The Assumptions for Creating Color

by Tom Wilson of Northstar Glassworks

In general, the making of glass is very structured, defined and logical. This article will provide an over view of our thought process, with some detail for those interested.

At Northstar Glass, we operate under a set of assumptions concerning the properties of glass, which then influence the approach taken in the manufacturing process.These properties are either related to the physical characteristics or the chemical characteristics. Typically, glass is sold by the physical properties. As the manufacturer we are concerned with the chemical properties. These are used in conjunction with specific processes to produce a certain range of physical properties.

Viscosity is a fundamental property for the manufacture and processing of glass. Viscosity is simply the resistance of a substance to sheer forces and hence to flow. Melting, conditioning, forming, working, and annealing occur at specific viscosities independent of glass composition. Many physical properties are defined by viscosity as well. These include the working, softening, annealing, and strain points.

Physical properties include:

-Density (mass per unit volume - g/cm^3)
-Thermal Expansion (fractional change in the length of a piece for a 1 degree Celsius change in temperature)
-Working Point (viscosity at which glass is soft enough to be worked and formed ~ 10^4 poise)
-Liquidus Point (viscosity at which glass begins to enter the crystalline phase or devitrify ~ 10^5 poise for 33 expansion)
-Softening Point (viscosity at which glass readily deforms under it's own weight ~ $10^{7.65}$ poise)
-Annealing Point (viscosity at which residual stress is released after several minutes ~ 10^{13} poise)
-Strain Point (viscosity at which residual stress is released after several hours ~ $10^{14.5}$ poise)

Chemical Properties include:

-Relative oxide percentages making up the glass (master batch, operating batch, and glass formula)
-Oxidation State (generally expressed as the ratio (Beta Ratio) of iron in two different valent states - Fe^{+3} / Fe^{+2})
-Transmission (radiant heat transfer)

There are number of different variables that must be taken into consideration during the development of a new color or the re-formulation process of an existing color. These include the clear glass that we start our process with (the base glass), the coloring chemicals (oxides) to be used, the processing steps, and the state of the end product (color shade, workability, repeatability melt to melt, compatibility, etc.). How these variables are manipulated is driven largely by the properties of the base glass and the different oxides employed.

We assume that the density, working point, liquidus, and softening point are not significantly affected by the introduction of coloring oxides. We assume the COE, transmission, strain and anneal points, and the oxidation state, are affected by the coloring oxides. In most cases, the impact is small, but there are those colors where the difference is large enough to potentially cause compatibility issues.

Compatibility involves more than just the COE. Equally important are the strain and anneal points, the viscosity curve (a graphical relationship between viscosity and temperature), and the radiant heat transfer of a given color. Two colors can have similar COE's but different annealing points (and/or strain points). This could lead to a situation where one color of a piece is properly annealed and another is not. If the slopes of the viscosity curves are different for two colors, the rate at which a piece transitions through the annealing "zone" can be different (this is not viewed as being a predominate situation). The radiant heat transfer aspect deals with the rate at which a given color accepts or radiates heat during working and/or the cooling portion of an annealing schedule. All of these situations can introduce stress points and may result in a cracking problem. Utilizing a controlled annealing cycle including a soak period around the strain point is essential not only for increasingly complex pieces geometrically, but also for the color scheme employed.

Oxidation/reduction relates to the development of the proper valent state of a coloring oxide during the melting process. Valence describes the combining power or total number of bonds an atom can form and the resulting electron configuration of the molecule. Many of the coloring oxides can form multiple states of valence. Depending on the oxide, some valent states can be colorless and others result in different colors. Oxidation state is a critical variable for melting color. This includes the requirements of certain batch formulas, as well as the impact of variation in the base glass. Clear glass can have a varying oxidation state from one manufacturer to another. Additionally, glass from the same company can vary from lot to lot. All of this can affect certain colors whether during re-melting or flameworking.

Color in glass is the result of either the transmittance and/or the reflection of light. Coloring oxides absorb different wavelengths of “white” light in the visible spectrum. Those wavelengths not absorbed are responsible for the perception of color. In certain colors, as crystals grow in the glass during striking, perceived color as the result of reflected light becomes more prominent. In general, crystal size is not necessarily responsible for color. The continuity (and/or discontinuity) of the metallic crystals in the glass is responsible for the different light absorption characteristics. An example would be the livering in the striking ruby colors and is due to a larger amount of reflected light due to increased crystal size.

All coloring oxides exhibit some form of bonding in the glass structure.

These bonds can be one or a combination of the following:

-Covalent (bond forms from shared pairs of electrons)
-Coordinate (covalent bond where the shared electrons are from one atom)
-Valence (two overlapping atomic orbitals localized between two adjacent atoms)
-Metallic (extreme de-localization of valence electrons)
-Ionic (Coulomb attraction)

A colloidal color may also exhibit some level of the equivalent of a condensed phase (the condensed state is characterized by tightly packed molecules held together by cohesive forces). The colloidal color is a mixture in which very small particles/molecules are uniformly dispersed in a supporting medium such that the result is in-between a true solution and a heterogeneous mixture.

Devitrification (phase transformation) occurs when the glass begins to change from an amorphous structure to a crystalline structure. Devitrification occurs at or around the liquidus viscosity (approximately 1000 - 1050 degrees c for 33 expansion) and is a time and temperature circumstance. Phase separation is the formation of two (or more) distinct glasses. Phase separation can occur in the melting (~ 10^2 poise), conditioning/forming (~ $10^{3.7}$ - $10^{4.5}$poise), working (~ 10^4 poise), and annealing processes (~ 10^{13} poise).

All of the re-formulations for compatibility, workability, improved quality, and/or consistency have been based on our set of assumptions. In addition, any of the new colors in the last 24 months as well as the six plus currently in the testing stage also were developed based on these assumptions.

Some examples of our assumptions include:

-Forest Green from a compatibility standpoint (lower COE by ~ 4 points and lower strain and anneal points by ~ 50 degrees c respectively)
-Cadmium colors to reduce boiling and improved intensity and opaqueness
-Repeatability of color shades in general
-Development of improved striking colors (including a self striking ruby line of colors)

Our set of assumptions is just that: assumptions. However, we believe in eliminating barriers and common beliefs that are inhibiting the growth and development of the boro market. The willingness to extend ourselves, and take risks by not accepting the norm is a fundamental requirement at Northstar. Dynamic growth comes from acknowledging what we do not know and making some basic assumptions. Then acting on those assumptions, evaluating the results, making adjustments, and starting the process again.