Value-Added Flat-Glass Products for the Building, Transportation Markets, Part 1

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This two-part series of articles addresses the concept of value-added products from the viewpoint of total value to the customer. The flat-glass customers in the building and transportation industries consist of the original equipment manufacturers (OEMs) of architectural windows, the automotive and other transportation industries, and the independent glass fabricators who are suppliers to the OEM and replacement markets.

The total-value viewpoint consists of an optimum combination of three main product qualities:

- Technically sound products that the consumer considers useful to sustain market demand;
- Low-cost products that allow competitive advantage for the glass supplier and the customer;
- Products that minimize downstream process or maintenance complexity, which allows the customers to serve their markets efficiently.

These attributes require technical innovation and discipline; a development team has to carefully balance all three qualities to produce a successful product. Because of serious competition from producers in low-labor-cost economies, delivering total value to the customer has taken additional urgency for flat-glass manufacturers and their employees in the Western industrialized countries.

Heat transfer through glass occurs by radiation, conduction and convection. Through use of insulated glass units with a low-conductivity gas fill between two or three panes of glass, conductive and convective heat loss can be significantly decreased. Radiative heat loss, which occurs at the infrared (IR) radiation range corresponding to room temperature, e.g., 21°C, can be decreased with low-emissivity coated-glass products that effectively reflect this radiation.

The relative spectral distribution of sunlight over the solar range is 300–2500 nm (Fig. 1).¹ The ultraviolet (UV) region makes up ~3% of the total solar energy and is responsible for causing sunburn and fabric fading. The visible region contains ~44% of the total solar energy and is responsible for color and brightness. The IR region contributes ~53% of

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the total solar energy and is mainly felt as heat.

To decrease solar heat load, it is desirable to filter as much of the IR radiation as possible. However, in dealing with the visible portion of solar radiation, we must be careful to maintain minimum acceptable visibility and to produce aesthetically desirable glass colors. For example, for motor vehicle safety, the minimum transmittances for visible light (LTA) in windshields in the United States and Europe are 70 and 75%, respectively. On the other hand, comfort and privacy preferences stipulate the use of dark glass in the rear sidelights and backlight of most minivans and SUVs.

An increasing preference for natural lighting in buildings has increased the use of high-visible-light transmittance glass, while architectural preferences for color in designing building facades continues to maintain a market for reflective or tinted flat-glass products at a significant level. In both cases, energy efficiency is important in product selection. In principle, an appropriate switchable transparency can address most of the aforementioned, at times contradictory, needs by controlling the level of light transmission in the visible or IR regions of the spectrum.

Despite the R & D on electro-chromic or other switchable technologies, an appropriate commercial solution is yet to be developed. Work in this area continues, and we refer the reader to existing reviews in the literature.

During the past several years, the development of self-cleaning glass products has opened a new category in the flat-glass market. These products, along with glass with hydrophobic surface quality, provide opportunities for the customer to offer additional value through convenience and safety in the building and transportation markets.

**Glassmelting/Glassforming**

The entire glassmelting and glassforming process can be easily depicted (Fig. 2). The principles of glassmelting technology for flat-glass manufacturing are described in detail elsewhere. The primary source of energy for melting glass is top heating by natural-gas or oil combustion with air as the oxidizing gas.

A major recent development in tank design has resulted from the introduction of oxy-fuel technology, where pure oxygen has replaced air in the combustion space. This technology has improved the combustion and energy efficiency of the furnace and has simplified tank construction by eliminating the need for regenerator superstructures, where, in the conventional design, air intake is preheated to recover some of the energy lost with the combustion exhaust.

There are several issues of significance that impact the melting of value-added products. Because heat is primarily delivered to the top of the glass batch and glassmelt, the spectral properties of the final product (e.g., its absorbance of IR and, to a lesser extent, visible light) have a corresponding impact on the heat-transfer efficiency through the
depth of the glassmelt and, thus, affect the convective flows and the refining of glass.

Therefore, generally speaking, melting a “darker” glass becomes more challenging. This, in turn, influences the cost of homogenizing the glass and refining it, because these glasses have to meet strict quality requirements.

Moreover, the chemistry of the product influences the chemistry of the glass batch, its melting rate and the concentration of refining gases, e.g., SO3, in the melt. All of these parameters are critical to the design of a cost-effective value-added glass product.

A final important factor to consider is the suitability of the melter for product change. A typical melter tank volume can contain up to 2000 tons of liquid glass with a throughput of several hundred tons per day. If the tank is viewed as a perfect mixing reactor, taking the range of volume to throughput ratios demonstrates that the time constant for a major product change (i.e., between products that have significantly different compositions) can be long—days or weeks in extreme cases—and costly.

Therefore, and to maintain relative consistency in the physical properties of glass supplied by various manufacturers, a basic soda-lime-silica composition has been maintained for use in the automotive and architectural markets. (One significant exception consists of several relatively small-volume ion-exchange compositions for the aircraft and projectile-resistant glass applications.)

Depending on customer specifications, the comparatively minor modifications in composition for spectrally selective glasses may result in long product changes; this requires careful attention to product change methodology and sequencing.

The float-glass forming process was developed >40 years ago.5 In this process, liquid glass is delivered to a pool of molten tin bath at ~1100°C, where it forms an equilibrium thickness defined by the respective surface energies of the glass melt and molten tin, and the interfacial energy between the two liquid phases. Subsequently, the melt is gradually cooled and its thickness is adjusted under externally applied mechanical forces to form a glass ribbon that exits the forming chamber at ~600°C.

Care must be taken to prevent the formation of excessive surface and bulk undulations, which cause optical distortion, in the ribbon as it is mechanically stressed while cooling through the glass transition temperature. This is particularly critical for thinner, often more valuable, flat-glass articles.

In addition, the forming chamber environment is generally maintained under an inert or reducing atmosphere of the molten tin. Upon exiting the forming chamber, mechanical stress in the formed ribbon is significantly decreased by slow cooling in a contiguous annealing lehr. After it exits the lehr, the ribbon is sufficiently stress-free, and can be cut and packed for shipping to customers.

**On-Line Coating Deposition**

The high temperature of the ribbon in the forming chamber and in the annealing lehr and the controlled atmosphere of the forming chamber provide intriguing possibilities for adding value to the surface of float glass. Some of these opportunities already have been realized.

Inside the forming chamber, several float-glass manufacturers have utilized thermally assisted chemical vapor deposition (CVD) methods to deposit thin films on the continuous ribbon. For example, one category of low-emissivity products, which is discussed later, is deposited using CVD. In this atmospheric pressure CVD process, usually an organometallic compound vapor flows over and in contact with the glass ribbon. The vapor is adsorbed and reacts on the glass surface to form an inorganic thin film, such as an oxide or a nitride.

To prevent contamination of the chamber atmosphere, a robust CVD reactor has to be well-isolated from the rest of the forming chamber. The reactor must be able to deposit the coating fast enough to be compatible with the ribbon speed, e.g., 10 m/min, and to give sufficient thickness uniformity across the glass ribbon, e.g., >4 m, to yield uniform spectral performance, e.g., color or emissivity.

External to the forming chamber, powder or liquid pyrolysis techniques also have been utilized as alternative methods of on-line thin-film deposition. A particular example of this technique is the use of organometallic particles suspended in an aqueous medium in a spray pyrolysis coater installed just outside the forming bath.
This technique is utilized to deposit a cobalt chromium iron oxide spinel onto the glass surface to provide a highly visible-light reflective coating on various tinted-glass substrates, used for design and energy efficiency purposes by architects. In both purposes, the relatively rapid temperature changes along the length of the ribbon provide opportunity for selecting the optimum temperature for the deposition without additional heating hardware, and relative to an off-line coater, the limitation of a maximum coater length along the same dimension. Another process point to consider is that yield losses because of the glassmaking or coating processes have an additive influence on the overall yield for online coated products.

**Off-Line Coating Deposition**

An alternative commercial coating process is based on physical vapor deposition (PVD), particularly using magnetron sputtering. In contrast with the processes described earlier, this is currently an off-line, but continuous process, where washed cut-size pieces of glass up to 3 m wide are continually cycled in and out of the coater through its entry and exit load locks. The coater consists of a multichamber vacuum system, where each chamber usually contains up to three sputter deposition targets.

The number of chambers and targets depends on the coating design, i.e., the number of individual layers and the materials used in a coating stack as well as the production cycle time. Direct-current (dc) magnetron sputtering, in the reactive mode for compound materials, generally has been used for industrial-scale large-area coating deposition. Recent developments in alternating current (ac) power supply technology, plasma monitoring with feedback systems and new target designs provide for increased deposition rates of insulating metal compounds, decreased coating defect density and improved thickness uniformity across the width of the coating.

These advances can, in turn, result in cycle time and yield improvements. Off-line deposition allows more flexibility in the coating design, choice of materials and production scheduling than on-line processes. On the other hand, coating hardness and chemical durability as well as substrate issues—surface condition of packed and stored glass—require more attention than the on-line processes, where the coating is deposited on a pristine glass surface at a high temperature.

**Flat-Glass Compositions**

There are several examples of high-performance, value-added glass compositions. For comparison, the solar performance properties, spectral transmission curves, chemical compositions and glass redox ratios of these new float-glass products need to be compared with previously made glass products.

Until the 1990s, a flat-glass product with a light-green color and moderate solar performance had been one of the products of choice for automotive glazing in North America for the previous 30 years. This glass was originally developed when automotive glazing was much thicker, ~6.5 mm. Thickness partially compensated for the moderate performance of this product.

Over the past decade, as glass products have become thinner, (4.0 mm or less) to decrease weight and improve gas efficiency, the solar performance of green glass has been improved to decrease the thermal heat load on the vehicle air-conditioning system and to enhance passenger comfort.

This improvement has been achieved primarily by increasing the total iron oxide content, which also brings the LTA much closer to the lower limit allowed by governmental regulations. At the same time, this increase in iron oxide increases the complexity of commercial production of solar performance glasses on conventional glassmelting furnaces. With improvements to the flat-glass melting process over the past decade, the range limits for the solar performance of new value-added flat-glass products have been significantly expanded.

The iron oxide content is critical to
producing value-added glass products because Fe$^{3+}$ and Fe$^{2+}$ contribute to UV and IR absorption, respectively (Fig. 3). Through proper control of the total iron oxide content and the glass redox ratio, glass color can be changed from yellow (when most of the iron oxide is present as Fe$^{3+}$) to blue (when most of the iron oxide is present as Fe$^{2+}$). Typical float glass that is produced on a conventional melting furnace has an iron redox ratio of ~0.25–0.30 (FeO:Fe$_2$O$_3$ ratio, in weight percent) and, therefore, has its familiar greenish edge color.

Other colorants, including transition-metal oxides (such as CoO, TiO$_2$, NiO or Cr$_2$O$_3$) as well as selenium (which often is used to make bronze and gray colors) and rare-earth oxides (such as CeO$_2$ to provide-added UV absorption, if necessary) are often used to make colored float-glass products. Because of their strong coloring power and absorption in the visible region, these colorants are typically present in lesser amounts than iron oxide. Of course, in high-transmittance glasses, all colorants need to be avoided.

**PROCESS ADVANCEMENTS**

Certain value-added glass products are now routinely made on conventional melting furnaces at throughput levels of 300–700 ton/d. Several process-related advancements have been achieved: the ability to adjust iron redox ratios for enhanced product attributes; lower environmental emissions for volatile glass colorants; shorter product transition times; increased production flexibility; and ability to supply lower-volume float-glass products for niche markets (shorter production runs have become economical for high-value-added products).

Product applications include photovoltaic glass, standard vision and privacy glass, and high-performance vision glass for architectural and transportation markets.

A typical transmission curve for a high-redox soda–lime–silica glass has been plotted (Fig. 4). The curve shows the familiar shape due to the addition of iron oxide to provide solar performance. However, in this case, glass redox can be viewed as an additional colorant. During commercial production, the shape of the curve is closely controlled by maintaining a constant total iron oxide level and by monitoring the glass redox ratio among the ferrous and ferric valence states.

The transmission curve for the more widely used solar-absorbing green color discussed above that has a total solar energy transmittance (TSET) of ~45% with iron redox ratios of ~0.25–0.30 also has been plotted (Fig. 4). Total iron oxide contents usually range from ~0.70 to 0.90%, depending on the actual glass thickness.

By increasing the iron redox ratio with a simultaneous decrease in the total iron oxide content, the TSET values can be further decreased to the 41–42% range while maintaining the visible transmittance requirements. This shift in redox ratio also results in a differentiating blue tint.

New glassmelting process improvements have been developed that include the use of novel heat-transfer schemes to adequately control the melting and refining processes. These improvements successfully produce a glass that meets acceptable float-glass quality requirements.

When the iron redox ratio is further increased, amber coloration occurs at a ~0.6 redox ratio or higher because of the formation of iron polysulfide coloring centers, which need to be avoided for most flat-glass applications.

This high-redox ratio blue glass has the highest IR absorption of any commercially produced float-glass product that is currently used in vision glass applications in automobiles, which is important, because ~50% of the solar energy that reaches earth is in the IR region. The resulting highest commercially available LTA/TSET performance ratio at ~1.70 is comparable with the level of performance achieved with coated automotive glass products, but without the added coating process costs.

This glass also shows a maximum in visible-light transmittance to solar heat gain ratio (LSG). The higher the LSG ratio, the better the glazing is at decreasing unwanted solar heat gain and maximizing desirable natural lighting for architectural applications. The DOE specifies glasses with a LSG ratio of 1.25 or better as “spectrally selective.” Currently,
architects frequently specify the use of spectrally selective glass products to decrease energy use in commercial buildings.

In addition to these vision products, several other value-added glasses have been commercially produced using conventional glassmelting processes during the past 10 years. These glasses, which include privacy glass products of various IR and visible transmittance levels, are currently used in automotive sunroofs, sidelights and backlights.

Besides high-iron-oxide glasses, the float-glass melting process also has been used to produce colorless glasses at the other extreme, namely with low-total-iron-oxide levels of ~0.01% or less. These products are needed when high transmittance or true color rendition is required, such as for furniture, display cases, appliances, photocopiers, solar collectors, photovoltaic substrates, aircraft windows, and for artwork protection.

When high-purity raw materials are used, commercial float glasses can be produced in thicknesses ranging from 3 to 20 mm. Once again, either oxidizing or reducing the iron oxide tramp impurities can achieve a wide range of iron redox ratios to obtain the desired glass properties and edge color required for a certain application. Here, a high-iron-redox ratio can produce an edge color with a slightly blue tint in a highly transparent glass, while, at a low-redox ratio (e.g., by adding CeO2 to further oxidize the Fe2+ to Fe3+), an even higher glass transmittance but with a slightly yellow edge color is manufactured.

The ability to accurately control the glass redox ratio and the glass colorant levels has led to the production of a variety of new value-added float-glass products with a wide range of aesthetics to meet the market demands for float glass.

As the ongoing development of new float-glass products continues at an even more rapid pace, improvements in the flexibility of the glass-melting process likely will provide even greater benefits in the future.

**Editor’s Note**
The second part of this two-part series will appear in the April 2005 issue of the *Bulletin*. It will include a discussion of flat-glass products, including a new self-cleaning glass.

**References**