Evolution of High Performance Environmentally Friendly Automotive Glass-Ceramic Enamels

Dr. George Sakoske,	Ferro Corporation, Washington, PA USA
Mr. Barry Reinherz	Ferro Japan
Mr. Gerhard Tünker,	Ferro GmbH

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Abstract

High performance automotive glass-ceramic enamels have evolved to meet and exceed industry challenges. Ever more demanding technical specifications for regional and global requirements must be understood and qualified. Improvements in fired film physical properties include opacity, scratch and abrasion resistance, color, adhesive bond strength, chemical durability, glass substrate strength, silver bleed through resistance, and silver solder adhesion. Functional performance during manufacturing is also critical as automotive glass forming processes become faster with more severe bends. Environmental initiatives regarding heavy metals and recycling also continue to shape and challenge the industry.

Introduction

Automotive glass enamels first appeared on US car models in 1968[1]. Since then, these glass-ceramic enamels have evolved to meet and exceed today's industry high performance challenges. Currently more than 2 million tons of automobile glass is produced annually[2]. Ever more demanding technical specifications for local, regional, and global requirements are becoming necessary to achieve the needs of the fabricating processes and the performance of the final automotive glass product.

Three criteria drive the specifications of glass enamels for automotive glass. They are:

1. Customer performance requirements that include physical and chemical properties of glass enamels such as durability, as well as the aesthetic properties such as color and surface texture which can affect adhesion to molding and encapsulation polymers, paints or adhesives.

2. Government regulations for individual countries, as well as international laws, and government industry initiatives aimed at reducing energy consumption, pollution, use of hazardous chemicals, and promoting recycling.

3. Glass fabricating process requirements including properties such as ease of application, firing temperature, rates, and mold release from press forming processes[3].

Customer Performance Requirements

To make sense of and respond to today's automotive glass fabricator's requirements, as well as the direction of future requirements, requires a local, regional, and global approach. The background behind specifications for glass enamels is best understood by looking at the evolutionary process .

As an example, in the early or mid 1990's motorists in western Japan were noticing erosion of the glass enamel applied to some kinds of automotive glazing where the glass had the potential to be exposed to some degree of weathering, such as hinged side-lights. It was believed that industrial pollution was causing acidic rain, which left stains and sometimes caused erosion of glass enamels under these circumstances. The glass enamels of this time period had not been developed to withstand any exposure to the elements, and still are not intended for applications that would directly expose them to weathering. In response to this complaint, however, Japanese automobile manufacturers intent on keeping their customers completely satisfied, established various standards for acid resistance aimed at reducing the vulnerability of the glass enamel on automotive glazing exposed to acid rain.

The evolution of technical requirements for acid rain in Japan began when one major automotive manufacturer reacted by specifying the acid rain resistance with an accelerated test, which they developed to closely reproduce the effects of acid rain. The artificial acid rain is a highly corrosive mixture of chemicals which are probably floating around in our atmosphere to some extent as the result of decades of industrial discharges. Other car makers also established specifications for chemical resistance such as exposure to 0.1N H2SO4 at elevated temperature for time periods that depend on the potential degree of exposure for the part in a vehicle. Glass which is at a higher risk of exposure is required to withstand well over 100 hours immersed in H2SO4 without exhibiting visible changes to the glass enamel when viewed from surface one.

Currently, one or more of the Japanese car makers specifies "acid rain resistance" of the glass enamel applied to glazing, which could be vulnerable to exposure. This would probably have been considered a local issue, if glazing was supplied to the Japanese car makers completely from within Japan. It is a fact however, that the glazing in a Japanese automobile could be supplied by producers in any of several nearby countries, depending on the model being made and the logistics involved. As such, this specification then becomes a regional requirement.

Likewise in Europe there is an accelerated weathering Kesternich-Test, for example, which is applied to determine resistance to "acidic moisture". DIN 50018 and a similar ISO 6988 test both expose glass enamels to the effects of acidic moisture, aimed at assuring the final product can resist the effects of air pollution or acid rain to some degree.

In the United States, where acid rain is less of a problem, American based car makers are not as a rule, currently specifying resistance to "acid rain" solutions, however, there are a significant number of chemical durability specifications for resistance to: acetic acid, citric acid, hydrochloric acid, sodium hydroxide, various solvents, unleaded gasoline, water, and even windshield wash solutions. As an example of these accelerated durability tests one can refer to ASTM C724. On the other hand, Japanese transplants now manufacturing automotive glass and automobiles in the Americas have to some extent adopted the same specifications as their Asian counterparts. As a result, what started as a local requirement in western Japan, and became a regional requirement for vehicles and parts imported to Japan, has evolved into a global requirement.

Color is another example of a specification that has evolved from local to regional and now global requirements. Almost all glass enamels applied to automotive glazing are black. However, black color space in the USA, EU, and Asia Pacific regions are often specified differently. One US car maker requires black to have a CIE *L value of less than 26, while fabricators in Japan and EU typically require lower *L values of 21 – 22. Similarly blue and red color value ranges can be specified. In some cases, regardless of geography, color is often just specified as "black" the implied meaning that blacker or lower *L value is better.

Opacity is a measurement of the hiding power of the glass enamel and is important for aesthetic as well as functional reasons. The black enamel, in addition to hiding the frame structure and mechanical parts beneath the glazing, is necessary to prevent the transmission of solar light energy that can degrade the strength of adhesives used to hold the glass in place. A securely bonded glass panel is necessary to provide structural strength to the vehicle frame assembly. Individual glass and car manufactures can have opacity specifications for visible light (380 to 780 nm), ultraviolet light (300 to 400 nm), and even total solar energy (300 to 2500 nm). Quality requirements for adhesive bonding are generally in the range of less than 0.1% for ultraviolet and visible light transmittance.

Because the specifications for each car maker and glass fabricator are almost always different, and details of their procedures are often required to be kept confidential, it is not surprising that a plethora of engineering standards and specifications exist, all to meet a commonly perceived need. Also, as automobile designs improve and reduce costs, so may additional performance requirements for automobile glass, enamels, and adhesives. For example, if automotive designers would like to eliminate the encapsulation seal strip, this would expose the glass-enamel-adhesive-paint-auto frame bonds directly to the elements as illustrated in Figure 1. Such a design change would require additional chemical durability for these components. Additional customer requirements based on design considerations and other functional glass coating present could include edge-to-edge printing and enamels for improved glass substrate mechanical strength.

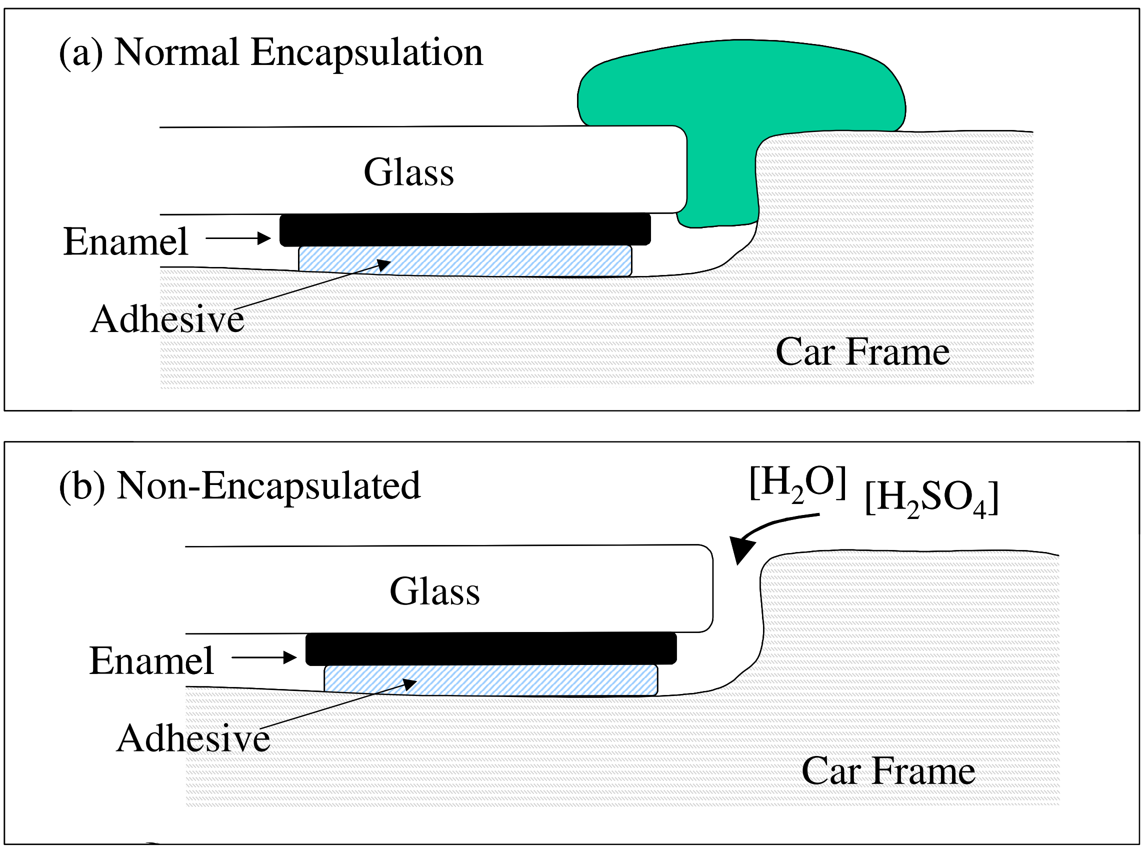

Figure 1. Encapsulated and Non-Encapsulated Automobile Glass Designs.

National or Regional Governmental Requirements

In some cases though, specifications are evolved from national or regional governmental or quasi-governmental bodies. These specifications concern issues such as vehicle crash strength and other safety related properties such as optical distortion. Glass enamels can influence these kinds of properties depending on the glazing design, and so must be specified as part of the whole.

As an example, almost all countries have some kind of requirement concerning the strength of bonding the glass to the frame of the vehicle in which it is installed. Additional accelerated weathering tests of the glass-ceramic enamel for adhesion to urethane are required to qualify in a variety of time, temperature, humidity, and light energy cycles. Because of the importance of the adhesive-enamel-glass bonding to the structural integrity of the vehicle, these types of "accelerated" tests can take up to two years to qualify and are extremely thorough and costly to complete. In Japan, testing is required in a weathering chamber with the capacity to expose samples to intense light from a carbon arc lamp, while undergoing extreme changes in temperature and humidity. In the United States and the EU a similar weatherability test is specified using a Xenon arc lamp, and in the EU a "Cataplasma Test" which uses a similar intense light source and temperature humidity cycles. Each major automobile manufacture has different adhesion testing specifications, for example General Motors GM3652, Daimler-Chrysler MS-CD927, Ford WSB-M2G316B and WSS-M28P1-B1. Any enamel accepted for use on a glass panel installed in automobiles by a given manufacturer must pass these engineering tests as required, for example, by the Production Part Approval Process[4]. In addition, automobile glass fabricators may have internal test specifications for glass-ceramic enamels. The main purpose of the weathering tests are to assure long term safety of the glazing units.

Other local and regional government legislation has shaped the evolution of the glass enamel industry. For example, automobile manufacturers in the USA were the first to request and then require lead-free compositions. This was initiated by the local costs of disposing glass fabricating plant waste streams. Currently in North America, industrial solid waste must meet Toxicity Characteristic Leaching Procedure (TCLP) specifications of less than 5 parts per million of lead, cadmium, and hexavalent chrome as tested[5] by Method 1311. Glass-ceramic enamels as well as automobile glass chemistries and raw materials are carefully monitored to meet these regulations.

In addition to managing industrial waste streams, different countries and geographic regions are initiating environmental legislation requiring recycling of end-of life vehicles (ELV). In the EU, the legislative basis for recycling of cars is European Union Directive 2000/53/EC. This Directive sets measures aimed at the prevention of waste from vehicles at the reuse, recycling, and other forms of recovery of ELV and their components so as to reduce the disposal of waste. In 1990, Germans disposed of approximately two million cars. Although 75 percent of the scrapped components were reused, more than 400,000 metric tons per year of the remaining plastics, rubber and glass are still placed in the waste stream. In the US, the average retirement rate from 1990 to 1996 was 11 million vehicles per year[6]. The average ELV composition contained about 86 lbs of glass, or about 3% of the total weight. Currently about 75% of a used car is recycled in EU and the share must be increased to 85% in year 2006 and 95% in 2015. Similar goals have been set in Japan and North America.

The definition of "recycling" means: the reprocessing in a production process of waste materials for the original purpose or for other purposes. Another goal is to increase overall energy efficiency with the re-use of previously melted glass cullet. Recycling of car glazing by re-melting back into clear automotive float glass may be too expensive. A clear float glass melting process needs very clean raw materials. Technology to remove all the undesired parts like rubbers, glues, and solder terminals from the glass before melting may not be available for reasonable costs compared to disposal depending on local issues. In addition, chromophores such as nickel and cobalt which can be used to make colored vehicle privacy glasses and can be used in enamels to give them black color and high opacity are not readily neutralized in the soda-lime silica glass re-melt to obtain an optically transparent glass. Recycling for use in the container, fiber glass, or pavement industries may prove to be more economical.

Key barriers to recovery and recycling of automotive glass are: collection, transportation, separation, and other technical as well as market issues. A value of US $50 – 70 per ton is regarded in the western economies as market price for clean glass cullet to maintain viable competition against primary raw materials[7]. Disposal costs, and government legislation, including cullet tariffs will ultimately drive the demand to recycle automotive glass. How to best recycle seems to be left to the industry segments and individual companies.

Glass Fabricating Process Requirements

Equally important properties of automotive glass-ceramic enamels are the ability to integrate cost effectively into automotive glass forming processes[8]. Glass-ceramic enamels are screen printed on pre-cut flat sheets of soda-lime-silica float glass, dried, and sintered during the forming and heat strengthening of the glass. The enamel must be designed around the thermal history requirements of a given size, thickness, shape of automobile glass, and process capabilities of a given furnace. These automotive glass forming processes have evolved significantly over the past 15 years to improve efficiencies and to meet automobile design trends requiring more glass surface area with more complex shapes for better aerodynamics, styling, and improved visibility.

For over 50 years industrial glass forming operations have used gravity-sag processes. Gravity-sag shaping uses steel jigs that support only the glass sheet edges as it is slowly passed through a furnace so that bending occurs when the glass sheet sags under its own weight into the shape of the jig. Several disadvantages of such processing include slow rates, inability to form severe bends, and the fact that many different jigs with exactly the same shape are required. Weight assisted sag forming operations can be used to improve bend shape, however, press bend or pressure forming technology has resulted in an evolutionary change within the automotive glass manufacturing industry. One part at a time is rapidly press formed by a single mould. Advantages 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 contact surface is covered with a knitted cloth made of stainless steel or glass fibers.

During the pressing operation, the enamel is in direct contact with the press mould cloth, and depending upon the furnace type, can be in the hottest temperature zone. Enamel anti-stick performance during bending is critical for glass yields. Production heating times can be shorter than 3 minutes from room temperature to forming temperatures between 600 to 700 ^{o}C for a tempering operation, and as long as 20 minutes for a sag-bend operation. Typical industrial press-bend forming pressures will be in the approximate range of $1.5 < P < 2.0$ psi or higher. Partial crystallization of the enamel controls melting properties, stress development, and anti-stick properties. Sticking can result in enamel defects, distortion of the glass, excessive wear of the press cloth, and even complete shut down of the line if the substrate does not release from the mould. Industrial automotive glass process times continue to decrease for increased productivities placing even more demands on the enamel and anti-stick properties. High performance high durability lead free bismuth silicate based enamel systems exhibit rapid kinetics of crystallization as shown in Figure 2 to meet these glass fabrication requirements. Antistick behavior of a high performance lead free enamel system is shown in Figure 3 as a function of temperature and pressing pressure. At temperatures above 690 ^{o}C, the float glass substrate with no enamel begins to soften and is very sticky, completely off the scale of the graph[3]. Enamel data above 690 ^{o}C is shown only as a trend line indicator. Enamel thermal energy transport properties are also important to glass fabricating process requirements.

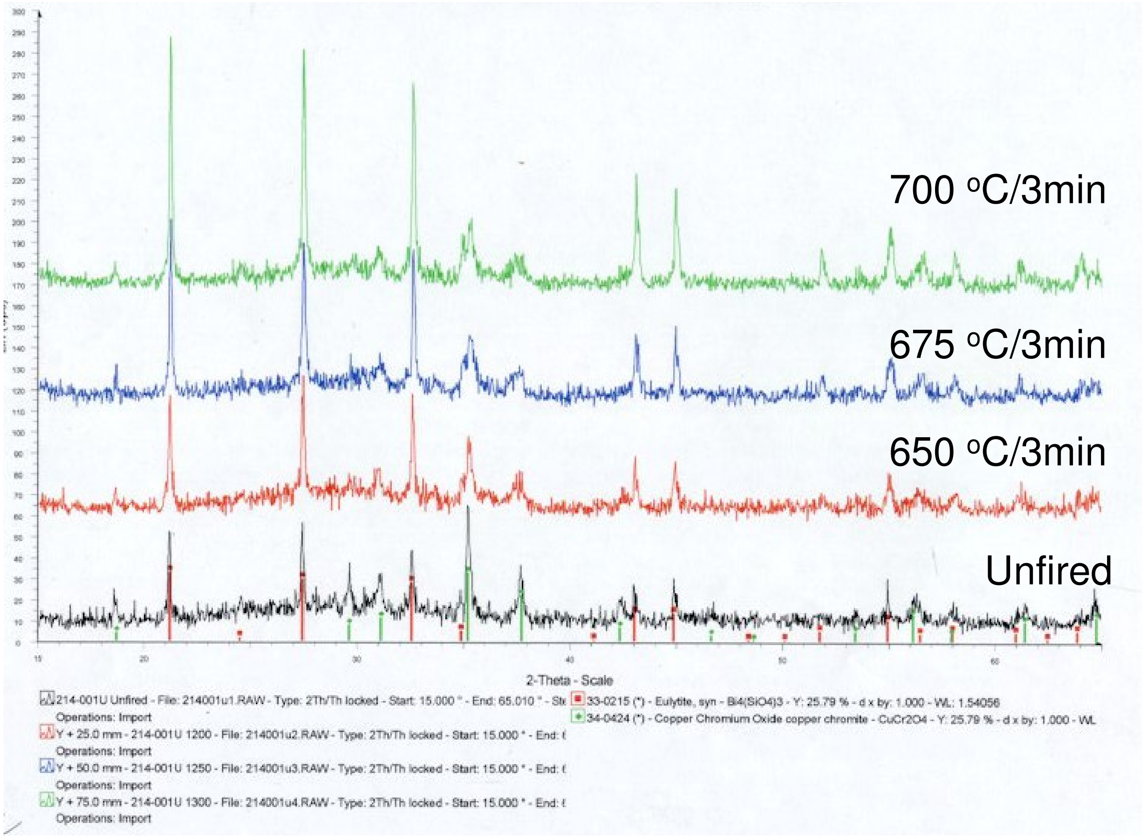

Figure 2. Crystallization of High Performance Lead Free Bismuth Silicate Based Enamel Systems

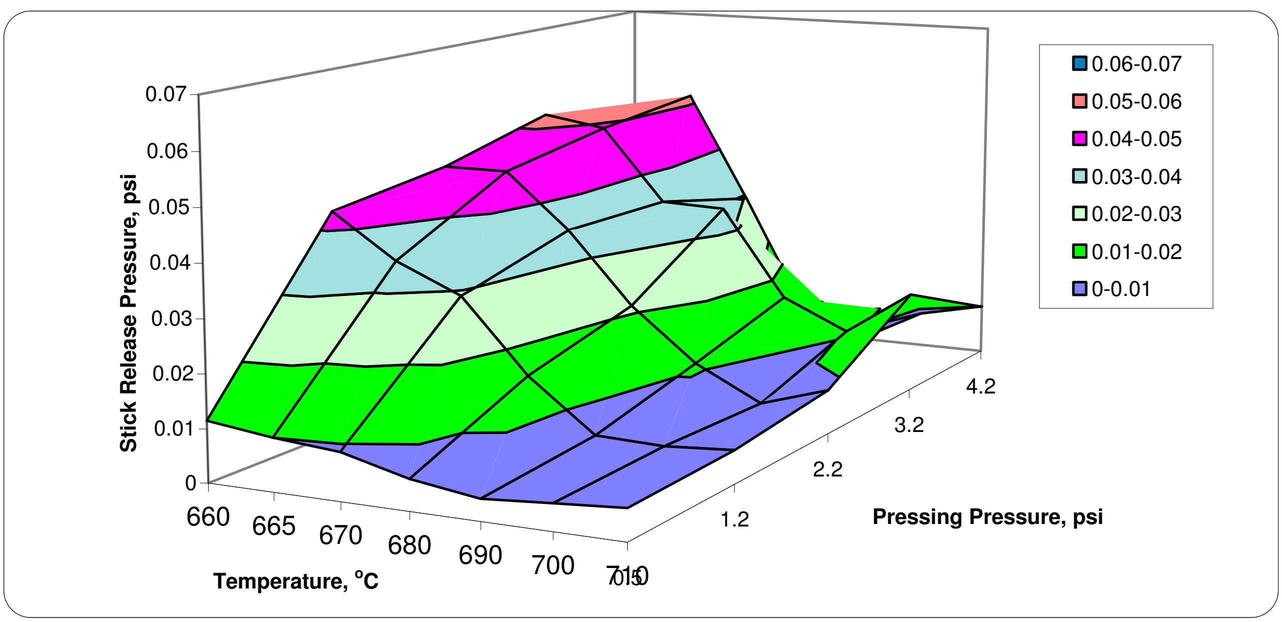

Figure 3. Anti-stick Pressure Forming Properties of a High Performance Lead Free Enamel

Important during the initial stages of heating processes is the ability of the printing medium to burn-out cleanly before the frit particles begin to sinter. Continued weight loss after the glass begins to sinter can result in entrapped porosity, reductions in scratch 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. Ease and consistency of application are also important glass fabrication process requirements that must meet specific properties such as: viscosity as a function of shear rate and temperature, stability, green strength, odor control, and clean-up to name a few.

The automotive industry is continuing innovations in some laminated glass product areas with surface 2 printing and single fire inside press windshield (IPW) processes. The glass enamel is printed on the second surface, and placed face up as in a tempering operation. However, to ensure the best possible shape match, the second piece of glass is placed on top of that. The process requirement for the enamel in this single fire process is to be able to burn-out printing vehicle completely while sandwiched between the two pieces of glass, and then sinter during the simultaneous press forming of the two matched pieces of glass without causing them to stick together. Front windscreens require annealing with the formation of high edge compression to minimize breakage during installation, low differential expansion stresses from the enamel, and low residual stresses elsewhere. The two pieces of glass are then laminated together with a layer of polyvinyl butyral (PVB) between them.

For rear window glass the dried enamel is typically overprinted with conductive silver enamel heater bands and bus bars before sintering. Thick film conductive coatings are also increasingly being used for global positioning, radio, TV, and other communication antennas, even on side and front automotive windows. Silver bleed through resistance or the ability of the enamel to resist silver staining where the enamels are overprinted with conductive silver enamels is an important property. Silver staining is dependent upon the forming process thermal history, the type of printing vehicles used, and the tin count of the substrate glass.

Conclusions

Ferro as a global supplier of products to the automotive glass industry has recognized that everyone in the world does need the same product, but all expect the highest level of quality. This is achieved by meeting or exceeding the automobile manufacturer's enamel product performance specifications and by meeting or exceeding the automobile glass fabricator's processing and enamel product requirements on local, regional, and global levels. If "globalization" continues as it has in recent years, and if glazing for automobiles continues evolution with design and fabrication innovations, it can be expected that the driving forces responsible for establishing the standards we rely on will give us a never ending supply of new targets and specifications to meet the needs of the automotive industry. As the leader in automotive glass-ceramic enamel technology, Ferro is committed to meeting and exceeding the challenges facing our industry for fired film properties, manufacturing process performance, and environmental initiatives.

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