PNNL-14227

Pacific Northwest National Laboratory
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Using Colored Cullet for Making Beautiful Glassware

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Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RL01830

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Using Colored Cullet for Making Beautiful Glassware (Report for G Plus Project for Fire and Light Originals)

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Abstract

Eight colored glasses from Fire and Light Originals (FLO) and three container cullet glasses were characterized for the viscosity, density, and thermal expansion, glass transition temperature, dilatometer softening temperature, color chromaticity, Fe(II)/Fe(total) redox ratio, and chemical composition. The results of the characterization were used to evaluate the options for the glass formulation development of colored glasses aimed at increasing the use of recycled container glass cullet. Out of several options considered, the possibility of using clear cullet for FLO's Citrus colored glass was selected and investigated in this study. It was shown that it is possible to use clear cullet to produce Citrus glass at the cullet oxide ratio of 90 mass% and the final color can be adjusted by controlling the nitrate level and alkali concentrations. From the present study, recommendations for further development efforts are provided to increase the container cullet usage or to replace partially or entirely the clear cullet by the amber cullet.

Acronyms

CIE	Commission International de L'Eclairage
DIW	Deionized Water
FLC	Fire and Light Citrus
FLO	Fire & Light Originals
ICP	Inductively Coupled Plasma
NIST	National Institute for Standards and Technology
VFT	Vogel-Fulcher-Tammann

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1.0 Introduction

One of the major efforts of the Environmental community for the glass industry is to recover and recycle 100 percent of available post-consumer glasses. Currently, Fire and Light Originals (FLO) (http://www.fireandlight.com) uses recycled cullet from clear glass containers to make beautiful glassware of various colors. Cullet from green and amber containers is not used. Batch raw materials without cullet are used for some of its special colored products. The purpose of this project is to develop the glass formulations that can lead to increased usage of recycled container glass cullet.

The first step of this project was to characterize the properties of FLO's current products and container glasses by measuring the viscosity, density, and thermal expansion and glass transition temperature by dilatometer, color chromaticity, redox, and chemical composition. Eight colored glasses distributed in the following three source categories

1. colors produced from clear container cullet and additional batch raw materials: Cobalt, Aqua, Celery, Plum, and Olive (will be referred to as "Clear Cullet" glasses in this report)
2. colors produced from 100 percent batch raw materials: Citrus and Lavender (will be referred to as "Batch" glasses)
3. color produced from the scrap of stained glasses: copper,

and three colors of container glass cullet (green, amber, and clear) were received from FLO for properties characterization.

Based on the results of the characterization, several options for the glass formulation development were reviewed to select one option to be tested in the present study. In this report, the results of property characterization and the glass-formulation tests are discussed, and recommendations for future work are provided.

2.0 Experimental Methods

This section describes glass preparation, the density of glass, the thermal expansion coefficient, the glass-transition temperature, the dilatometer softening point, chromaticity, iron redox, viscosity, and the analysis of chemical composition.

2.1 Glass Preparation

The as-received container glasses were washed with acetone to remove glue, melted twice at 1450°C for 1 h, and poured into a Pt-10%Rh mold to make roughly 10-mm thick glass bars, which was moved to a preheated furnace and held for 2 h at 550°C. Then the furnace was shut off to allow the glasses to slowly cool to room temperature.

For density, dilatometer, and chromaticity measurements, both the FLO product glasses and remelted container glasses were subjected to the same annealing treatment. The FLO glass blocks were cut into roughly 10-mm thick samples to prepare similar size glass to remelted container glasses. The glasses were annealed by heating to 550°C, holding for 4 h, and then slowly cooling to room temperature. Annealed glasses were examined under the polarized light for any remaining stresses.

2.2 Density by Gas Pycnometer

Annealed glasses were cut to obtain solid specimens with a nominal volume sufficient to fill at least 10 percent of the gas pycnometer sample chamber. Samples were washed with deionized water (DIW), placed into a glass beaker filled with ethanol, and ultrasonically cleaned for 10 min before analysis. The sample dry mass was determined with a calibrated four-decimal-place balance. The glass density was measured using an Accupyc® 1330 Gas Pycnometer calibrated before and after the experiment with a National Institute for Standards and Technology (NIST) traceable standard, tungsten carbide ball. After five runs for each glass, the average glass densities were calculated.

2.3 Thermal Expansion Coefficient, Glass Transition Temperature, and Dilatometer Softening Point by Dilatometer

Annealed glasses were cut to obtain solid bars of approximately 5×5×25 mm and with parallel ends. They were washed with DIW, and their length was set using calipers. The length of solid sample matched closely the length of the sintered alumina reference specimen. The thermal expansion of glasses heat treated 2°C/min from 30°C to 650°C was measured with the differential dilatometer Dilatronic I. The thermal-expansion coefficient, dilatometic transformation temperature, and softening point were determined from the expansion versus temperature curves.

2.4 Chromaticity

The Commission International de L'Eclairage (CIE) 1931 Chromaticity Diagram with x, y coordinates is one of the most widely used ways of specifying the colors of light visible to humans. The glass color coordinates for transmitted light, x, y, and a, are

$$x = \frac{X}{X+Y+Z}\,,\quad y = \frac{Y}{X+Y+Z}\,,\quad z = \frac{Z}{X+Y+Z} \tag{1}$$

$$x + y + z = 1 \tag{2}$$

where X, Y, and Z are the red, green, and blue tristimulus values calculated from

$$X = k\sum_{380}^{780} S_\lambda \bar{x}(\lambda)\tau(\lambda),\quad Y = k\sum_{380}^{780} S_\lambda \bar{y}(\lambda)\tau(\lambda),\quad Z = k\sum_{380}^{780} S_\lambda \bar{z}(\lambda)\tau(\lambda) \tag{3}$$

where S_λ is the spectral energy distribution of the illuminant, $\bar{x}(\lambda)$, $\bar{y}(\lambda)$, and $\bar{z}(\lambda)$ are color-matching functions (also called distribution coefficients), $\bar{\tau}(\lambda)$ is the spectral transmission of glass, and the constant k is given by

$$k = \frac{1}{\sum_{380}^{780} S_\lambda \bar{y}(\lambda)}\,. \tag{4}$$

The color coordinate of glass is typically represented by x, y, and Y. Here Y represents the average transmission of the glass.

Another popular color space is the CIE Lab (also designated as L*a*b*) system in which the following L^*, a^*, and b^* values are plotted at right angles to one another to form a three-dimensional coordinate system:

$$L^* = 116\sqrt[3]{\frac{Y}{Y_N}} - 16\,,\quad a^* = 500\left[\sqrt[3]{\frac{X}{X_N}} - \sqrt[3]{\frac{Y}{Y_N}}\right],\quad b^* = 200\left[\sqrt[3]{\frac{Y}{Y_N}} - \sqrt[3]{\frac{Z}{Z_N}}\right] \tag{5}$$

where X_N, Y_N, and Z_N are the X, Y, and Z values of the illuminant. The L* represents the lightness, a^* represents the redness/greenness axis, and b^* represents the yellowness/blueness axis. The advantage of the CIE Lab chromaticity system is that the equal distances in the space approximately represent equal color differences to human eyes.

Annealed glasses were cut and polished to obtain samples with roughly 20×20×6.35 mm. The thickness of 6.35 mm was used to match closely to the $^1/_4$-in.-diameter sample size for color determination at FLO. The spectral transmission of light for the wavelength region from 380 to 780 nm was measured in steps of 1 nm on a double beam, double out-of-plane Littrow monochromator spectrophotometer (Cary 500 Scan, Varian). The x, y CIE chromaticity values and L^*, a^*, b^* color difference values have been calculated under the conditions of illuminant D65 with a 2° observer. The measurements were carried out at an ambient temperature of 24±2°C.

2.5 Iron Redox [β = Fe(II)/Fe(Total)] by Wet Colorimetry

To perform wet colorimetry for measuring the ratio of Fe(II) to Fe(total), glass samples were first ground in a tungsten carbide mill for 2 min. The fine glass powder of each sample with ammonium metavanadate added to prevent Fe(II) from oxidizing was dissolved in a mixture of sulfuric and hydrofluoric acids. Iron-fluoride complexes were disassociated by adding boric acid. Ferrozine reagent forms purple complexes with Fe(II). The absorption of light by the Fe(II)-Ferrozine complex was measured using an ultraviolet visible near infrared (UV-VIS-NIR) spectrophotometer (Cary 500 Scan, Varian) with Cary WinUV software in a scan range 400 to 800 nm with a scan rate of 300 nm/min. By adding ascorbic acid, Fe(III) in solution was reduced to Fe(II), and the absorption of total Fe(II)-Ferrozine complex in solution was measured. A buffered ferrozine solution was used for baseline measurement. The ferrous ion is quantified spectrophotometrically at a wavelength of 560 nm.

2.6 Viscosity by Spindle Viscometer

The glass samples (as-received glass blocks for FLO products and as-received broken pieces for container glass cullets) were broken into 5- to 25-mm pieces and added to a beaker filled with alcohol to measure 50±5 mL of glass. Dried samples placed into the platinum crucible were transferred to the melt furnace heated to 1500°C, the highest temperature at which the samples were tested. The measurement began at 1500°C after the glass samples were completely melted, and the temperature was steady. Then the temperature was decreased to the lowest temperature, 1200°C, by 50°C intervals with a 20-min dwelling time at each temperature.

The viscometer was calibrated using NIST 710a soda-lime-silica glass, for which

$$\log(\eta) = A' + \frac{B'}{T - T_0} \tag{6}$$

where η is the viscosity, T is the temperature in °C, and A', B', and T_0 are Vogel-Fulcher-Tammann (VFT) coefficients that have the following values: T_0 = 240.8°C, A' = –1.7290 (for η in dPa·s), and B' = 4560.0 K. The calibration data were used to calculate the spindle factor, F, defined as

$$F = \eta \frac{\omega}{\tau} \tag{7}$$

where τ is the torque, and ω is the spindle speed. The temperature range for calibration on the automated viscometer varied from 1200°C to 1500°C. The measurement began at 1200°C. For each subsequent measurement, the temperature was increased by 100°C. The highest temperature was 1500°C. Then the temperature was decreased to 1200°C by 100°C intervals. Calibration data are presented in

The measured viscosity data were fit to the Arrhenius equation:

$$\ln(\eta) = A + B/T \tag{8}$$

where A and B are Arrhenius coefficients for viscosity, and T is the absolute temperature.

Table 2.1.

The measured viscosity data were fit to the Arrhenius equation:

$$\ln(\eta) = A + B/T \qquad (8)$$

where A and B are Arrhenius coefficients for viscosity, and T is the absolute temperature.

Table 2.1. Viscometer Calibration Data

T **(°C)**	***η*** **(Pa.s)**	***F***
1199	107.2	9.58
1298	38.5	9.69
1398	16.3	9.92
1498	7.9	10.36
F_{avg}		9.89

2.7 Chemical Composition Analysis

The chemical composition of glass was determined by inductively coupled plasma (ICP) spectrometer Model IRIS/AP using the glass powder ground in a tungsten carbide mill for 2 min. Two fusion methods were applied: Na_2O_2 fusion in a Zr container and K_2O_2 fusion in a Ni container. The average concentration from two fusion methods was used except for components that can be determined from one method only, such as Na, K, Ni, and Zr.

3.0 Glass Characterization Results

Table 3.1 summarizes the results of chemical analysis by ICP for three container glasses. It can be noticed that there are some analytical errors based on the fact that the concentration of all components analyzed do not sum close to 100%. No attempts were made to pursue this issue. The present results provided information needed to identify general trends in glass composition that allow establishing correlations between the key glass properties and major components and between chromaticity and colorant.

Table 3.1. Chemical Composition of Container Glass Cullets Determined by ICP

Comp.	Clear Cullet	Green Cullet	Amber Cullet
SiO_2	65.40	67.99	67.48
Na_2O	13.17	14.52	16.11
K_2O	1.48	1.07	1.35
Li_2O	0.03	0.04	0.01
CaO	9.39	9.99	9.20
MgO	0.21	1.40	0.39
Al_2O_3	1.54	1.66	2.11
B_2O_3	0.06	0.07	0.07
SO_3	0.24	0.28	0.16
CoO			
Cr_2O_3		0.26	
Fe_2O_3	0.099	0.337	0.310
MnO_2	0.01	0.02	0.01
CuO			
CeO_2			
TiO_2	0.06	0.06	0.09
Nd_2O_3			
NiO	0.07	0.07	0.07
P_2O_5			
SrO	0.03	0.02	0.03
ZnO	0.01	0.01	0.01
ZrO_2	0.22	0.02	0.03
BaO	0.07	0.04	0.11
Sum	92.09	97.86	97.53

Table 3.2 summarizes the following glass properties: the thermal expansion coefficient (α), the glass transition temperature (T_g), the dilatometer softening temperature (T_s), the density (ρ), the Fe(II)/Fe(total) ratio (β), the Arrhenius coefficients (A, B) for viscosity (η), the temperatures at 10 and 1000 Pa·s, and the chromaticity by both the CIE (x, y) Coordinate and CIE Lab (L^*, a^*, b^*) Coordinate systems. The temperatures at 10 and 1000 Pa·s were calculated from Arhenius coefficients, which are used for as-reference temperatures for melting and forming.

Table 3.2. Summary of Glass Properties

	"Clear Cullet" glasses					"Batch" Glasses			Container Glass Cullets		
Property	**Aqua**	**Celery**	**Cobalt**	**Olive**	**Plum**	**Citrus**	**Lavender**	**Copper**	**Clear Cullet**	**Green Cullet**	**Amber Cullet**
$\alpha_{30\text{-}400^\circ C}$ (10^{-6}°C^{-1})	11.15	10.93	10.98	10.98	11.25	11.47	11.46	10.53	9.82	9.70	10.01
T_g (˚C)	523	524	525	526	520	514	506	521	563	568	564
T_s (˚C)	563	565	562	570	563	553	541	568	599	609	604
ρ (g/cm^3)	2.533	2.531	2.532	2.539	2.539	2.598	2.539	2.501	2.501	2.513	2.512
β	0.36	0.29	0.33	0.19	0.25	0.17	0.29	0.24	0.18	0.27	0.47
A for η (η in Pa·s)	-10.10	-10.53	-10.44	-10.35	-10.57	-9.80	-10.33	-10.91	-11.19	-11.49	-10.18
B for η (K)	20326	20932	20877	20758	20885	18917	20486	21888	23323	23663	21413
T (˚C) at 10 Pa·s	1366	1358	1365	1368	1349	1290	1348	1384	1456	1443	1443
T (˚C) at 10^3 Pa·s*	922	927	931	930	922	859	915	956	1016	1013	980
Y (%)	35.55	33.92	26.62	38.62	13.26	36.73	28.03	30.68	77.59	38.16	3.07
x	0.304	0.314	0.29	0.32	0.356	0.337	0.291	0.343	0.328	0.318	0.575
y	0.332	0.338	0.307	0.346	0.325	0.365	0.302	0.347	0.339	0.485	0.423
L^*	66.18	64.9	58.62	68.47	43.16	67.08	59.92	62.23	90.59	68.14	20.32
a^*	-4.28	-2.65	-0.81	-3.21	12.37	-3.48	1.42	4.51	2.66	-42.18	19.87
b^*	-0.30	2.71	-8.33	5.87	3.56	13.14	-9.70	8.62	6.01	40.83	51.71

*Extrapolated to the temperature outside the temperature range viscosity data were obtained.

Figure 3.1 shows the dilatometer curves and Figure 3.2 the Arrhenius plots of viscosity data for all FLO glasses and container cullet glasses. For the glass properties by dilatometer, α, T_g, and T_s, there is a clear difference among glasses with different source categories as shown in Figure 3.1. For T_g and T_s, the order of higher values is Container glasses > "Clear Cullet" glasses > "Batch" glasses. The thermal expansion coefficient is in exactly opposite order. The variation in these properties is believed to be related mainly to the alkali contents in these glasses. The Container glass cullets had the lowest concentration of total alkali and so the highest T_g and T_s and the lowest α. The difference between "Clear Cullet" glasses and "Batch" glasses is relatively small and is a combined result of different alkalis, Al_2O_3, and B_2O_3 concentrations.

For a high-temperature viscosity, the temperatures at 10 and 1000 Pa·s have a very similar trend as T_g and T_s, except for Lavender, which is closer to the values for "Clear Cullet" glasses rather than to Citrus (see Figure 3.2). The difference between Citrus and Lavender is likely caused by the slight difference in colorants (CeO_2 and TiO_2 in Citrus, Nd_2O_3 in Lavender). For Copper glass, the α and T's at 10 and 1000 Pa·s are between "Clear Cullet" glasses and Container glass cullets whereas the T_g and T_s are closer to "Clear Cullet" glasses. This glass is a standalone composition produced without any modification at FLO.

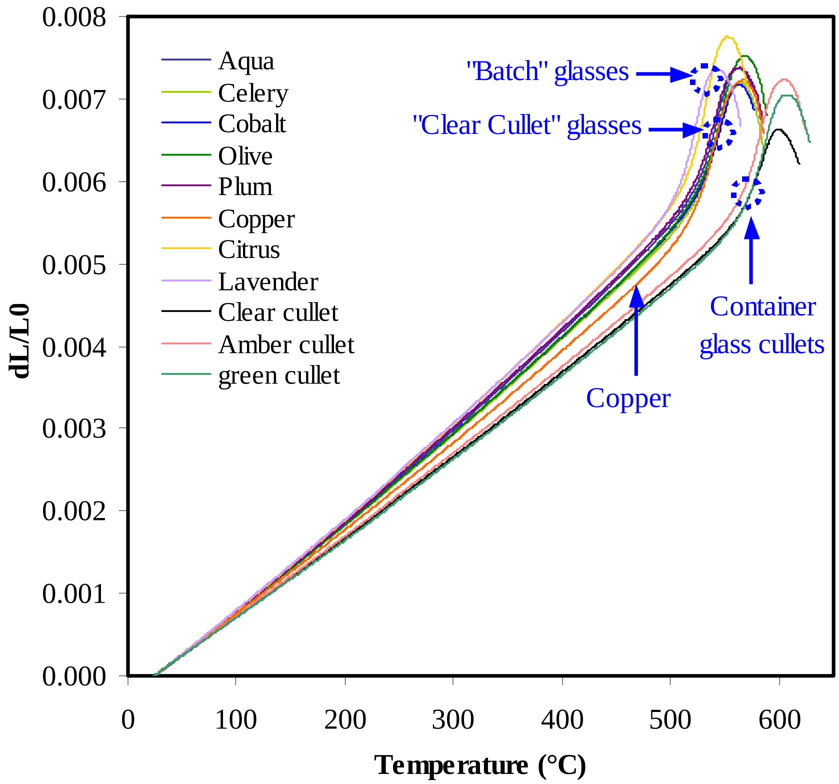

Figure 3.1. Expansion vs. Temperature for FLO and Container Cullet Glasses

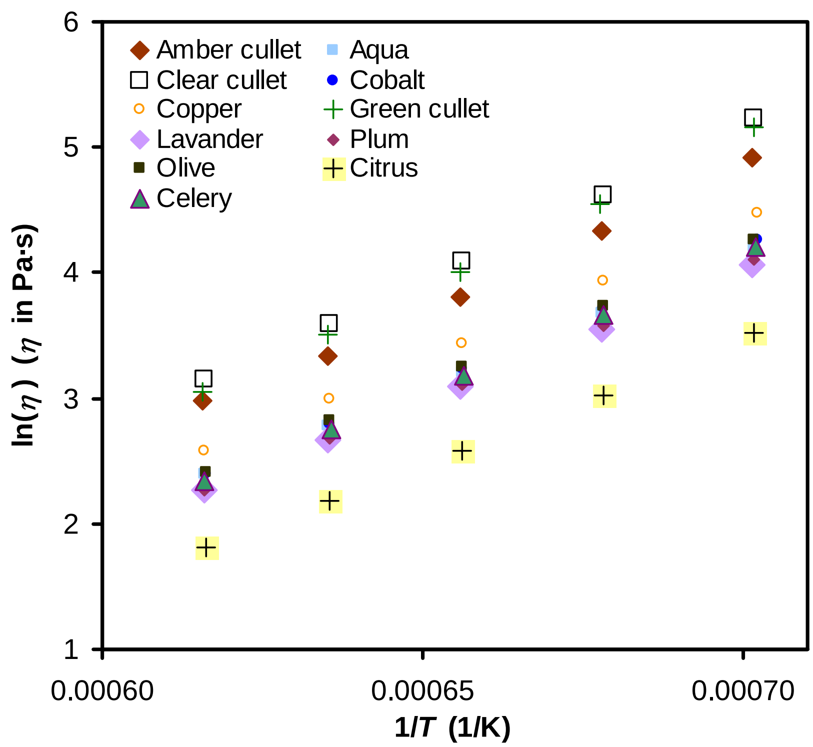

Figure 3.2. ln(η) vs, 1/T for FLO and Container Cullet Glasses

For density, the “Clear Cullet” and “Batch” glasses have similar values, which are higher than those of Container glasses as can be expected from their lower alkali concentrations. The relatively higher density of Citrus glass is obviously the result of addition of CeO_2 and TiO_2 (total ~5.5 wt%).

The iron redox will be dependent on both glass composition and batch formulation, assuming the same melting conditions. The major factor that affects the redox would be the concentration of nitrates used in the batch. Figure 3.3 shows the β value as a function of the amount of nitrate in moles per 150 lb of clear cullet used in the “Clear Cullet” glasses. There is a general trend—as the nitrate used in the batch increases, the β value decreases, except for one outlier glass, Plum. The main difference of this Plum glass from the other four glasses is that the Plum glass has a higher content of MnO_2, but it is not clear if this high MnO_2 is responsible for redox behavior deviation. Among container glasses, the amber glass shows the clearly higher β value for which this is the reduced condition to produce the amber glass. Citrus in “Batch” glasses and Clear glass in container glasses had the lowest β value.

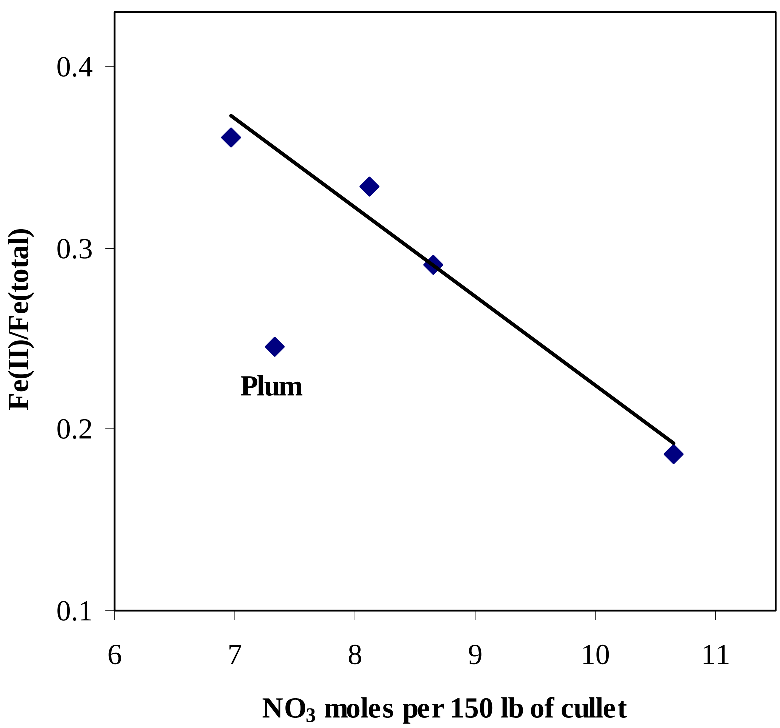

Figure 3.3. Effect of Nitrate on the Iron Redox for FLO “Clear Cullet” Glasses

The spectral transmission curves for FLO and remelted container glasses are in Figure 3.4 and Figure 3.5. Figure 3.6 shows the CIE *x*, *y* chromaticity coordinates for the FLO glass products and remelted container glasses. All the FLO glasses and clear cullet are near the central point of the neutral color (white to black) while the green and amber cullet glasses are closer to the pure colors. (Note that the color representations in Figure 3.6 may not be accurate and are dependent on the display/reproduction equipment.)

Figure 3.7 shows the *x*, *y* chromaticity coordinates for the FLO glass products and remelted clear cullet glass, which are clustered in Figure 3.6. Figure 3.8 shows the CIE Lab coordinates for the same glasses in Figure 3.7. The color labels with arrows in Figure 3.7 and Figure 3.8 roughly indicate the general direction of the color as the coordinate changes. Not included in Figure 3.7 and Figure 3.8 is information on the transmission (Y) or lightness (L*). The color coordinates well agree with the description of each color. One exception would be Lavender, which exhibits a well-known dichroism caused by several very sharp absorption peaks as shown in Figure 3.4.

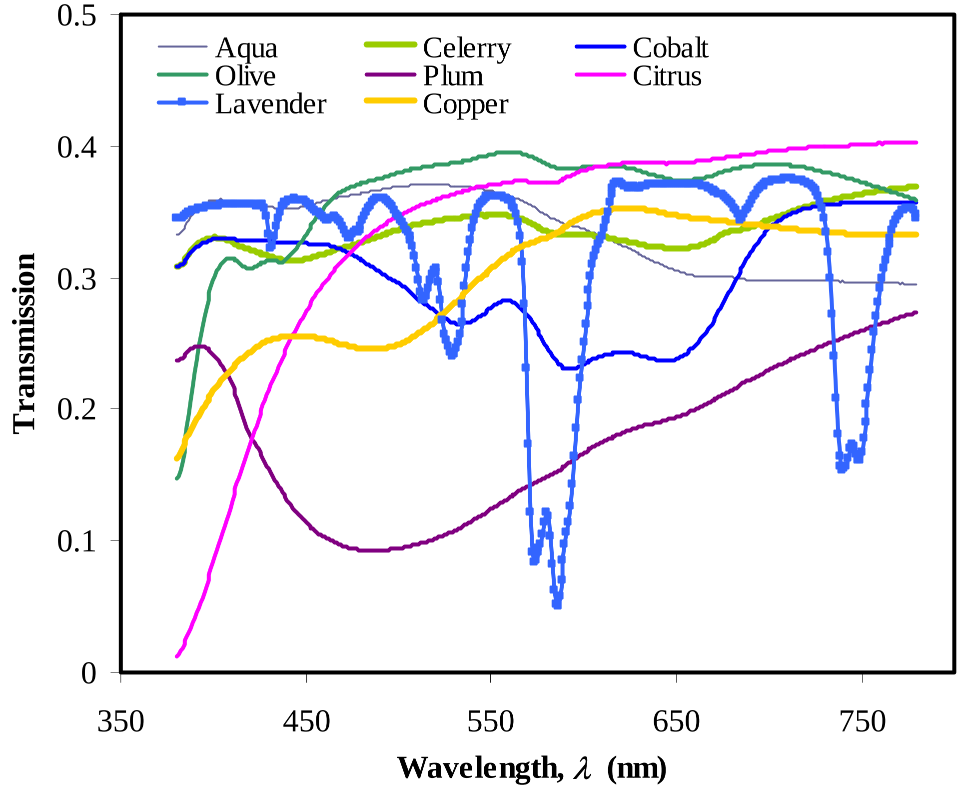

Figure 3.4. Spectral Transmission for FLO Glasses at a Glass Thickness of 6.35mm

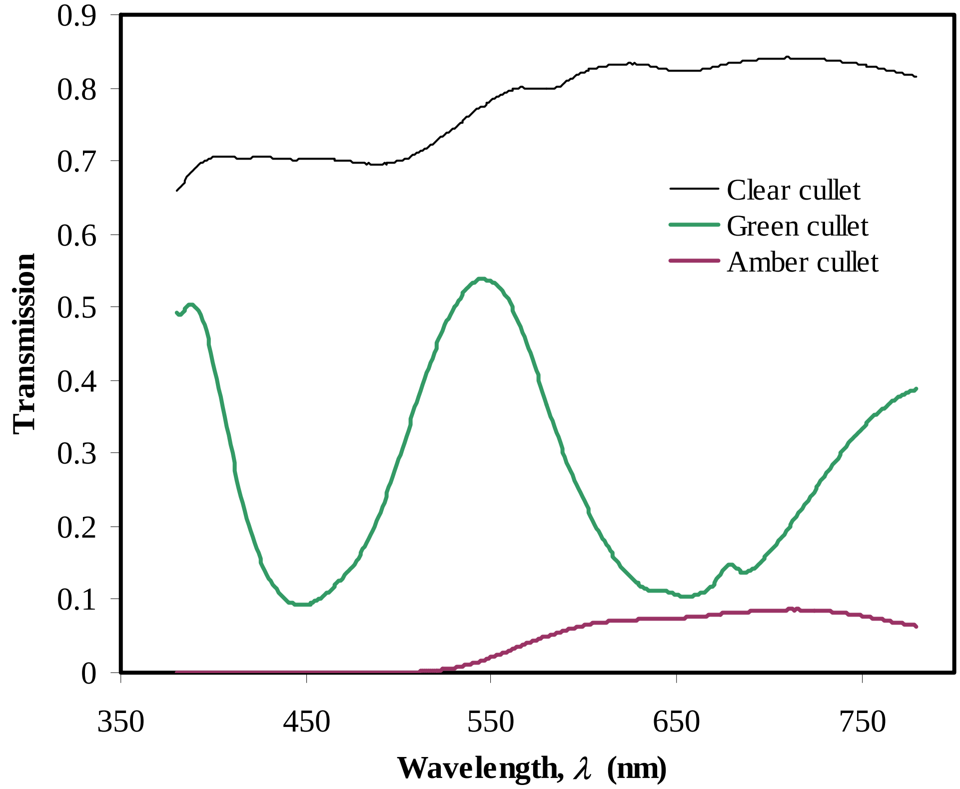

Figure 3.5. Spectral Transmission of Container Glasses at a Glass Thickness of 6.35mm

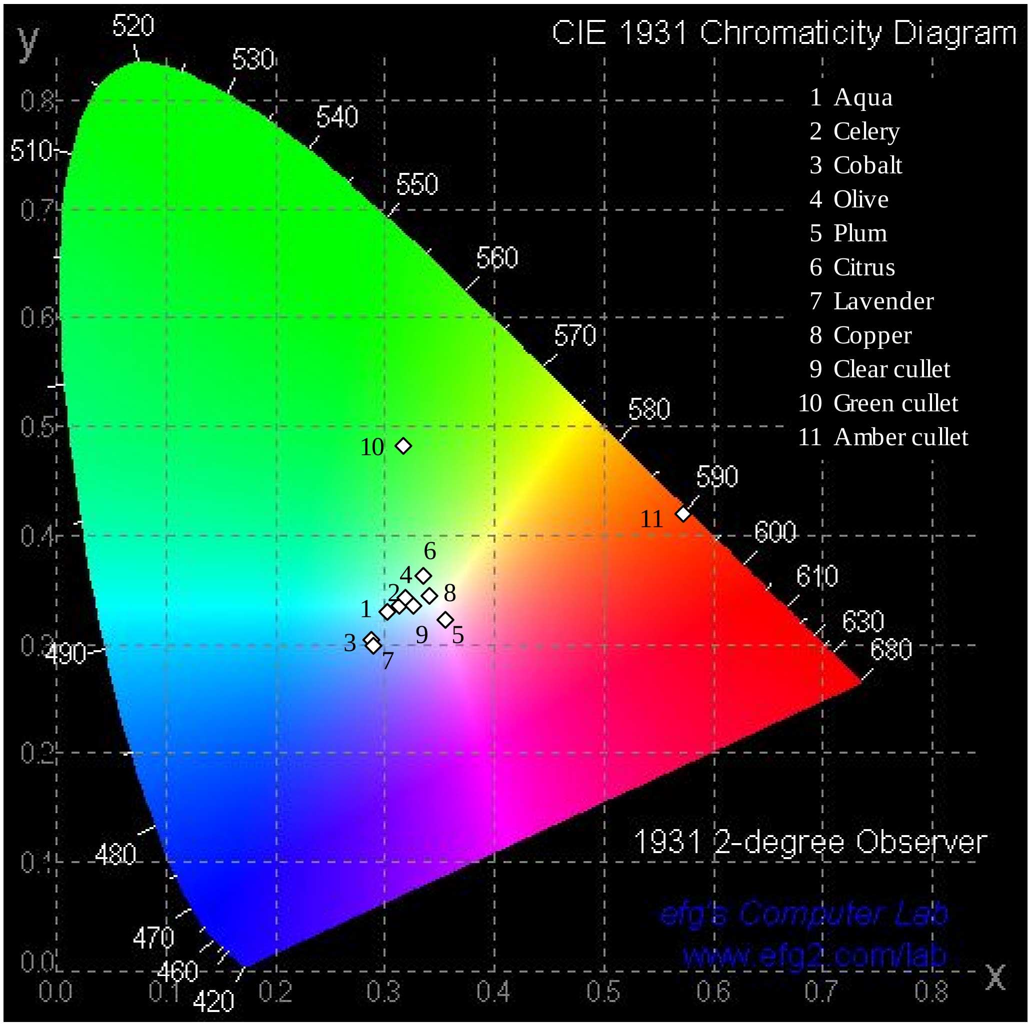

Figure 3.6. Chromaticity x,y Coordinate for all FLO and Container Glasses (note that the color representation is for illustration purposes and may not be accurate)

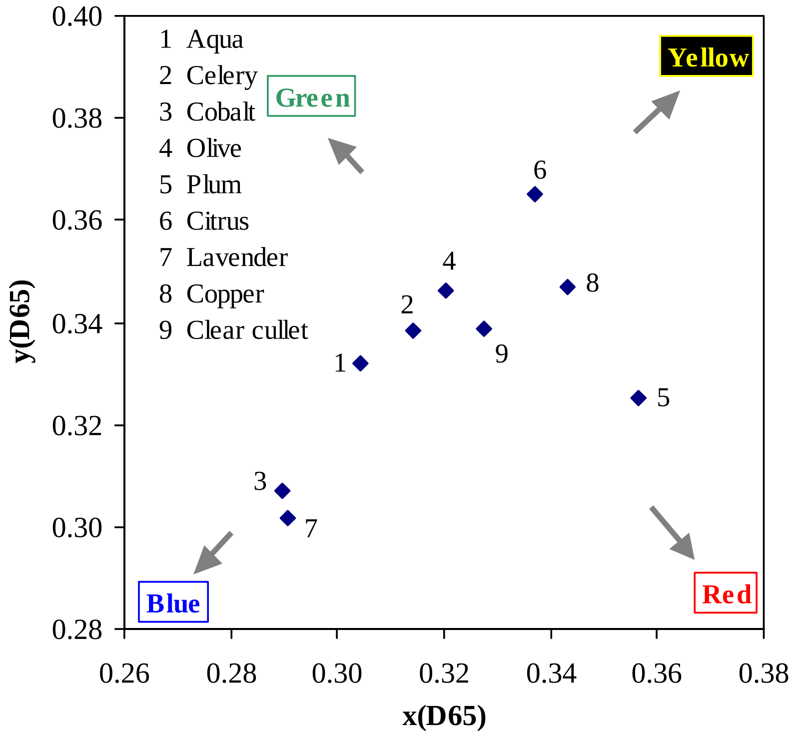

Figure 3.7. Chromaticity x,y Coordinate for all FLO Glasses and Clear Cullet

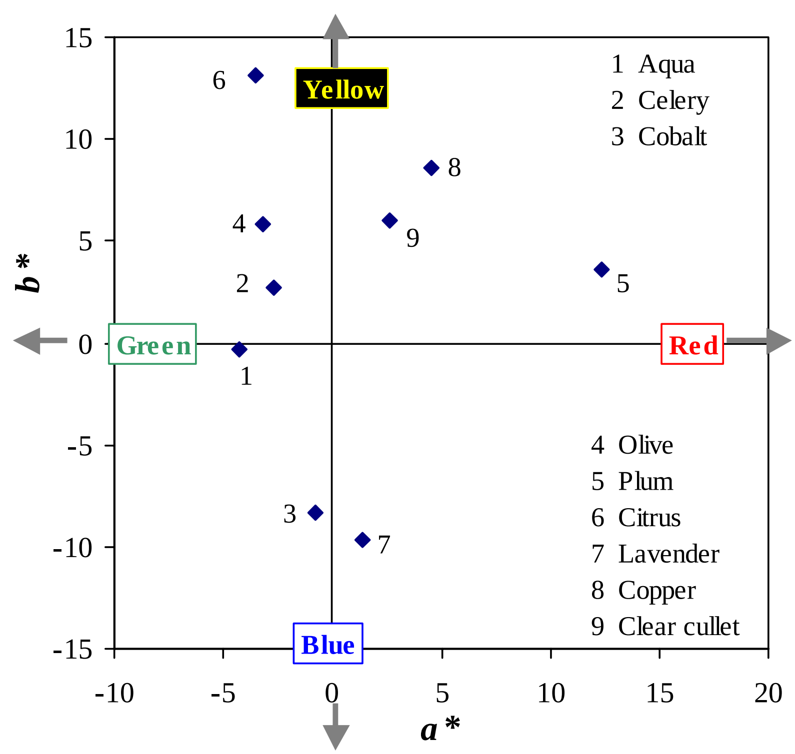

Figure 3.8. Chromaticity a*,b* Coordinate for all FLO Glasses and Clear Cullet

4.0 Glass-Development Tests

Any color development should include the effect of glass composition on other properties that affect the glass-processing operation. However, this study first focuses on the chromaticity only to determine the feasibility of different options. Additional steps of formulation testing would be required for complete color development.

It would be most economical if colored container cullet (green or amber) could be used to produce FLO's current "Batch" glasses. However, it is obvious that green cullet glass cannot be used for any FLO glass production. The green container glass is colored mainly by Cr_2O_3 with some CoO. The green coloring by Cr_2O_3, represented by strong absorption bands centered at 450 and 650 nm as shown in Figure 3.5, is too strong to be corrected by any decolorization techniques. Celery is the only FLO's product that uses Cr_2O_3 as a coloring agent, but the concentration is much less than $^1/_{10}$ of that in the typical green container glass. Therefore, the cullet fraction achievable will be too low to be practically usable.

Below are two possible options that can be considered:

1. Using amber cullet to produce "Clear Cullet" glasses.
2. Using clear cullet to produce "Batch" glasses.

In Option 1, the obvious first choice would be Olive because the major colorant in this glass is Fe_2O_3. Depending on the effect of Fe_2O_3 on each color, partial or full replacement of clear cullet by amber cullet would be possible for other colors. It is required to oxidize the ferrous and sulfide ions in amber cullet glasses. The effect of oxidizing agents and the melting condition on the behavior of iron and sulfur in amber glass needs to be studied to fully explore this option. However, Option 1 has a lower priority, considering that the advantage from replacing clear cullet by amber cullet is minimal compared to Option 2. Out of two colors in Option 2, Citrus was selected for development in this study.

One major issue with Option 2 is also the relatively high concentration of iron in clear cullet and its effect on each color produced by unique colorants. The known traditional methods of decolorization of iron are:

- adding arsenic
- adding selenium
- increasing nitrate.

Among these methods, only the third method of using nitrate will be considered in this study because arsenic is highly toxic and selenium can cause problems and be difficult to control with its highly volatile nature.

The method of using nitrate is based on the fact that the color produced by iron is mainly by ferrous iron, and the ferric iron has only very weak absorption at the ultraviolet end of the visible spectrum, producing virtually no noticeable impact on color at the relatively low concentration being considered here, < 0.1 wt%. Nitrate is added to oxidize the melt to form ferric iron, thus minimizing the concentration of ferrous iron. However, the Citrus color produced by the combination of CeO_2 and TiO_2 is also dependent on the redox state of the glass and the basicity of glass, which is determined by glass composition.

As a first step in this study for Citrus development, the glass and batch composition were varied in six glasses. The batch composition of these Fire and Light Citrus (FLC) series test glasses is summarized in Table 4.1. All glasses were formulated to have a cullet loading of 90 mass% in oxide basis. The estimated glass compositions are in Table 4.2. The amount of raw materials in the batch and the amount of nitrate in terms of NO_3 moles calculated per 150 lb of cullet are also included in Table 4.1 for comparison with the values used in the plant.

Table 4.1. Batch Composition of Glasses Used in Formulation Tests for Citrus Glass

Materials (g)	**FLC1-1**	**FLC1-2**	**FLC1-3**	**FLC2**	**FLC3**	**FLC4**
Na_2CO_3	2.51	2.97	2.04	2.25	2.77	3.02
$NaNO_3$	1.20	0.45	1.95	0.38	2.01	0.38
KNO_3	0.97	0.97	0.97	1.93	0.00	1.93
Li_2CO_3	2.97	2.97	2.97	2.97	2.97	1.85
$Na_2B_4O_7$-$10H_2O$	2.88	2.88	2.88	2.88	2.88	2.88
CaF_2	0.68	0.68	0.68	0.68	0.68	0.68
Na_2SO_4	0.53	0.53	0.53	0.53	0.53	0.53
Sb_2O_3	0.33	0.33	0.33	0.33	0.33	0.33
CeO_2	3.30	3.30	3.30	3.30	3.30	3.30
TiO_2	4.95	4.95	4.95	4.95	4.95	4.95
Batch Total	20.31	20.02	20.59	20.19	20.41	19.85
Clear Cullet	135	135	135	135	135	135
Total	155.31	155.02	155.59	155.19	155.41	154.85
For comparison with current FLO “Clear Cullet” glasses						
lb batch per 150-lb cullet	22.56	22.25	22.88	22.44	22.68	22.05
NO_3 moles per 150-lb cullet	11.9	7.5	16.4	11.9	11.9	11.9

In FLC1-1 through FLC1-3, the amount of total nitrate was varied for the same glass composition. In FLC2 through FLC4, the glass composition was modified from FLC1 glass by varying the ratio of alkali oxides while keeping the total concentration (in mass%) of alkali oxides constant. In FLC2 and FLC3, the concentration of K_2O was increased or decreased by 0.3 wt% at the expense of Na_2O. In FLC4, the K_2O was increased, replacing the Li_2O. In FLC2 to FLC4 glasses, the total number of moles of NO_3 per 150-lb cullet was kept constant. It is expected that the iron redox will be slightly shifted in favor of ferric iron by replacing Na_2O or Li_2O by K_2O. However, the major effect of the above changes may be in the coloration by CeO_2 and TiO_2. The nitrate variation will affect Ce redox, and the glass-composition variation will influence the oxygen coordination of Ce^{3+} and Ce^{4+} ions, which are known to affect the CeO_2 and TiO_2 coloration. The extent of these effects is not well established and needs to be determined empirically for specific glass composition and melting conditions.

Table 4.2. Target Glass Compositions

Component	FLC1	FLC2	FLC3	FLC4
SiO_2	64.19	64.19	64.19	64.19
Na_2O	14.67	14.37	14.97	14.67
K_2O	1.75	2.05	1.45	2.05
Li_2O	0.83	0.83	0.83	0.53
CaO	9.54	9.54	9.54	9.54
MgO	0.20	0.20	0.20	0.20
Al_2O_3	1.52	1.52	1.52	1.52
B_2O_3	0.76	0.76	0.76	0.76
F	0.22	0.22	0.22	0.22
SO_3	0.43	0.43	0.43	0.43
Sb_2O_3	0.22	0.22	0.22	0.22
Fe_2O_3	0.098	0.098	0.098	0.098
MnO_2	0.010	0.010	0.010	0.010
CeO_2	2.20	2.20	2.20	2.20
TiO_2	3.36	3.36	3.36	3.36
Sum	100.00	100.00	100.00	100.00

For preparation of the FLC test glasses, the glass batch consisting of reagent-grade chemicals and clear cullet was melted in a Pt-Rh crucible placed in the electrical heating furnace. The clear glass cullet was ground before mixing with a raw-materials batch to overcome potential inhomogeneity from small-size melting. The melting procedure was modified from normal methods because of severe foaming observed during initial melting. It is likely that foaming was caused by using ground-glass particles instead of bigger-sized crushed pieces. The glass batch was heated to 900°C at 5°C/min, quenched, and crushed. The crushed glass was then put into a furnace at 900°C, heated to 1400°C at 10°C/min, and held at 1400°C for 2 h. The glass melt was poured into a Pt-mold placed on a heater, which was put into the annealing furnace to anneal the glass according the same schedule as was used for all other FLO glasses. The color of the sample was measured according the procedure described in Section 2.

Table 4.3 summarizes the chromaticity results of the FLC series glasses. The spectral transmission of these FLC glasses is in Figure 4.1, and the chromaticity a^*,b^* diagram is in Figure 4.2. The coordinate for the FLO's Citrus glass product is also included in Figure 4.1 and Figure 4.2 for comparison. In terms of chromaticity coordinates, all the FLC series glasses are shifted towards yellowness and slightly greenness compared to the FLO Citrus product. This overall shift in color coordinates may be caused by the slightly different CeO_2 and TiO_2 ratio expected between product and lab-melting glasses. Considering the inherent errors in glass chemical analysis, it was not attempted to exactly match the colorant concentration to that in the FLO product glass at this point. The following discussion is valid in terms of the relative effect of iron redox and the alkali ratio on the glass color, which can be used to fine tune the batch composition to produce the exactly matching color in the plant.

In FLC1-1 through FLC1-3 glasses, as the nitrate content in the batch increased, the yellowness and transmission (or lightness) decreased without a noticeable effect on the redness/greenness (see Figure 4.2). Based on the transmission change and spectral pattern, it seems that the chromaticity change was mainly affected by the Ce redox rather than the iron redox. The decrease or increase of K_2O replacing Na_2O in FLC2 and FLC3 glasses had little effect on the color coordinate while it decreased the transmission. The increase of K_2O replacing Li_2O in FLC4 increased yellowness significantly and decreased the transmission. Although not tested within this study, it is expected that increasing Li_2O at the expense of Na_2O or K_2O would decrease yellowness, which will make the color closer to the FLO's current Citrus product if desirable.

In summary, it can be concluded from the current studies that the desirable color close to the current Citrus product can be obtained by controlling the nitrate level and alkali concentrations. It is also noted that the decrease of transmission, which implies stronger absorption, may be used to reduce the amount of colorants to produce the same color and transmission as the current product.

The color produced in these six glasses satisfies the current color specification at FLO. It should be noted that the plant-melting condition may give different results compared to these glasses prepared in the laboratory. However, the effect of nitrate and glass composition identified in the present study can be used to fine tune the glass color under the plant melting condition. More detailed study on these effects of nitrate and alkali contents and additional study on the effect of CeO_2 to TiO_2 variation would be needed to develop the "optimized" glass composition, including the glass composition for best economics.

Table 4.3. Chromaticity Results of FLC Series Test Glasses

	FLO Citrus	FLC1-1	FLC1-2	FLC1-3	FLC2	FLC3	FLC4
Y (%)	36.73	35.07	36.41	31.08	31.03	28.79	33.02
x	0.337	0.340	0.342	0.339	0.342	0.344	0.348
y	0.365	0.372	0.374	0.370	0.373	0.375	0.380
*L**	67.08	65.80	66.83	62.58	62.53	60.59	64.18
*a**	-3.48	-4.46	-4.39	-4.16	-4.02	-4.03	-4.36
*b**	13.14	15.04	16.17	13.95	15.13	15.52	18.09

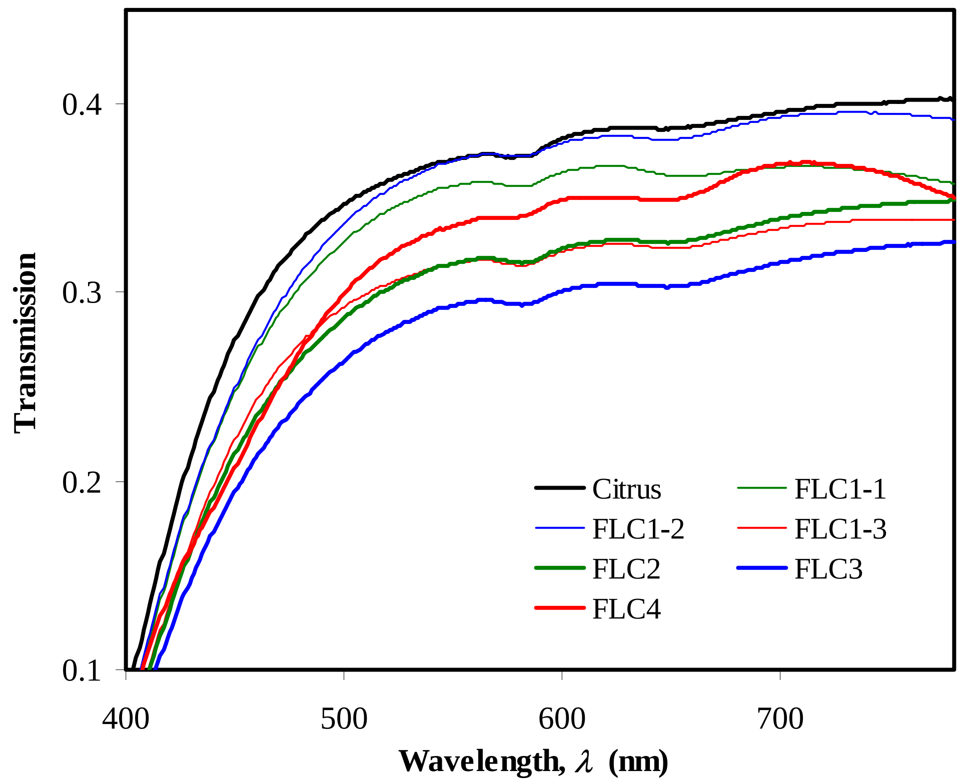

Figure 4.1. Spectral Transmission of FLO Citrus Glass and FLC Series Test Glasses at a Glass Thickness of 6.35mm

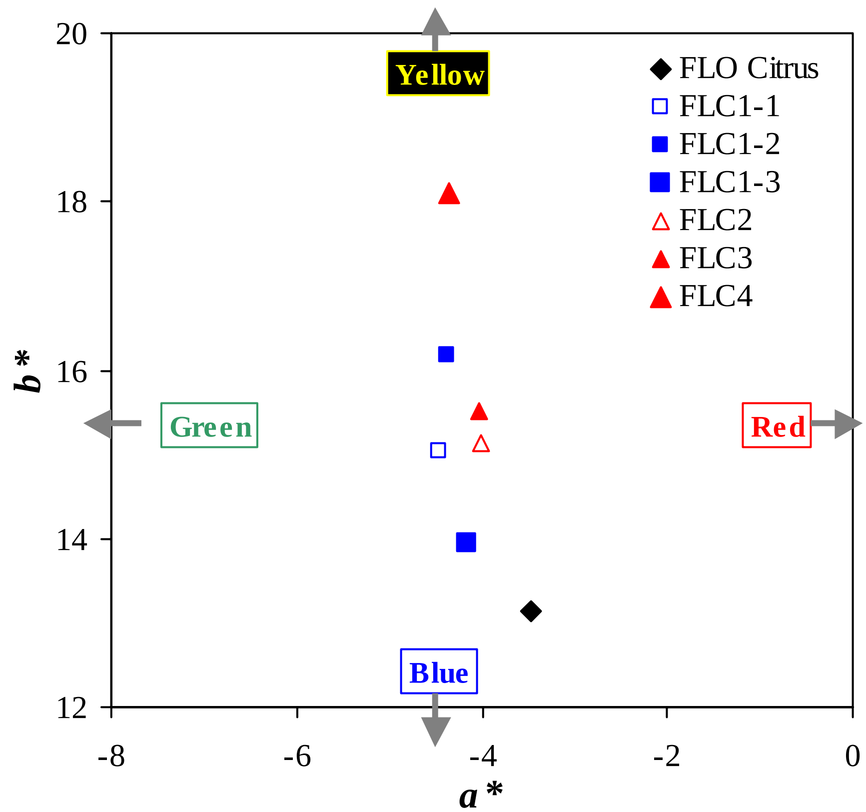

Figure 4.2. Chromaticity a*,b* Coordinate for Clear Cullet, FLO Citrus Glass, and FLC Series Test Glasses

5.0 Conclusions

Based on the test results on six glasses formulated with varying nitrate addition and alkali ratio, it was shown that it is possible to use clear cullet to produce Citrus glass at the cullet oxide ratio of 90 mass% and the final color can be adjusted by controlling the nitrate level in the batch and alkali concentrations in glass. The current study focused on matching the color of the current Citrus product. However, the final development may require additional steps of matching other glass properties important for the production processes.

The results from the study for the Citrus glass development suggest that the similar development for Lavender glass will be possible. There are no anticipated major obstacles for producing lavender color using clear container cullet. It is also recommended that the formulation development to replace partially or entirely the clear cullet by the amber cullet for the current "Clear cullet" glasses be performed. It is suggested that the development of the Olive glass that uses Fe_2O_3 as a colorant is the first option to start with, and then the development efforts can be expanded to other colors. The use of amber cullet will provide some cost benefits and will become very helpful, especially, in case there is a difficulty to provide enough supply of clear cullet.

6.0 Bibliography

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Appendix A

Viscosity Raw Data

Appendix A: Viscosity Raw Data

Aqua		Celery		Cobalt	
T (°C)	η (Pa·s)	T (°C)	η (Pa·s)	T (°C)	η (Pa·s)
1496.7	4.08	1496.3	3.83	1496.0	4.19
1449.3	5.62	1448.0	5.13	1448.3	5.33
1400.2	7.80	1399.0	7.24	1399.6	7.49
1350.6	10.98	1350.4	10.40	1350.2	10.98
1301.3	16.15	1300.0	15.64	1300.6	16.47
1251.4	24.58	1250.5	24.20	1251.3	25.59
1202.1	39.66	1201.4	39.17	1201.7	41.33
1152.5	67.05	1151.7	66.83	1151.0	70.88

Olive		Plum		Citrus	
T (°C)	η (Pa·s)	T (°C)	η (Pa·s)	T (°C)	η (Pa·s)
1494.4	4.18	1495.2	3.48	1495.0	2.57
1448.0	5.67	1448.2	4.87	1448.0	3.42
1399.6	7.78	1399.5	6.75	1399.0	4.38
1350.0	11.17	1350.3	9.73	1350.0	6.10
1300.5	16.76	1300.4	14.55	1300.4	8.81
1251.2	25.88	1251.3	22.49	1251.3	13.29
1201.6	41.69	1201.6	36.01	1201.6	20.66
1152.4	70.54	1152.4	60.80	1152.4	33.91

Lavender		Copper		Clear Cullet	
T (°C)	η (Pa·s)	T (°C)	η (Pa·s)	T (°C)	η (Pa·s)
1498.0	3.48	1495.3	4.27	1496.7	7.55
1449.5	4.78	1448.6	6.14	1449.0	10.85
1400.4	6.73	1400.0	8.96	1400.0	15.63
1350.7	9.69	1350.4	13.26	1350.3	23.36
1301.3	14.30	1300.6	20.00	1300.7	36.57
1251.5	21.92	1251.4	31.28	1251.3	59.73
1202.2	34.86	1201.8	50.82	1201.7	101.57
1152.9	57.74	1151.0	87.28	1152.5	186.36

Green Cullet		Amber Cullet			
T (°C)	η (Pa·s)	T (°C)	η (Pa·s)		
1498.5	6.74	1496.4	6.92		
1451.0	9.50	1450.0	10.15		
1401.6	13.88	1401.0	13.91		
1351.5	21.08	1351.0	19.56		
1301.6	33.47	1301.5	28.26		
1252.1	55.02	1251.8	45.08		
1202.5	94.75	1202.4	76.54		
1152.4	173.22	1152.8	137.43		