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Liquid Flame Spraying for Glass Coloring

K.A. Gross, J. Tikkanen, J. Keskinen, V. Pitkänen, M. Eerola, R. Siikamaki, and M. Rajala

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The liquid flame spraying process has been developed to uniformly color hot glass objects. A solution consisting of a metal nitrate dissolved in alcohol or water is fed to an oxyfuel torch and atomized in the flame. The liquid evaporates from the droplet, and subsequent reactions produce metals or metallic oxides that impact the hot glass surface. Flame spraying of Co, Cu, and Ag solutions onto soda-lime silica glass at 900 to 1000 °C have produced blue, blue-green, and yellow colors. Typical spraying times are 5 to 20 s. Other colors have been produced by using a combination of transition metal ions. This method has found application in studio production and in volume manufacturing of glassware.

Keywords atomization, coloring, glass technology, impactor, nanoparticles, pyrolysis

1. Introduction

Color in glass has industrial significance in producing an item with the desired appearance. Crown glass, typically used for window panes and bottles, exhibits a slight green color. This is attributed to the iron impurity in the glass, which, when present as Fe^{2+}, preferentially transmits green light. The addition of manganese oxide can remove this effect by partially undergoing reduction while forcing an oxidation of the ferrous iron to a ferric state. The coloring effect of the remaining ferrous irons is removed as the manganese produces a purple color; thus providing a complementary color resulting in a uniform absorption across the spectrum (Ref 1). This example of removing a certain color is important in the glass industry when working with impure source materials. Significant effort, however, is directed at producing coloring effects.

Materials that produce color in glasses can be broadly classified into two groups. The first group includes transition metallic oxides that enter glasses in true solution form. The resulting color depends on how the nature of the glass and coordination of the metallic constituents affects the energy level of the electrons (Ref 2, 3). A blue color, thus, is obtained by adding cobalt to a soda-lime-silica glass; however, pink is observed in phosphate glasses. Light with a wavelength corresponding to the electronic transition of the metal ion is absorbed, imparting a color that is made up of the remaining wavelengths in the visible spectrum (Ref 4). The intensity of the color is dictated partly by the intrinsic absorption of each transition metal (Table 1) and the concentration of the metal in the glass.

Colloidal or striking glasses typically produce colors with a longer wavelength such as red, orange, and yellow. The striking process refers to the necessity to reheat the glass for nucleation of crystals. Diffraction from the colloidal particles then produces the coloring effect (Ref 2, 4). The colored glasses produced in the work for this article employed both coloring mechanisms.

Colored glasses are usually made in devoted glass furnaces where the composition is fixed. The number of colors available is, therefore, dictated by the number of glass furnaces. Furthermore, a change of glass color requires the furnace to be cooled and, possibly, the replacement of the refractory lining. A long homogenization time is typically required to establish a uniform color throughout the glass tank. This leads to a delay in the production cycle associated with glass color changes.

Coatings represent a faster means of producing a colored article. In the Middle Ages, copper (Cu) and silver (Ag) were diffused into the surface of a colorless glass to produce a red or yellow stained glass window (Ref 1). Today, many processes are available for modifying the surface. For a glass artist, simple techniques exist such as the addition of a transition metal oxide powder or the melting of a colored glass rod onto the surface of a hot glass article. Several colors can be applied to a single glass article in this fashion. Uniformity of coloring a surface, however, cannot be achieved easily using these methods. Tikkanen et al. (Ref 5) thermally sprayed colored glass particles onto hot glass objects and achieved deeply colored surfaces (Fig. 1; see cover of journal for color version). The uniformity of the color was in part dictated by the size of the glass particles, 20 to 120 μm. Periods of a day at high temperatures (between 500 and 600 °C) were required to allow diffusion to produce a more even concentration on the surface while the residual stress was re-

Table 1 Intrinsic coloring ability of different transition metals based on Ligand theory (Ref 4).

Coloring ion	Absorption coefficient	Coordination	Color
Co^{2+}	30-45	Tetrahedral	Intense violet blue
Ni^{2+}	14	Octahedral	Yellow, brown
Fe^{2+}	9	Octahedral	Blue green
Cr^{3+}	6	Octahedral	Green
Cu^{2+}	3	Octahedral	Blue, green
Fe^{3+}	0.3-1	Tetrahedral	Pale yellow-green

The corresponding colors produced by transition metals in soda-lime-silicate glasses is given to show the range of colors that is possible.

K.A. Gross, J. Tikkanen, J. Keskinen, and **V. Pitkänen**, Department of Physics, Tampere University of Technology, Box 692, FIN 33101 Tampere, Finland; and **M. Eerola, R. Siikamaki,** and **M. Rajala,** University of Art and Design, Faculty of Ceramics and Glass Design, Hämeentie 135C, FIN 00560, Helsinki, Finland. K.A. Gross is presently at Department of Materials Engineering, Monash University, Clayton, VIC 3168, Australia. Contact e-mail: karlis.gross@eng.monash.edu.au.

lieved. Such a long duration could be overcome by depositing a thinner layer of colored glass. Since the coloring is dependent on the effective diffusion of the metallic ions into the glass, thermal spray methods capable of depositing material more uniformly at a high temperature could be used. This article addresses the use of liquid flame spraying for producing colored glass in glass-shop and factory settings.

2. Methods and Materials

2.1 Flame Spraying

A flame spray torch was designed to deliver liquid axially to the flame through a needle with a 1.5 (internal) and 2.5 mm (external) diameter. Hydrogen gas flowing at 40 L/min circumferentially around the needle was used to atomize the liquid and act as the fuel gas. Flow rates slower than this produce a larger droplet size and were not used (Ref 6). Oxygen gas delivered through a larger eccentric ring was added in a stoichiometric quantity to produce a neutral flame. Two torches were used simultaneously to increase the feed rate of the solution.

The droplet diameter is dependent upon the atomizing gas velocity, liquid viscosity, liquid surface tension, liquid feed rate, and internal diameter of the needle. It was determined that the mean droplet diameter was 20 μm for water but 10 μm for methanol when a feed rate of 3.3 mL/min was selected. Methanol was selected as the preferred solvent. The lower surface tension of methanol compared to water allows a finer droplet size to be atomized. Consequently, a smaller droplet size promotes faster evaporation of the solvent before decomposition of the metal salt at higher temperatures. Because the rate-limiting step during evaporation of the droplet is the solute diffusion (Ref 7), methanol can be transported more quickly to the droplet surface to facilitate droplet shrinkage.

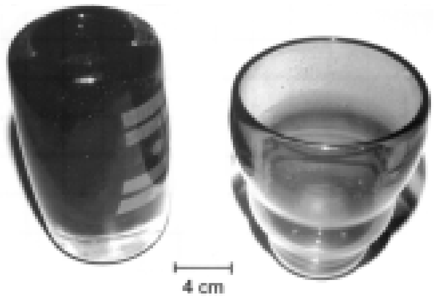


Fig. 1 Glass articles made by spraying blue glass powder. The article on the left has been flame sprayed with cobalt-containing glass and subsequently with copper. A mottled effect can be observed in the vase on the right. (See the front cover of this issue to see this figure printed in color.)

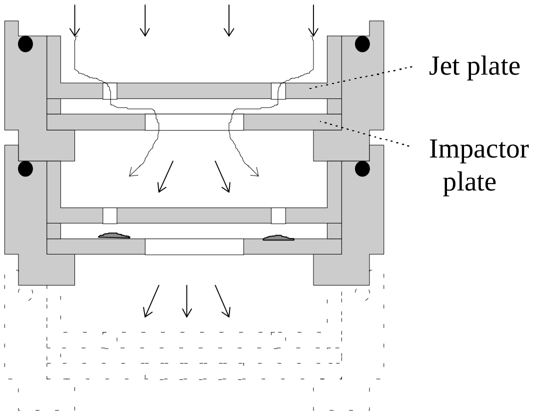


Fig. 2 A section of an impactor showing three stages, each stage consisting of a jet plate through which fluid passes, and an impactor plate, where particles above a critical particle size are collected. Small deposits on the second impactor stage show where powder is collected.

Metallic salts dissolved in methanol or water were delivered as liquids to the torch. The choice of metallic salt was dictated by its solubility in methanol or water and a low decomposition temperature. A more soluble salt implies a greater mass transfer rate from the solution to the target. Chlorides, carbonates, sulfates, hydroxides, and nitrates were considered. Metallic nitrates satisfy the above criteria. Cobalt and copper nitrates were dissolved in methanol, but water was chosen as the solvent for silver nitrate.

Liquid flame spraying was used for the production of metal oxide particles that were in turn used to manufacture colored glass articles in a glass shop and glass bowls on an automatic assembly line with a gob feeder machine. The resulting particles produced within the flame were collected and analyzed with a ten-stage low-pressure impactor. The mass distribution, phase composition, and morphology of the powders could then be determined. Characterization methods are discussed in more detail in subsequent sections.

For making vases in the glass shop, a metal pipe inserted into the glass furnace was used to remove a gather of glass. The gob was shaped to a cylindrical form, and an air pocket was introduced by blowing into the pipe. A second gather was used to increase the size of the workpiece. The glass article was then heated in a gas-operated glass heater (also known as a glory hole) to increase the temperature and, hence, the workability of the glass. The liquid flame spray torch at a stand-off distance of 10 cm then applied a layer of fine particulate to the glass surface for a period of 10 to 20 s as the glass article was slowly turned. This was followed by more heating in the glory hole (to facilitate diffusion into the glass), and a second gather of glass was added on the outside to make up the final mass of the workpiece. After several forming stages in a wooden mold, the cylinder was placed into an annealing furnace at 510 °C for 8 h and furnace cooled overnight.

Liquid spraying was also adapted to an automated gob feeder in a factory setting. A gob of glass fell into a metallic mold, which, on rotation, produced a bowl form. The liquid flame spray torch then sprayed the inside of the bowl with a cobalt nitrate solution for a period of 5 s. A period of less than 10 s remained before the glass was cooled with air jets, ejected from the mold, and then forwarded to an annealing furnace.

2.2 Powder Collection

A Berner-type low pressure impactor (Ref 8) positioned 20 cm from the torch was used to collect powder produced within the flame. The sample was taken through a short, straight, and thin walled tube. Sampling was not isokinetic. The impactor consists of ten stages, each with a jet plate and an impaction plate. Aerosol particles suspended in hot gas pass through a nozzle in the jet plate. The heavier particles with more inertia impact the aluminum foil placed onto the collector (or impactor) plate, but lighter particles are deflected and follow the streamlines to the next stage (Fig. 2). Classification takes place on the basis of aerodynamic diameter. Thus, a denser particle of a given size will be collected earlier in the impactor than a lighter particle of the same size. Each stage has successively smaller nozzle diameters in the jet plate, allowing particles to be collected between 20 nm and 20 μm. The cascade impactor was heated to 150 °C during collection to avoid condensation of the steam produced within the flame. After cooling, the aluminum foils seated on the collector plate were weighed to determine the distribution of the collected powder. Impactor cut sizes were recalculated for the sampling conditions.

2.3 Characterization Techniques

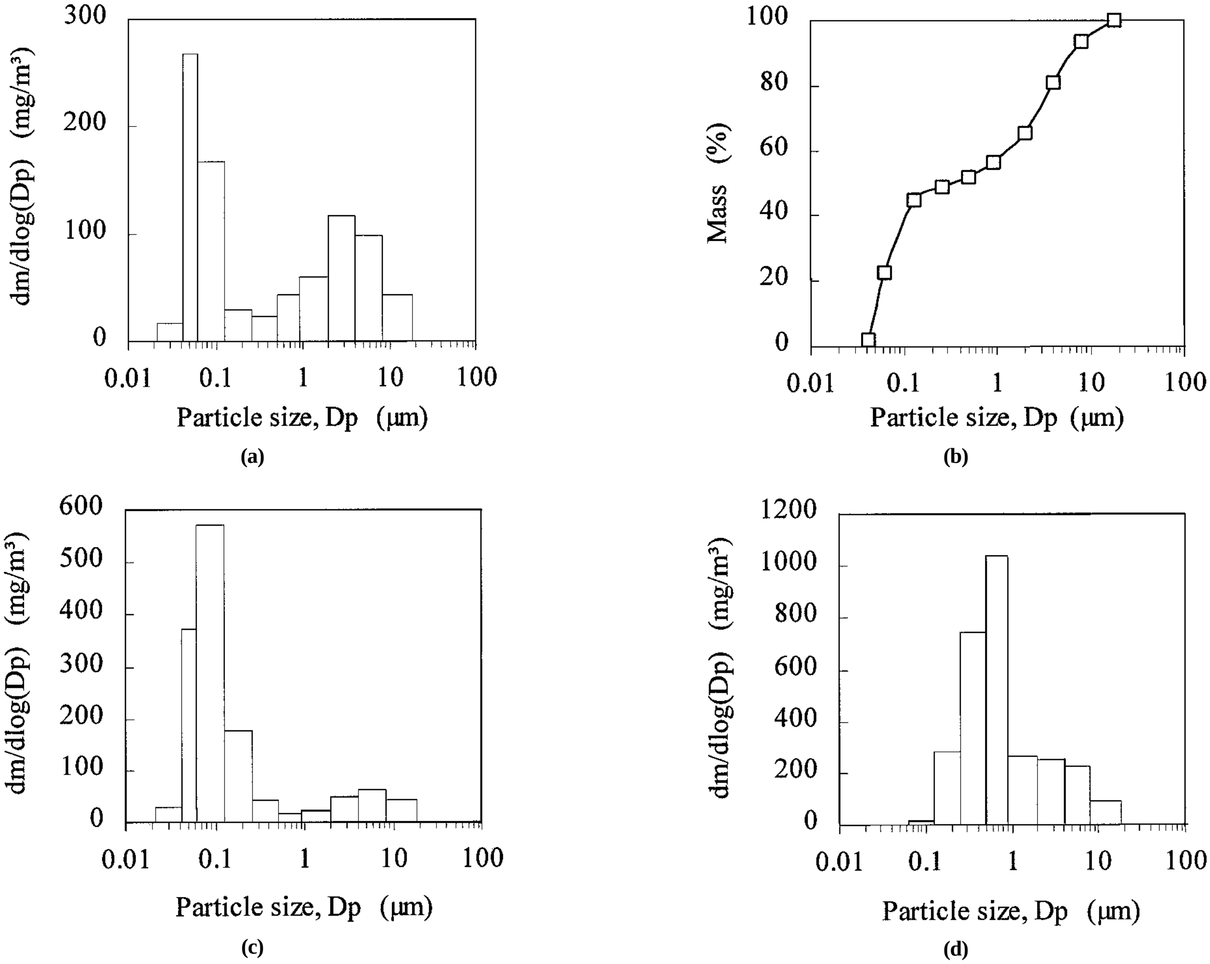
Powder was analyzed using x-ray diffraction (XRD) and scanning electron microscopy (SEM). The powder was removed from the collection foils and fixed to a plate with adhesive. Copper Kα1 radiation was used in a Philips (The Netherlands) XRD, and the pattern was collected using a sampling time of 1.5 s for every 0.1° step. An angular range of 30 to 80° was investigated. Samples were coated with carbon and then examined with the Philips XL30 SEM (The Netherlands) at an accelerating voltage of 20 kV.

The intensity of the coloring and the absorption spectra were measured using a Lambda 2 UV/VIS spectrophotometer (Perkin-Elmer Corp., Norwalk, CT). The light transmission was measured in reflection and employed an RSA-PE-20 reflectance spectroscopy accessory.

3. Results and Discussion

3.1 Characterization of Particles

Liquid flame spraying of metallic nitrates nebulized into the flame and produced a bimodal particle size distribution (Fig. 3). Use of a cobalt nitrate solution resulted in a particle size centered at 50 nm and 3 μm (Fig. 3a). The fine particles contribute a total of 50% of the total mass (Fig. 3b). Spraying of copper nitrate produced the same two particle ranges (Fig. 3c), but 85 wt% of powder consisted of finer particles. Silver nitrate sprayed into the flame produced a smaller separation between the two peaks. Particle size was mainly centered about 800 nm (Fig. 3d).



(a)

(b)

(c)

(d)

Fig. 3 Weight distributions [*dm*/*d*log(Dp)] of particles collected in the low pressure impactor after spraying (a) cobalt nitrate, (c) copper nitrate and (d) silver nitrate solutions. The weight distribution shows whether more than one particle mode is present. The cumulative mass distribution of cobalt nitrate is shown in (b).

Analysis of particles centered at 3 μm, produced by liquid flame spraying of cobalt nitrate, revealed that the peaks corresponded mainly to CoO with a trace of Co_3O_4 and with the main peak being positioned to the right of the CoO peak at 36.8° (Fig. 4a). This suggests that methanol was released by combustion, and the high temperatures within the flame removed both structural water and nitrates by decomposition to produce cobalt oxide. The duality of the oxidation state of cobalt in Co_3O_4 could be attributed to the deficiency of oxygen within the core of the particle.

The finer powder (less than 0.2 μm) was not analyzed due to an insufficient quantity for XRD. It is believed that the finer mode is (feasibly) generated through evaporation of the metal in reducing conditions. Reducing conditions are caused by the use of hydrogen gas as the fuel gas and methanol as the solvent. When evaporated metal reaches the flame perimeter where the oxygen gas concentration is high, the vapor becomes oxidized, thus producing a dramatic decrease in the vapor pressure. This causes nucleation into very fine particles and consequent growth by coagulation and condensation. When methanol solvent is used, the burning particle creates a reducing local atmosphere. In this case, the particle generation process is well described by Helble (Ref 9).

X-ray diffraction of particles (approximately 800 nm) produced by spraying silver nitrate showed that the product was silver (Fig. 4b). The reaction was able to proceed to a further stage. Decomposition occurs at a relatively low temperature (at 440 °C in oxidizing conditions) (Ref 10), but at 600 °C in reducing conditions (Ref 11). Furthermore, silver nitrate has no structural water, like cobalt nitrate, and thus requires less energy from the flame for decomposition. Silver nitrate can be directly decomposed to metallic silver at the flame temperatures. It seems plausible that silver nucleates as pure metal. Compared to gas phase oxidation, the temperature drop in the flame would produce a much lower supersaturation and, thus, a lower number of particles, which would grow with time, would be nucleated. The difference in the particle size compared to cobalt nitrate can additionally be attributed to the difference in particle density. Silver, with a density of 10.5 g/cm^3, would impact earlier in the impactor than cobalt oxide, with a density of about 7.1 to 7.4 g/cm^3.

Large droplets traversing through the flame have insufficient time to undergo the decomposition reaction. This could arise

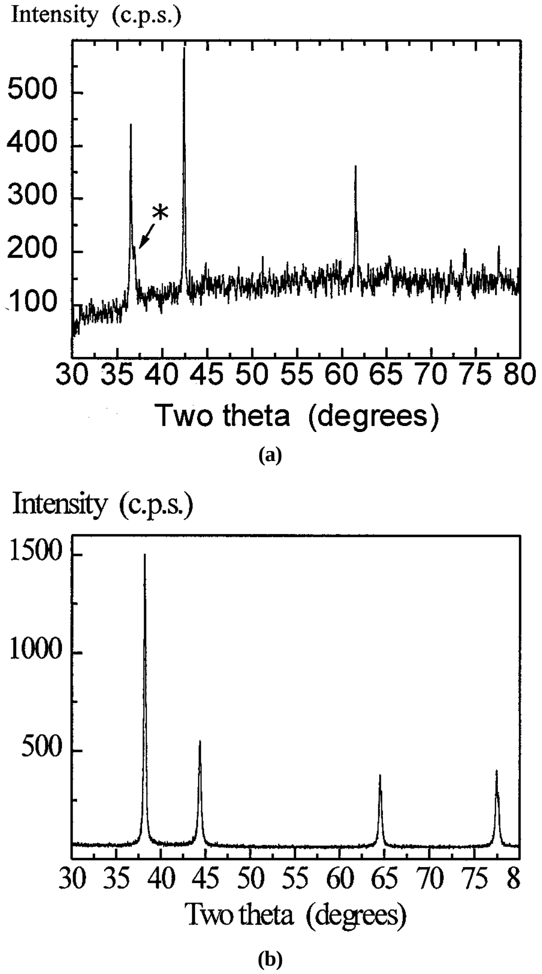


Fig. 4 X-ray diffraction patterns of (a) the 5 to 10 μm powder, consisting mainly of CoO, collected after spraying cobalt nitrate dissolved in methanol and (b) the 0.6 μm silver powder, produced by spraying silver nitrate dissolved in water. The asterisk in (a) represents Co_3O_4.

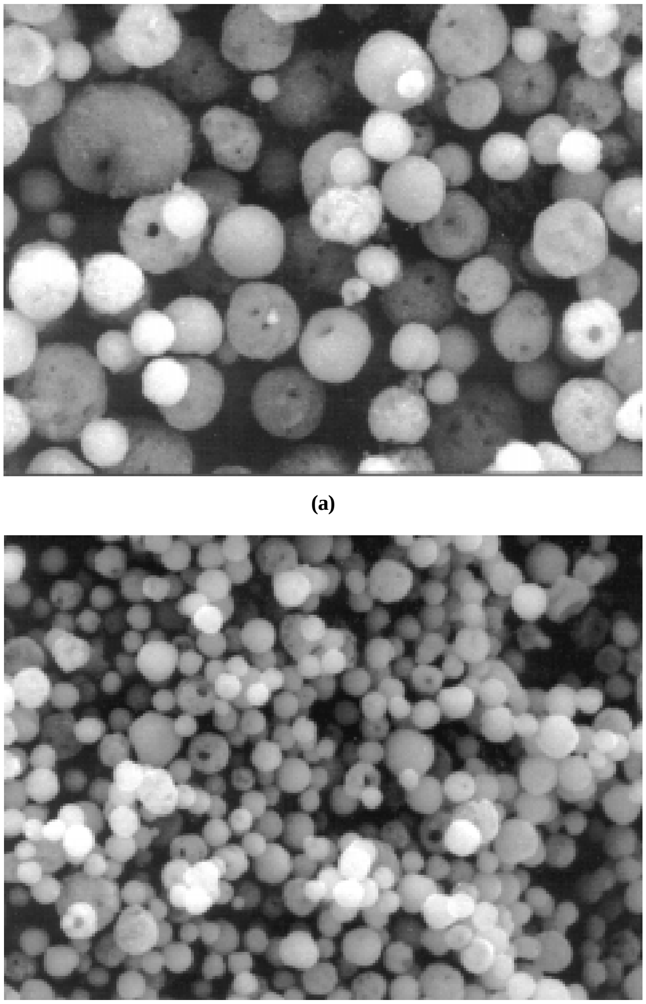
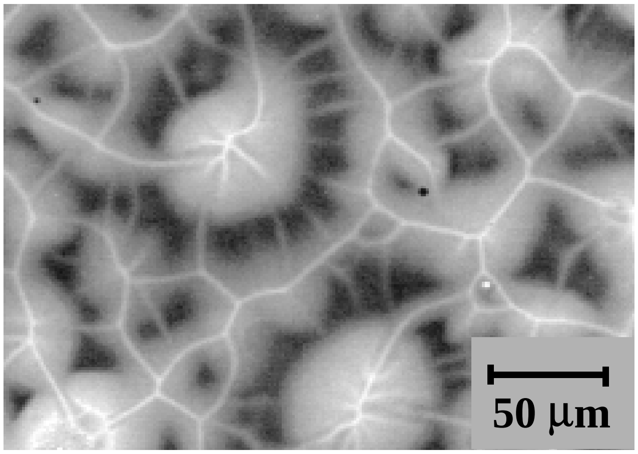


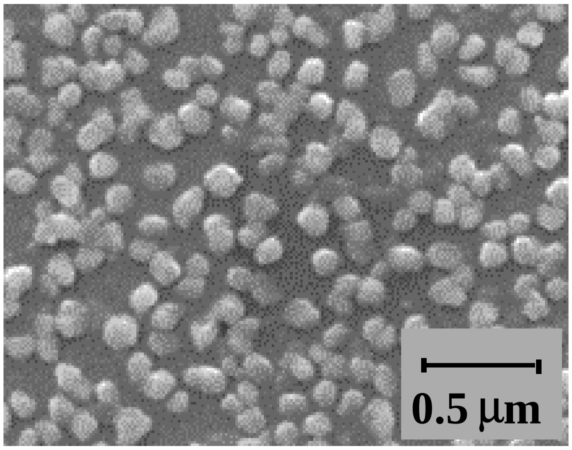
Fig. 5 Cobalt oxide powder collected in (a) stage 8 and (b) stage 9 of the impactor

from droplets being dispersed in a cooler region of the flame or from a consumption of the available flame heat from an excessively high localized droplet concentration. The skin can undergo decomposition, but the core of the droplet will consist of unreacted product, possibly with some evolved gases. Trapped gases from smaller particles can escape by forming a blowhole, giving the particle a resemblance to a doughnut. Alternatively, small pinholes can be formed uniformly on the surface as a result of slower heating and cooling conditions (Fig. 5). Similar morphological features have been observed in spray dried particles where an organic binder is typically released from the drying particle (Ref 12, 13).

Smaller droplets decompose at an earlier stage, allowing the pores to be removed by a process of densification within the flame. The extent of the densification stage then depends on the temperature and time of the particle within the flame. The porosity, therefore, depends on the mechanism of particle formation. If gases are evolved from the droplet, leaving the metallic oxide, then the porosity would be a characteristic of the gas escape path.



(a)



(b)

Fig. 6 Surface of liquid sprayed glass showing (a) deposition of a droplet containing unreacted products in the core and (b) the 100 nm sized particulate that uniformly covers the surface. The jagged nature of the ultrafine particles indicates insufficient diffusion time.

3.2 Coloring of Glass

Liquid flame spraying onto glass at 900 °C for 5 s at a high liquid feed rate (>10 mL/min) produces a grayish-blue appearance, even after annealing at 500 °C for 12 h. The discoloration occurs from one of two sources. Firstly, the coverage of flattened particles on the surface decreases the light transmission and, hence, results in a dull surface. Alternatively, the color could arise from an oxide such as Co_3O_4 that is naturally black in appearance. Observation of the surface with SEM indicates islands with folds in the surface. These areas do not appear to have diffused into the glass (Fig. 6a). Assuming that the molten droplet flattens to 5 times the original particle diameter (Ref 14), the size of the original molten droplets can be calculated. The larger lamellae observed in Fig. 6(a) have been produced by particles approximately 5 to 10 μm in size, in agreement with the larger size of the bimodal distribution in Fig. 3(a).

The effect of liquid feed rate on the finer-particle size range is such that a sixfold-higher feed rate will produce a particle twice as large (Fig. 7). Typical solution feed rates for producing a blue color correspond to about 3.3 mL/min. Flow rates at this level enable the torch to deposit submicron particulate effectively onto the hot glass surface (Fig. 6b). The small particles have a smaller thickness and, thus, require a shorter time for diffusion to produce the desired coloring effect. A compromise exists between the ease of particle delivery to the surface and the ability to color the glass effectively. A small particle can be deflected from the surface more easily as it follows the streamlines of the hot deflected gas, thus, producing a lower deposition efficiency. However, smaller particles present a smaller particle volume for diffusion and subsequent incorporation into the glass structure.

The diffusion of metallic ions into the surface can be promoted by the addition of soda that decreases the viscosity of the glass surface. The modification of the glass structure will produce an accompanying change in the surroundings of the metallic ion. Glasses with a high alkali content have shown a color change from blue through green-blue to green-yellow (Ref 15).

The absorption spectrum from a liquid flame sprayed cobalt onto a hot glass surface was compared with a sample containing 0.01 wt% Co_2O_3 at a constant composition through the thick-

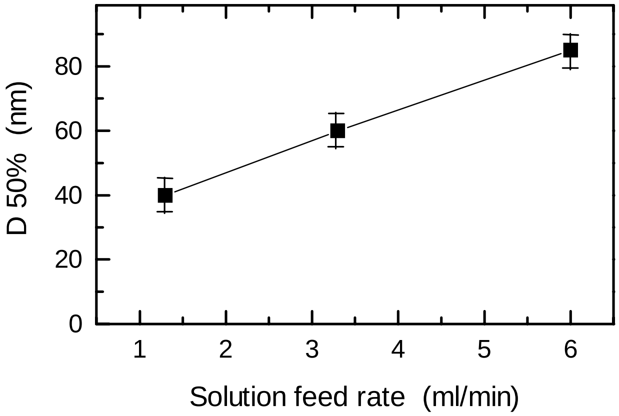


Fig. 7 The size variation of cobalt oxide particles with solution feed rate

ness (Fig. 8). The shape of the absorption spectra from the surface-colored sample was identical to the glass reference, indicating that the location of the cobalt ion within the glass network is identical. This is expected because it is only the coating that can possibly contain a metastable phase; however, consequent diffusion places the metallic ion into definite positions.

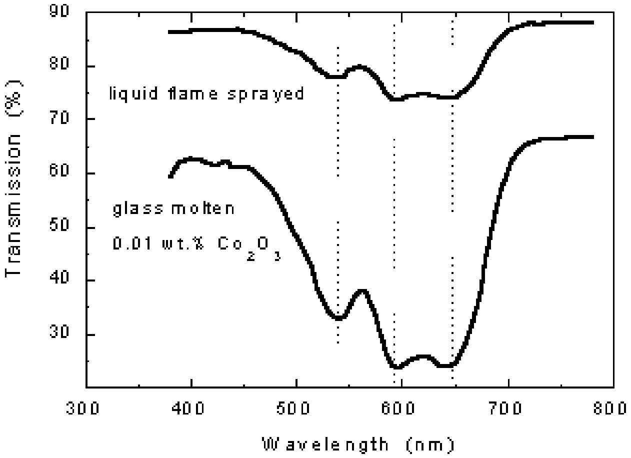


Fig. 8 Absorption spectra of cobalt colored glass produced by liquid flame spraying and by conventional glass making methods

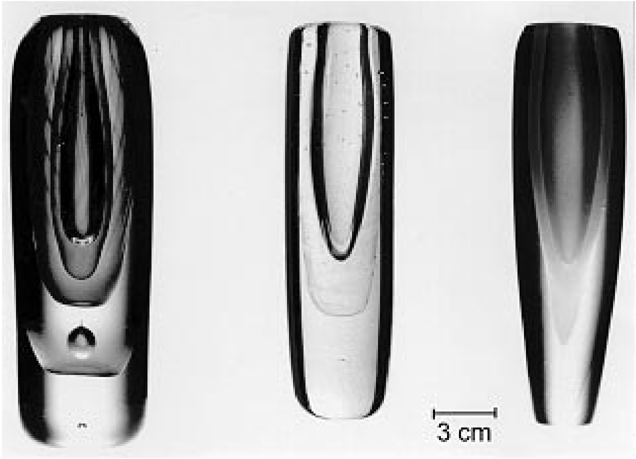


Fig. 9 Blue, blue-green, and yellow colored vases produced by glass blowing. The light blue-green color indicates the weak but eloquent coloring effect of copper ions.

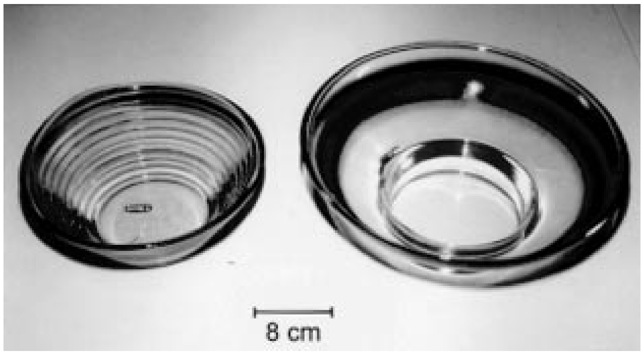


Fig. 10 A light blue hue is only possible by liquid flame spraying cobalt nitrate in a factory process, whereas the use of cobalt glass powder can give more intense coloring.

3.3 Glass Coloring in the Glass Studio

Spraying of cobalt nitrate solutions onto glass blown objects produces a uniform blue color (Fig. 9). Placement of the glass in the glory hole increases the temperature of the glass and promotes diffusion of the metal or metallic oxides. The second gather of glass also subjects the metal layer to high temperatures, thereby facilitating diffusion from the outer surface into the newly applied layer of hot glass. This process enables the coloring metal to be incorporated with higher initial concentrations compared to those in the coloring of a free surface. The use of copper, which has a lower coloring intensity, is also able to produce reasonable results (Fig. 9).

Coloring with silver depends on the initial surface concentration and glass temperature. If the spraying time is too long, a silver coating will be produced from the high surface concentration. This silver layer can be broken up by further blowing the glass object and producing a white silver oxide layer. A lower surface concentration of silver is necessary to produce the yellow coloring. The glass blown object heated in the glory hole then allows diffusion of the silver into the glass to produce light scattering centers (Fig. 9).

3.4 Glass Coloring with an Automated Gob Feeder

The flame spraying process has the advantage of delivering the glass coloring material while heating the glass object. Spraying onto hot glass that is spun into a mold allows the deposition to be performed onto a glass gob that is originally at 1100 °C. The decrease of the glass surface temperature with time dictates the depth to which the metal oxide is able to diffuse. In a production line process, this time can be limited to a period of 8 s. Figure 10 shows the lightly colored cobalt regions after 4 s of spraying and 4 s for diffusion. The glass bowl is then air cooled and annealed at 510 °C for 12 h.

Because the production line process is subjected to a cooling regime, only coloring from transition metals can be produced. The fast cooling of the glass article limits the coloring option to cobalt, which has the most intense effect of all the transition metals (Table 1). A short diffusion time does not facilitate establishment of a definite colored area, and so the coloring appears to have occurred throughout the entire object.

In comparison with other glass coloring processes, such as physical vapor deposition (Ref 16) and sol gel (Ref 17), the liquid flame spray process is able to produce more gentle tones of different colors. Furthermore, liquid flame spraying can be applied to the production of articles in the glass studio where only a short period of time is available for coloring. The flexibility of isolating the colored region to a given axial location in glass studio-produced articles presents more flexibility in the regions that can be colored compared to a sol-gel technique, which can require dipping into a solution.

4. Conclusions

Liquid spraying of metallic nitrates produces metallic or metal oxide particles with a particle size between 50 nm and 10 μm. Larger sized particles produced within the flame are porous and are not useful for glass coloring. Coloring of hot glass is faster with dense submicrometer particles that have good contact with the molten glass. Glass coloring using the liquid flame spraying process has been shown to be suitable in a glass studio and also on a production line. Coloring in glass blowing operations produces more intense coloring with the option of a wider variety of colors.

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