

# Color Modification of Post Consumer Glass Cullet



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## **Re-TAP PROTOCOL**

*Prepared by:*

### **The Recycling Technology Assistance Partnership (ReTAP)**

A program of the  
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The Recycling Technology Assistance Partnership (ReTAP) is an affiliate of the national Manufacturing Extension Partnership (MEP), a program of the Commerce Department's National Institute of Standards and Technology. The MEP is a growing nationwide network of extension services to help smaller U.S. manufacturers improve their performance and become more competitive. Other major support comes from the U.S. Environmental Protection Agency and the American Plastics Council

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## ReTAP Protocol

# **COLOR MODIFICATION OF POST-CONSUMER GLASS CULLET**

## **Introduction**

Recycled container glass is generally available in only clear, amber, and green. The lack of availability of a fuller color pallet is a barrier to the use of recycled container glass by small-scale businesses remelting glass for casting or pressing. The use by small businesses of recycled container glass could help to increase the market options available for recyclers, especially in rural areas. The Recycling Technology Assistance Partnership conducted a technology validation project in 1995 to demonstrate that by re-melting brown and green cullet and modifying its chemistry, a broad range of colors can be produced. Pressed glass tile manufacturing, in particular, has been identified by the Clean Washington Center as a

potential high-value market for recycled glass.<sup>1</sup> In the course of the study, separate batches of 25 to 30 pounds each of cullet were melted, pressed into four-inch square tile molds, and annealed. Nine transparent colors, two blacks, and a series of opals were produced using green, brown and clear bottle cullet. Each formula was evaluated for workability, color and melt quality, and formula economy.

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<sup>1</sup> For the purpose of this protocol, low-value is considered to be less than \$20 per ton aggregate markets, intermediate value is considered to be \$20-60 per ton, the approximate range of the value of collected recycled glass to container manufacturers, and high-value is considered to be greater than \$60 per ton.

This protocol reviews basic methods of decolorizing brown and green bottle cullet, and summarizes the details of the prototype melts described above, in the following five sections:

- ◆ Brown Bottle Cullet
- ◆ Green Bottle Cullet
- ◆ Opal Glasses
- ◆ Experimental Procedure
- ◆ Color Modification Formulas

Although resulting colors will vary widely depending on the source of glass cullet, furnace conditions, and the chemical additions used, the procedures presented here may help to make post - consumer glass a more attractive feedstock for small hot-glass operations.

## **Project Background**

Prior to conducting the prototype melts, a literature search was performed, previously tested methods of color modification were reviewed, and a series of small lab melts were conducted to test various formulas of interest.

The properties of available glasses and melting procedures were then reviewed by a panel of business, market, and technical glass experts to establish testing priorities for prototype melts. Classes of chemical modifications were chosen based on their recommendations and a search of relevant literature.

## Brown Bottle Cullet

Brown bottle glass is produced with a sulfur-iron colloidal solution under reducing conditions. Brown bottle cullet can be decolorized by taking advantage of the greater affinity of the  $S^-$  anion, called a ligand, for the free  $Zn^{2+}$  ion over the free  $Fe^{2+}$  ion. At a certain level of zinc oxide, brown glass will be decolorized to a neutral blue/green hue glass, due to the free ion of  $Fe^{2+}$ . Erbium oxide ( $Er_2O_3$ ) and manganese oxide ( $Mn_2O_3$ ) balance the pale blue/green hue. By adding ZnO to the batch and melting with a neutral atmosphere, the hue can be varied from dark amber (0.5% ZnO), to honey amber (0.75% ZnO), to a light hue of blue/green (1.5% ZnO). By adding 2.0% ZnO by weight and 2.0%  $Er_2O_3$  by weight, brown glass can be color balanced to produce a nearly colorless glass. From this base, other colors can be produced with some of the common oxide colorants, such as cobalt, manganese, titanium, and copper.

## Green Bottle Cullet

Green bottle glass gets its color from small amounts of  $Cr_2O_3$  dissolved in the glass. The green color of green bottle cullet is principally due to the chromium ion  $Cr^{3+}$ . A 0.05% of  $Mn_2O_3$  melt yields a neutral hued glass -- that is, the transmittance spectra of the glass is spread out, minimizing predominant spikes in the transmittance curves. With this formulation, the  $Cr^{3+}$  ion is color balanced by the reduction-oxidation equilibrium with  $Mn^{3+}$  ion. Although the glass is neutral, it has a gray smoky hue to it. Chrome has two primary valence states,  $Cr^{3+}$  and  $Cr^{6+}$ , with the  $Cr^{3+}$  state yielding the characteristic emerald (bottle) green. By oxidizing the melt, shifting the chrome redox equilibrium toward  $Cr^{6+}$ , the hue of the glass can be shifted from the intense green to a yellow/green. If a green or blue glass is desired, decolorization may be unnecessary, as the green color of the cullet may be utilized or diluted by combining it with clear glass before colorants are added.

Dark colored glasses can also be produced using green glass without adding manganese oxide. The density of the transparent colors made with green cullet result from the additive properties of coloring ions in solution. The glass is not decolorized but masked with complementary

coloring ions in sufficient quantities to overpower the chrome yielding dense transparent colors.

## Opal Glasses

Both the client and the advisory committee expressed a great deal of interest in creating opal glasses, which generally have higher market values. Fluorine-based opal glasses can be produced using either clear, green, or brown cullet.

Opals may be produced by one of two different methods. The two methods of producing a fluorine-opal glass have extremely different melting and heat treating requirements.

The first method involves adding a phosphoric acid and fluorspar mix. This mix requires very high melt temperatures and high working temperatures, and produces relatively translucent opals. This mix, however, is also highly corrosive to crucibles.

The other method of producing fluorine-based opals is with a high fluorine-content salt called PAF ( $Al_3K_6F_9$ ). PAF is a by-product of the aluminum refining process and contains 30% potassium oxide, 20% alumina, and 49% fluorine. PAF melts fluxed with borax require very low melting temperatures and low working temperatures. Further, PAF melts do not attack refractories as aggressively as do the phosphate-fluorine opals. PAF melts are extremely volatile, however, making it necessary to use an excess of fluorine and to melt and fire the batch as quickly as possible.

From an opal base, many different opal colors can be readily produced. With both clear cullet and green cullet, coloring oxides can be added to the opal bases to produce corresponding opal colors. The oxides that have a tendency to reduce easily need to be stabilized in the melt or they will be reduced.

Fluorine-based opal glasses create a white backdrop for the coloring oxides, making darker colors easier to see. (Similar colors produced without opalizers may appear black.) In the absence of additional coloring oxides, the chrome already present in the green cullet yields an opal

green colored opal glass when opacifying agents are added.

Procedures for melting and heat-treating opal glasses vary widely, and must be fine-tuned for each individual facility.

### **Important Safety Note:**

**The volatilization of fluorine is a serious health hazard.** It is important to keep water out of the batch materials. Water increases the tendency of fluorine to volatilize. Adequate ventilation must be provided when fluorine is used. Fluorine becomes volatile during the melting process. Fluorine is also corrosive to the furnace refractories, frosts the windows in the studio, and is harmful to the lungs.

## **Experimental Procedure**

The prototype melts were designed to simulate the melt conditions at the client's facility. This included procedures for beneficiating the base recycled glass, sourcing glass-maker chemicals, controlling melting conditions, press-forming the final product and annealing the samples. Further, a flexible melt sequence was required to accommodate daily results/failures. Each aspect of the process was fully documented.

### **Source of Glass Cullet**

The glass was obtained from Rabanco at their Seattle plant. Three types of glass (clear, green, and brown) are collected through their curbside recycling program. The glass is presorted into the truck at the curb.

The glass was crushed with a hand-crusher to obtain a cullet sizing of two-inch-minus and washed to remove gross contamination. Ceramics, metals, lead wrappers, and some plastic were also removed. All paper, foils, and other colored glasses were left in the cullet. The debris was weighed to determine the percentage of material that was removed. This was generally less than one percent by weight for all the glass received.

This cullet worked fine for transparent glasses. Repeated trials revealed, however, that two-inch-minus cullet was too coarse for the opal glasses, for reasons that will be discussed below. To produce quality opal colors, the cullet should be pulverized to at least a 150 mesh size.

### **Batch Chemicals**

The majority of the chemicals were sourced from local suppliers, such as the local pottery supply house in Seattle. The chemicals added to the base glasses in the test melts consisted of fluxing agents, coloring agents, and opacifiers.

#### *Fluxing Agents*

Several different fluxes were used to facilitate melting the base glasses, including borax, potash, ( $K_2CO_3$ ) and tin dioxide ( $SnO_2$ ), which acts to keep the colorant in solution. Silicon carbide was added as a batch reducer.

#### *Colorants*

Colorants were added to the batch to either color balance and/or colorize the base glasses. Copper was added as copper carbonate. Cobalt was added as cobalt carbonate, sodium as sodium nitrate, and zinc as zinc oxide. Manganese was introduced as manganese dioxide. The rare-earth ion  $Nd^{3+}$  was introduced as 96% purity neodymium oxide,  $Nd_2O_3$ . Cerium was added as cerium oxide, and titanium as titanium dioxide,  $TiO_2$ .

#### *Opacifying Agents*

Two sets of opacifying agents were used during the laboratory melts to obtain opal colors, as described above. The first used phosphorus and fluorine, added as phosphoric acid,  $H_3PO_4$ , and calcium fluoride,  $CaF_2$  (fluorspar). The second used PAF. In one instance, bone ash was introduced for phosphorous content, replacing phosphoric acid.

### **Melting Procedure**

Each melt day, four separate batches of 25 to 30 pounds each were weighed out and mixed thoroughly. Each batch was charged into separate crucibles in an experimental test furnace that contained four free-standing crucibles, each with a capacity of 30 pounds. The charge cycle was varied according to the glasses being melted. Generally, each crucible was charged regularly at four intervals, with the last two charges being the smallest. The melt temperature was then allowed to

increase slowly for one to two hours to complete the melt. Finally the furnace setting was turned down to allow the glass to slowly cool to the working temperature required the following day. Melting and working temperatures are shown in Figures 1 through 5.

### **Sample Forming**

Samples of each glass formulation were pressed in a hand-press using a patterned four-inch square tile mold. This stage of the process is critical in that this is the stage at which all the working characteristics of the glass determined.

The glass melt was initially gathered in a gob from which a thread was pulled. From the thread pull, an initial read on the viscosity was taken and the temperature was adjusted as required. Once the melt temperature was satisfactory, the tiles were pressed. Thread samples were also pulled to determine the annealing temperature of each formula melt. Set times were short, as desired for pressing molds, between five and ten seconds. The sample tiles pressed each day were annealed through a cooling down cycle of eight hours.

### **Color Contamination**

Cross-contamination was a major concern during the melt progressions. Since the project could not afford a new crucible for every formula, the melts were organized to minimize prior melt contamination. Formulas were sequenced in crucibles that utilized similar colorants and base glasses. For instance, the pot used to melt copper colored opals was initially used to melt transparent colors. Once a sequence ran its course, the crucible was exchanged for a new one. To keep track of contamination, the melt progressions were fully documented with each melt listing the crucible number and prior melt formula number.

### **Color Modification Formulas**

Thirteen target colors were chosen as the most promising, given technical and economic considerations, by the client and review panel, and a total of 45 separate formula melts were conducted during the course of this study in an effort to generate these colors. The colors were specified as follows:

#### *Target Colors for Green Cullet:*

- translucent grape purple
- translucent amethyst
- translucent blue/pink dichromatic
- opal mint green
- opal purple
- opal cobalt blue
- opal turquoise

#### *Target Colors for Brown Cullet:*

- translucent honey amber
- translucent bright red

#### *Target Colors for Clear Cullet:*

- translucent amethyst
- translucent swimpool blue
- dichroic blue/pink
- translucent yellow-green
- translucent honey amber
- opal white

Clear bottle cullet is chemically modified by container manufacturers every day to produce transparent colors. The primary goal of this project was to validate techniques to recolorize green and brown bottle cullet. During the course of this study, only seven or eight of these colors were successfully attained (three of which used clear cullet as a base glass), although it may be possible to attain the remaining colors with minor modifications to the formulas described in this protocol.

The significant trial melts are listed in Tables 1 through 5. The tables are organized according to the type of base glass used. Transparent colors are listed in the first three tables with each table representing a different base color; the last two are the opal glass formulas, which use clear and green bottle cullet, respectively, as base glasses.

The formula number is given for each melt listed, as is the sample number which is composed of the melt day followed by the formula number. Melt temperatures and work temperatures used for each melt are also included in each table. The chemical additions are given in percent

by weight. Base glass percentages are also given by weight.

The color listed at the bottom of each column is the actual color of the sample obtained from the melt. By convention, when describing a transparent glass, 'light' refers to a lightly colored glass, easily seen with a minimum of lighting. 'Dense' is used to refer to a transparent color that is discernible when light is directed through the glass, but appears to be black against a white background. If a color is listed without a qualifier, the color is in between light and dense. In the case of a transparent glass yielding an opaque sample, a phosphate has been used and the melt was not complete.

### **Green-Based Transparent Glasses**

From mixed-green bottle cullet, a series of colors, grape purple, amethyst, steel blue, smoke gray and black, were produced using different proportions of manganese dioxide and cobalt carbonate as colorants with various proportions of green and clear bottle cullet. A sufficient amount of the  $Mn^{3+}$  ion is used to balance the  $Cr^{3+}$  ion, or decolorize the glass. Table 1 lists the melts based on this class of colorization with green bottle cullet.

With the first formulation (sample #17-1/1), a black appearing glass was obtained. When held up to a bright light, a beautiful grape purple can be seen. The successive melts attempted to lighten the color intensity. The next two melts in this sequence cut the colorants to 25-percent and 50-percent of the colorants used in formula 17-1 yielding a dense smoke green and a dense smoke gray, respectively. From these results, it became obvious that the melt was favoring the  $Mn^{2+}$  state which is a weak brown as opposed to the  $Mn^{3+}$  state which is a deep purple. To favor the  $Mn^{3+}$  state, sodium nitrate was introduced in the remaining melts at a ratio of 1.2 times the weight of manganese dioxide pushing the melt into an oxidation state favoring  $Mn^{3+}$  formation. To further lighten the color intensity, formulas 17-5 through 17-7 used a 25/75 mix of green and clear cullet, respectively. By adjusting the colorant proportions, three different transparent colors were obtained; grape purple, amethyst and steel blue. To obtain a light amethyst, the green glass was eliminated and all clear cullet used as shown in formula 17-8.

### **Brown-Based Transparent Glasses**

Using mixed-brown bottle cullet, a honey amber was developed in two ways. By diluting brown cullet with clear according to formula 5-4, a less intense amber is produced. With melt formula 5-3, the S-Fe ligand is completely eliminated with 1.5-percent zinc oxide yielding a light transparent blue/green. By decreasing the percent zinc oxide to 3/4-percent, a nice honey amber is obtained that is very near to the same color as obtained with formula 5-4.

Another set of chemical color modifications were attempted with brown cullet. A dense bright red was attempted by shifting the emission spectra with copper carbonate and phosphoric acid. This produced a copper ruby based color when the S-Fe ligand was eliminated (decolorizing the brown glass) with three percent zinc oxide. The phosphoric acid/copper carbonate combination in formulas 15-1 and 16-1 were difficult to completely melt. With the next melt of formula 15-2, the melt temperature was increased to 2500°F. Still a complete melt could not be obtained; an opaque, grainy glass was the result from these melts. A complete melt was reached when raising the melt temperature to 2600°F. However, this high temperature and darkness of the melt, makes this approach economically unfeasible.

The next trial, formula 15-3 was formulated without phosphoric acid, relying on residual contamination from the prior melt and adding silicon carbide as a batch reducer. With this melt, a partially struck (opal) copper ruby was obtained. For the last trial, formula 15-4 was melted with an increase in copper carbonate and silicon carbide with the addition of bone ash for a source of  $P_2O_5$  oxide. The resultant color was a very dense copper ruby or black.

Additional research is necessary to identify a formula that will successfully yield a bright red colored glass.

### **Clear-Based Transparent Glasses**

Several melts were conducted from a base of clear cullet. These melt formulas are listed below in Table 3.

The first formula listed, formula 1-1, used copper carbonate to obtain a successful swimpool blue. Formula 3-1 was a 50/50 mix of green and clear cullet with neodymium yielding a bluish/green glass. The green cullet

appears to darken or over-power the effects of neodymium.

The next three formula melts, formulas 4-1, 5-1, and 5-2 use titanium dioxide and cerium oxide to develop a series of colors from light yellow/green to honey amber. Formula 4-1 yielded a light yellow/green glass that was quite seedy. The glass seediness is attributable to the 2.5 percent cerium oxide (a foaming agent). With an increase of titanium dioxide in formula melt 5-1, a very light amber was obtained. By increasing the melt temperature in melt 5-2, a nice transparent yellow-green color was obtained.

### **Opal Glasses**

The client and market advisors expressed a high level of interest in glasses capable of reflecting distinctive colors. Thus, an extensive portion of the study examined the fluorine based (opaque) glass modifications. Initially, the formulas developed earlier for transparent glasses were used as baseline formulas for the opal glasses. The two methods of introducing fluorine into these formulas were then tested and formulations were adjusted to obtain the desired colors.

#### *Clear-Based Opal White Glasses*

The client expressed a strong interest in obtaining an opal white. Based on a separate series of test trials, it was determined that a white could not be obtained, within the scope of this project, from brown or green cullet. Therefore, a white opal was formulated using clear bottle cullet as a base glass. These clear based melts are listed below in Table 4.

Two methods of introducing fluorine into the glass were examined. In melt 13b-1, two opacifying agents, phosphorus as phosphoric acid ( $H_3PO_4$ ) and fluorine as fluorspar ( $CaF_2$ ), were used. The effects of the phosphoric acid were similar to those that we had seen during earlier attempts to produce a red transparent glass. Again we had a formula utilizing phosphoric acid that required a melting temperature of 2600°F. A stiff, grainy glass was obtained with a normal 2400°F melt temperature and a 2100°F to 2250°F working temperature. When using a high melt temperature and work temperature, this class of modification yielded a

consistent opal. An opal white was obtained with clear cullet; an opal green was made using green cullet.

To decrease the costs associated with high melting and working temperatures, attempts were also made to develop a white opal using PAF, a complex opacifying agent. Formula melts 13a-1 through 13a-5 were conducted with varying percentages of PAF and melting conditions.

At normal melt temperatures, melt 13a-1, formulated with ten percent PAF, yielded a clear glass sample. In melt 13a-2, the PAF was increased to twelve percent and zinc oxide was added to stabilize the fluorine. Initially, a clear glass sample was obtained from the press. The anneal cycle of the sample was adjusted to check for strike occurring upon heat treatment. The soak temperature was incrementally increased and held for two hours at each increment. At 1000°F with a two hour soak, the samples began to strike, turning a translucent white.

To increase the degree of opalization, the PAF was increased to 18-percent in melt 13a-3. An inconsistent glass was obtained. During sample forming, the glass at the top of the crucible was extremely loose in workability, and yielded a very dense opal sample similar to an enamel white glass. The glass near the bottom of the crucible was very stiff. These samples yielded a clear glass with swirls of opal white. This formulation appeared to have a high tendency to separate with the fluorine concentrating at the top of the crucible. Also, the samples made with this high fluorine content glass were very incompatible and unstable. The samples inherently pull apart in layers following the fluorine striae.

During the melts, it was noted that an extreme amount of discharge from the furnace exhaust was occurring during the PAF melts. To decrease the amount of fluorine being burned off, the melt temperature was lowered in melt 13a-4 and the PAF was backed off to 15-percent. Further, in this melt only, a finely crushed (flour) window glass was used for the base clear glass. This was done to see if the cullet size has any affect on the melt conditions. A lower melt temperature was used yielding a consistent, good working light opal green (whitish mint green).

The final formulation for opal white was melt 13a-5 using 13-percent PAF and melt temperature of 2250°F. Again

we used clear cullet of 2-inch minus simulating the procedures of the client. This melt yielded an inconsistent glass body with fluorine-rich swirls. Again there was a high degree of vapor discharge from the melt and the samples were inherently incompatible.

### *Green-Based Opal Glasses*

PAF melts with various coloring agents such as copper carbonate, chromium, and cobalt carbonate were conducted using green bottle cullet as the base glass. The approach was similar to the approach used to produce the clear-based opals.

Green-based copper PAF formula samples 8-1/4, 8-2/5 and 8-3/6 (not shown in tables) were melted at the same time as the opal whites, melts 13a-1/4, 13a-2/5 and 13a-3/6 described previously. Melt 8-1/4 with ten percent PAF and no zinc oxide yielded a dense transparent green, no fluorine strike, similar to the clear in melt 13a-1/4. The next melt, melt 8-2/5, was twelve percent PAF and 1.5-percent zinc oxide, and exhibited a heavy reduced copper ( $\text{Cu}^0$ ) state and a white fluorine swirl. As with white melt 13a-3/6, melt 8-3/6 was formulated with 18-percent PAF and 1.5-percent zinc oxide, using the two-inch-minus cullet. Again, the green-based copper PAF performed similar to the white sample, exhibiting extreme separation with the top of the batch being extremely rich in fluorine and the bottom being the color of the base glass.

For the last three days of PAF melts (days seven, eight and nine), attempts were made to obtain other consistent opal colors. The same approach used for the green-based transparent colors was used to obtain green-based opal colors. Blue and purple were obtained with cobalt and manganese, respectively. A turquoise was produced in melt 78-1/9 with copper and cobalt.

With formula #10 run each of the last three PAF melt days, the green cullet's chromium,  $\text{Cr}^{3+}$  state, was used as an inherent colorant to obtain an opal mint green. With melt 10-1/7, a PAF content of 15-percent was melted at normal temperature (2400°F). The next melt 10-1/8, the PAF content was kept constant and the melt temperature lowered to 2250°F. The final melt 10-2/9 had 13-percent PAF and melted again at 2250°F. As with the melts of the opal white, all three of these melts showed a tendency

to separate. At the top of each melt, fluorine-rich striae samples were obtained. As the glass samples came from a lower level in the crucible, less dense striae of fluorine appeared in a dense transparent green base.

In all of the trials in this category, the fluorine exhibited a tendency to separate in the melt, producing inconsistently colored tiles with streaks and swirls. It was concluded, therefore, that a finely pulverized base glass is critical to obtaining a consistent (well blended) melt.

## **Conclusion**

Pre-sorted post-consumer bottle glass can be readily remelted and chemically modified to produce a wide variety of colors. Test trials demonstrated that brown cullet can be decolorized to a nearly colorless, neutral hue, and then recolorized into transparent colors. Green cullet was color balanced using manganese, and then recolorized into other relatively dense transparent colors. Further research is required to obtain lighter green-cullet based transparent colors.

The results of this study suggest that it is also possible to generate a wide range of opal colors from green, brown, or clear cullet. Each color formula must be developed on site, however, to make adjustments for workability, color concentration, color hue, melt redox equilibrium, melting environment and raw material sourcing. Strict control over the melting, forming and annealing processes is also required, whether using phosphate-fluorine opacifiers or the alumina-fluorine opacifiers. Minimizing melt times will help to reduce fluorine volatilization.

For the various green-based colored opals and the clear-based white opals, the fluorine was difficult to blend, and separated in the melt, using two-inch-minus cullet. Several attempts were made to improve the melt conditions and arrive at appropriate PAF concentrations. The best results were obtained using a 150 to 200 mesh pulverized glass sand and a shortened melt time. If these adjustments are made, a whole set of opal colors can be obtained from recycled glass

The transparent glass formulas produced relatively consistent and satisfactory results. Successful formulas were developed for producing grape purple, amethyst, honey amber, swimpool blue, and yellow-green colors. The only transparent color that was not successfully attained was bright red.

Further trials with brown cullet could yield better results by adding additional agents to neutralize the brown cullet.

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Ro Purser (Langley, WA) provided a prototype press to press the formula melts. Initial test melts and spectral analyses were conducted by Don McPherson of Bay Glass Research, Berkeley, CA. The prototype melts were conducted at the Randal Dalbey's glass products development facility in Seattle, WA.

**Table 1:  
Formulas for Green-Based Transparent Glasses**

Formula #	17-1	17-3	17-4	17-5	17-6	17-7	17-8
<b>Objective Color</b>	Grape Purple	Grape Purple	Grape Purple	<b>Grape Purple</b>	Grape Purple	<b>Amethyst</b>	Amethyst
<b>State</b>	Transp.	Transp.	Transp.	<b>Transp.</b>	Transp.	<b>Transp.</b>	Transp.
<b>Melt Temp</b>	2400 <sup>o</sup> F	2400°F	2450°F	2400°F	2420°F	2420°F	2450°F
<b>Work Temp</b>	2250°F	2090°F	2070°F	2180°F	2120°F	2190°F	2070°F
<b>Melt Atmosphere</b>	Oxidation	Oxidation	Oxidation	Oxidation	Oxidation	Oxidation	Neutral
<b>Clear cullet</b>				60.5%	63.8%	63.8%	85.5%
<b>Green cullet</b>	80.3%	81.0%	80.8%	20.2%	21.3%	21.3%	
<b>Borax (10mole)</b>	16.4%	16.4%	16.4%	16.4%	8.2%	8.2%	8.2%
<b>Zinc Oxide</b>	3.0%	3.0%	3.0%	3.0%	3.0%	3.0%	3.0%
<b>Potash</b>	8.8%	8.8%	8.8%	8.8%	8.8%	8.8%	8.8%
<b>Manganese Dioxide</b>	1.1%	0.275%	0.55%	0.55%	0.275%	0.385%	0.275%
<b>Cerium Oxide</b>	1.0%	1.0%	1.0%	1.0%	1.0%	1.0%	1.0%
<b>Cobalt Carbonate</b>	0.032%	0.008%	0.016%	0.032%	0.022%	0.016%	
<b>Sodium Nitrate</b>				0.66%	0.33%	0.462%	0.33%
<b>Sample No.</b>	<b>17-1 /1</b>	<b>17-3 /3</b>	<b>17-4 /4</b>	<b>17-5 /5</b>	<b>17-6 /6</b>	<b>17-7 /7</b>	<b>17-8 /11</b>
<b>Sample Color Results</b>	Black to Dense Purple <sup>2</sup>	Dense Smoky Green	Dense Smoky Gray <sup>3</sup>	<b>Dense Grape Purple</b>	Steel Blue	<b>Dense Amethyst</b>	Amethyst
<b>Translucent</b>	semi	yes	yes	yes	yes	yes	yes

<sup>2</sup> The tile produced was very similar in both color and translucency to Spectrum® medium purple Cathedral color #146W.

<sup>3</sup> The smoky gray tile produced was slightly more yellowish in hue but similar in intensity to Spectrum® pale gray Cathedral color #180.8W.

**Table 2: Formulas for Brown-Based Transparent Glasses**

Formula #	5-3	5-4	5-5	15-1	16-1	15-2	15-3	15-4
<b>Objective Color</b>	Honey Amber	<b>Honey Amber</b>	<b>Honey Amber</b>	Bright Red	Fuschia Red	Bright Red	Bright Red	Bright Red
<b>State</b>	Transp.	<b>Transp.</b>	<b>Transp.</b>	Transp.	Transp.	Transp.	Transp.	Transp.
<b>Melt Temp</b>	2450°F	2350°F	2350°F	2400°F	2500°F	2500°F	2450°F	2350°F
<b>Work Temp</b>	2070°F	2250°F	2250°F	2200°F	2280°F	2280°F	2070°F	2250°F
<b>Melt Atmosphere</b>	Neutral	Neutral	Neutral	Oxidation	Neutral	Neutral	Neutral	Neutral
<b>Clear cullet</b>	23.9%	48.5%						
<b>Brown cullet</b>	71.7%	48.5%	96.3%	84.9%	84.9%	84.9%	90%	90%
<b>Borax (10 mole)</b>	5.5%	8.2%	8.2%					
<b>Zinc Oxide</b>	1.5%		0.75%	3.0%	3.0%	3.0%	3.0%	3.0%
<b>Potash</b>				8.8%	8.8%	8.8%	8.8%	8.8%
<b>Tin Dioxide</b>				1.0%	1.0%	1.0%	1.0%	1.0%
<b>Copper Carbonate</b>				0.14%	0.07%	0.14%	0.14%	0.35%
<b>Cobalt Carbonate</b>					0.08%			
<b>Silicon Carbide</b>							0.04rw%	0.11rw%
<b>Phosphoric Acid (75%)</b>				9.2%	9.2%	9.2%	prior melt residual	
<b>Bone Ash</b>								0.25rw%
<b>Sample No.</b>	5-3 /11	5-4 /12	5-5 /12	15-1 /3	16-1 /10 <sup>4</sup>	15-2 /10	15-3 /11	5-3 /11
<b>Sample Color Results</b>	Light Green	<b>Honey Amber</b>	<b>Honey Amber</b>	Opaque Blood Red	Opaque Copper Blue (very grainy)	Opaque Blood Red (swirly)	Transparent blue/green w/ some Cu Ruby strike	Very Dense Cu Ruby (Black)
<b>Translucent</b>	yes	yes	yes	no	no	no	yes	no

<sup>4</sup> The opaque copper blue tile produced (#16-1) was less translucent but similar in color to Spectrum® dark blue Cathedral color #136s.

**Table 3: Formulas for Clear-Based Transparent Glasses**

Formula #	1-1	3-1	4-1	5-1	5-2
<b>Objective Color</b>	<b>Swimpool Blue</b>	Dichroic Blue/Pink	Yellow Green	<b>Honey Amber</b>	<b>Yellow Green</b>
<b>State</b>	<b>Transparent</b>	Transparent	Transparent	<b>Transparent</b>	<b>Transparent</b>
<b>Melt Temp</b>	2400°F	2500°F	2400°F	2450°F	2500°F
<b>Work Temp</b>	2250°F	2280°F	2250°F	2070°F	2280°F
<b>Melt Atmosphere</b>	Oxidation	Neutral	Oxidation	Oxidation	Neutral
<b>Clear cullet</b>	79.8%	37.8%	80.3%	71.4%	71.4%
<b>Green cullet</b>		37.8%			
<b>Borax (10mole)</b>	16.0%	27.4%	16.4%	6.85%	6.85%
<b>Zinc Oxide</b>	5.0%				
<b>Potash</b>	8.8%		8.8%	22.1%	22.1%
<b>Cerium Oxide</b>			2.5%	2.5%	2.5%
<b>Copper Carbonate</b>	0.7%				
<b>Neodymium</b>		10%			
<b>Titanium Dioxide</b>			2.5%	7.5%	7.5%
<b>Sample No.</b>	<b>1-1 /1</b>	<b>3-1 /10</b>	<b>4-1 /3</b>	<b>5a-1 /4</b>	<b>5-2 /10</b>
<b>Sample Color Results</b>	<b>Swimpool Blue<sup>5</sup></b>	Light Green to Blue-Green <sup>6</sup>	Light Yellow to Yellow-Green	<b>Light Amber to Clear</b>	<b>Light Yellow to Yellow-Green</b>
<b>Translucent</b>	yes	yes	yes	yes	yes

<sup>5</sup> The tile produced was very similar in both color and intensity to Spectrum® medium blue Cathedral color #533-1s.

<sup>6</sup> The tile produced was not opaque but similar in color to Spectrum® medium green color #823-72s.

**Table 4: Formulas for Clear-Based Opal White Glasses**

Formula #	13b-1	13a-1	13a-2	13a-3	13a-4	13a-5
<b>Objective Color</b>	Opal White	White	White	White	White	White
<b>State</b>	Opal	Opal	Opal	Opal	Opal	Opal
<b>Melt Temp</b>	2400°F	2450°F	2400°F	2420°F	2250°F	2250°F
<b>Work Temp</b>	2250°F	2070°F	2100°F	2120°F	1940°F	1950°F
<b>Melt Atmosphere</b>	Oxidation	Oxidation	Oxidation	Oxidation	Oxidation	Neutral
<b>Clear cullet</b>	84.2%	85.7%	83.6%	77.6%	78%*	82.6%
<b>Borax (10mole)</b>	8.2%	8.2%	5.5%	5.5%	5.5%	5.5%
<b>Zinc Oxide</b>			1.5%	1.5%	1.5%	1.5%
<b>Fluorspar</b>	8.85%					
<b>Phosphoric Acid (75%)</b>	7.36%					
<b>PAF (Al<sub>3</sub>K<sub>6</sub>F<sub>9</sub>)</b>		10%	12%	18%	15%	13%
<b>Sample No.</b>	<b>13b-1 /1</b>	<b>13a-1 /4</b>	<b>13a-2 /5</b>	<b>13a-3 /6</b>	<b>13a-4 /8</b>	<b>13a-5 /9</b>
<b>Sample Color Results</b>	Grainy White (opal at 2600°F)	Clear (no strike)	Translucent Opal White	Opal White (separation)	Light Opal Green <sup>7</sup>	Light Opal White (separation)
<b>Opaque</b>			no	yes	yes	yes

<sup>7</sup> The tile produced was similar in both color and intensity to Spectrum® green #325-2s.

**Table 5: Formulas for Green-Based Opal Glasses**

Formula #	10-1	10-1	10-2	12-1	12-2	12-3	7-2	78-1
<b>Objective Color</b>	Mint Green	Mint Green	Mint Green	Purple	Purple	Purple	Cobalt Blue	Turquoise Blue
<b>State</b>	Opal	Opal	Opal	Opal	Opal	Opal	Opal	Opal
<b>Melt Temp</b>	2420°F	2250°F	2250°F	2420°F	2250°F	2250°F	2250°F	2250°F
<b>Work Temp</b>	2190°F	1900°F	1950°F	2190°F	1900°F	1950°F	1900°F	1950°F
<b>Melt Atmosphere</b>	Oxidation	Oxidation	Neutral	Oxidation	Oxidation	Neutral	Oxidation	Neutral
<b>Clear cullet</b>						60.6%		
<b>Green cullet</b>	80.6%	80.6%	82.6%	80.6%	81.3%	20.2%	78.8%	83.1%
<b>Borax (10mole)</b>	5.5%	5.5%	5.5%	5.5%	5.5%	5.5%	5.5%	5.5%
<b>Zinc Oxide</b>	1.5%	1.5%	1.5%	1.5%	1.5%	1.5%	1.5%	1.5%
<b>Manganese Dioxide</b>				1.1%	0.385%	0.385%		
<b>Copper Carbonate</b>								0.7%
<b>Cobalt Carbonate</b>				0.08%	0.016%	0.016%	0.16%	
<b>Sodium Nitrate</b>						0.42%		
<b>PAF (Al<sub>3</sub>K<sub>6</sub>F<sub>9</sub>)</b>	15%	15%	13%	15%	15%	13%	14%	12%
<b>Sample No.</b>	<b>10-1 /7</b>	<b>10-1 /8</b>	<b>10-2 /9</b>	<b>12-1 /7</b>	<b>12-2 /8</b>	<b>12-3 /9</b>	<b>7-2 /8</b>	<b>78-1 /9</b>
<b>Sample Color Results</b>	Opaline Green <sup>8</sup> (separation)	Mint Green (separation)	Opaline Green (separation)	Dense Blue (separation)	Pinkish Brown	Mauve (separation)	Cobalt Blue (swirly)	Turquoise <sup>9</sup> w/ some white swirls
<b>Opaque</b>	yes		yes				yes	no

<sup>8</sup> The tile produced was very similar in both color and translucency to Spectrum® green Cathedral color #329-1s.

<sup>9</sup> The cobalt blue tile (#7-2) was denser but similar in color to Spectrum® blended medium blue color #533-1W.