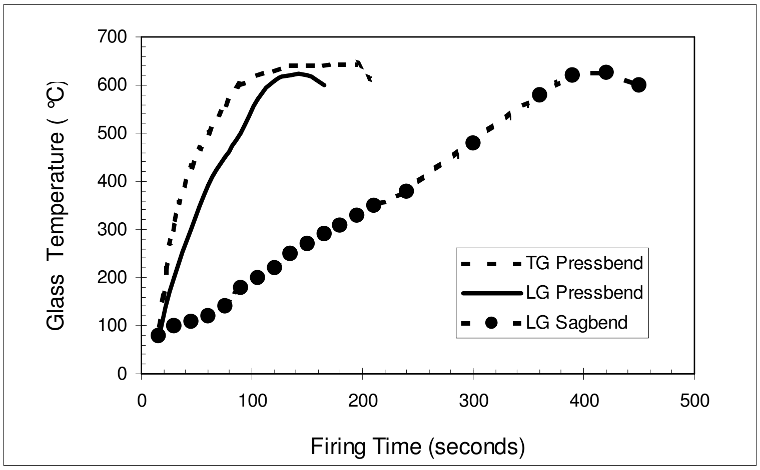


Figure 1- Weibull Plot of Enamel Coated Soda-Lime-Silica Glass Substrate



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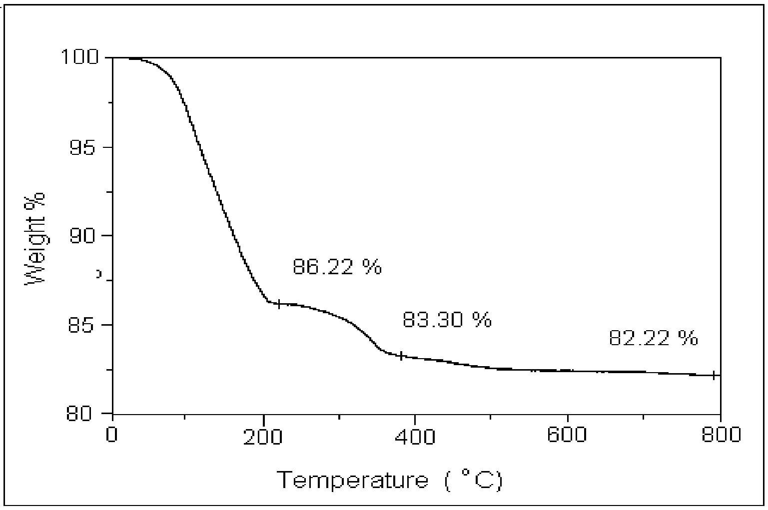
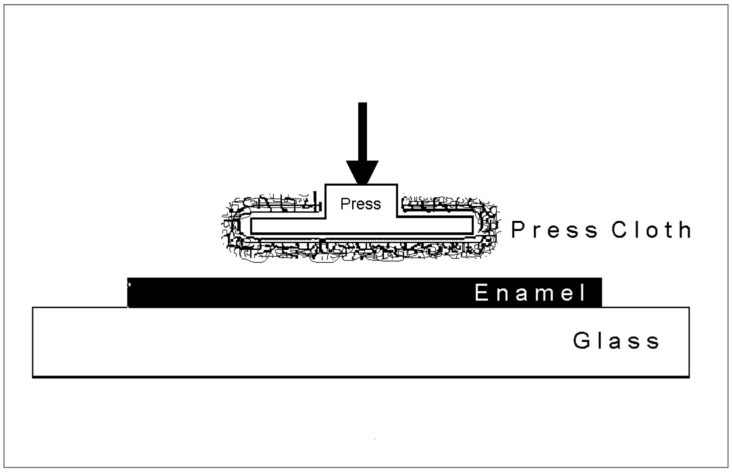


Figure 3- Medium Burnout in a High Loading Lead Free Enamel Syste



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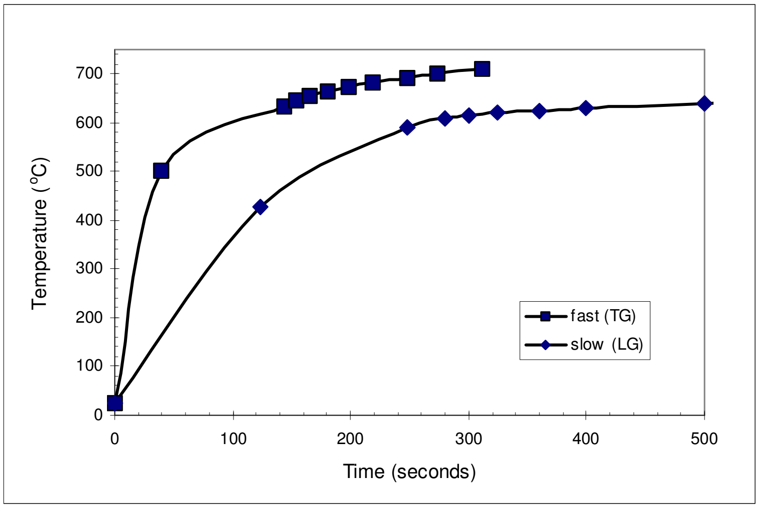

Figure 5- Typical Slow and Fast Laboratory Heating Rates

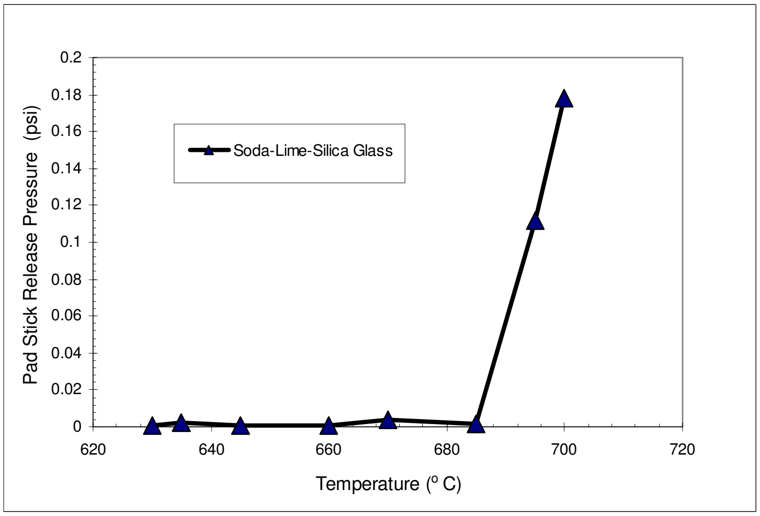

Figure 6- Soda-Lime-Silica Glass Substrate Stick Response Curve at 2.2 psi Pressing Pressure

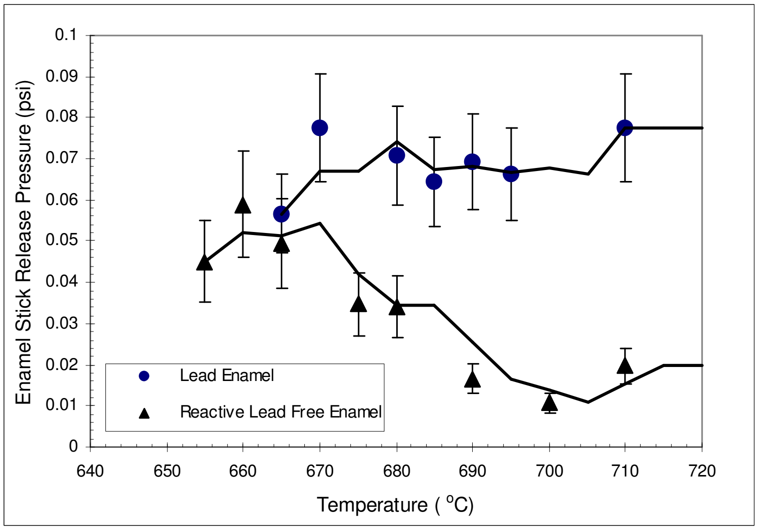

Figure 7- Lead and Lead-Free Stick Response Curves at 3.2 psi Pressing Pressure

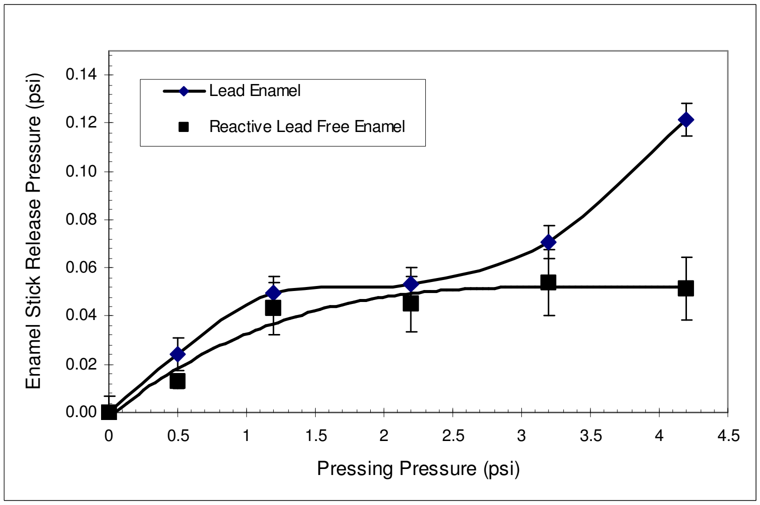

Figure 8- Lead and Lead-free Peak Stick Release Pressure as a Function of Pressing Pressure

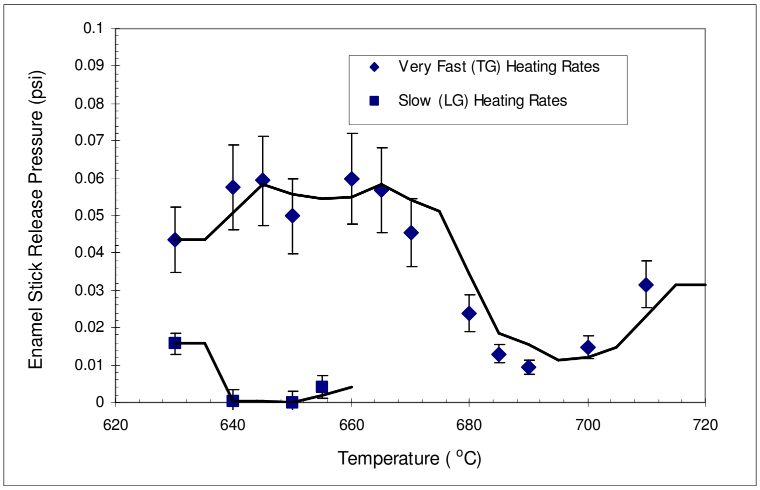

Figure 9-Lead-free Reactive System Stick Response Curve at 2.2 psi Pressing Pressure as a Function of Heating Cycle Times.

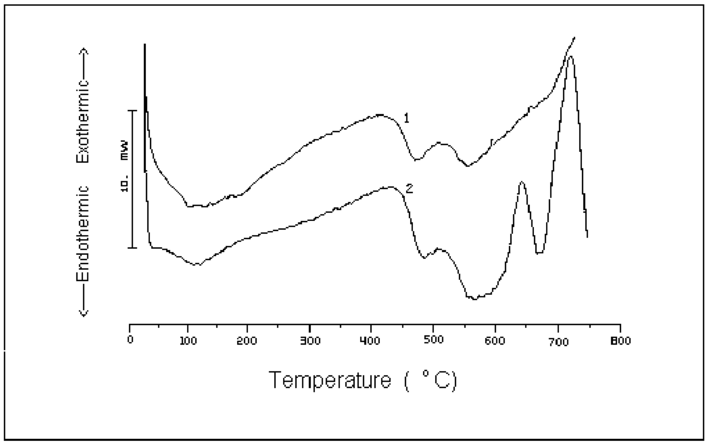

Figure 10-DSC Curves for a Lead-free Reactive System and a Non-Reactive System.