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THE FIFTY-THIRD ANNUAL

SYMPOSIUM
ON THE
ART OF SCIENTIFIC GLASSBLOWING

2008

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Papers

Amazing Characteristics of a Simple Coil / Elasticity in Glass

by

Scott Bankroff[a] and Mathew Puskar

ABSTRACT

The construction of a three-foot long coil is fairly straightforward. The characteristics the completed coil took on present an amazing study in the movement of glass.

Last year a customer ordered a 3' long x 6" o.d. coil. Pretty straightforward I thought, but of course it did not turn out that way.

Dimensions for the coil were not critical so an Arabica Pyrenees Receptacle (coffee can) was used as the mandrel. (Figure 1) The idea for the mandrel came from a technical paper that Allan Brown presented at the 1994 ASGS Symposium in Pittsburgh (Allan Brown, "An Elliptical Glass Coil," *Proceedings of the 39th Symposium on the Art of Scientific Glassblowing* (Pittsburgh, PA: June 1994): 7-21).

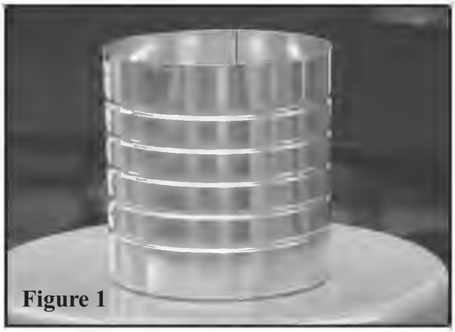
Figure 1

With the mandrel chucked in the lathe, Figure 2 shows the warming of a large area of 8 mm x 1.5 mm wall tubing. Since the medium wall tubing would need a lot of fire, a large soft flame from a Miller burner was used. Note that the end of the tube has been bent in preparation for hooking into the lathe chuck arm.

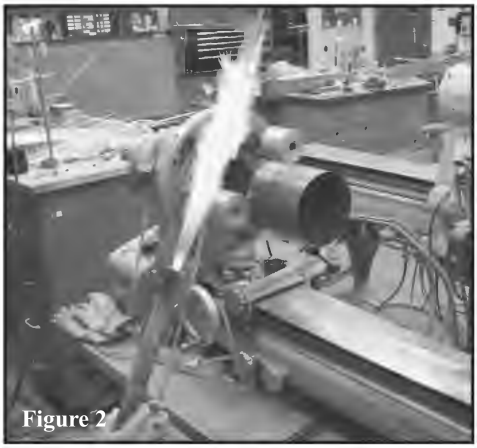
Figure 2

Figure 3 shows the tubing starting to soften onto the mandrel. The lathe is turned to its slowest speed.

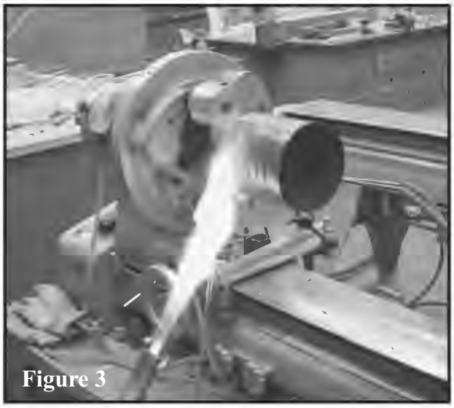
Figure 3

Knowing that the lathe runs haltingly at its slowest speed, I used my hand to manage a smooth and consistent rotation. (Figure 4)

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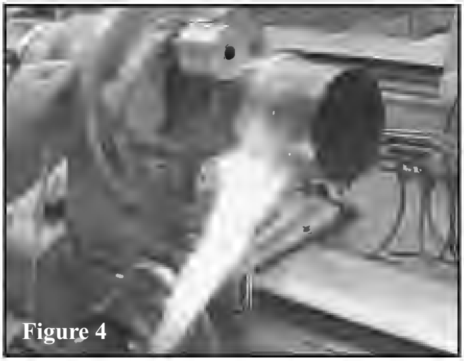
Figure 4

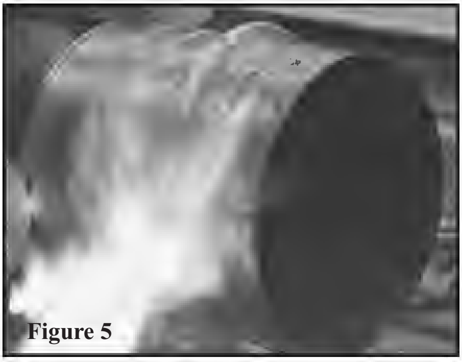
Figure 5

The mandrel did start to oxidize (Figure 5), though the metal never got hot enough for the glass to stick to it. One four-foot length of tubing made a single "wrap" of coil. The circumference of each wrap is 20". Each wrap is approximately 1.5 turns and 3.5" in width.

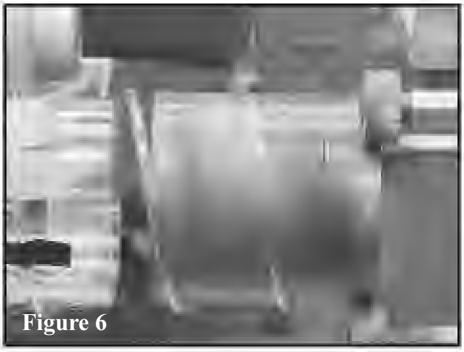
Figure 6

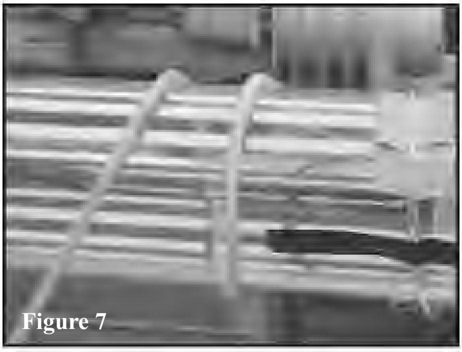
Figure 7

To hold the wraps for assembly of the coil, one wrap was held onto the mandrel and another wrap was secured to a length of 150 mm tubing (Figure 6) using a high temperature woven cloth. The first two wraps of the coil were very loose on the 150 mm, having very little surface area, so my blow hose was used to hold the wraps securely. (Figures 7 & 8)

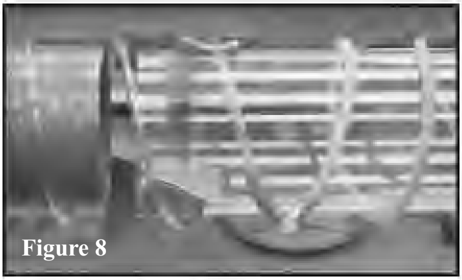
Figure 8

Preparing the ends for sealing was critical: the bottom of each end was pulled off with fire as there was no rotating of the glass due to the looseness. A small flame (Figure 9) was used to make the simple seal and hand annealing was important due to the flexibility and handling of the coil. After each wrap was added, the coil was pushed onto the 150 mm until the desired length was achieved. From this point on, the coil did not come off the 150 mm until all adjustments were made.


Figure 9

Figure 10 shows the main body of the coil; note the uneven spacing.

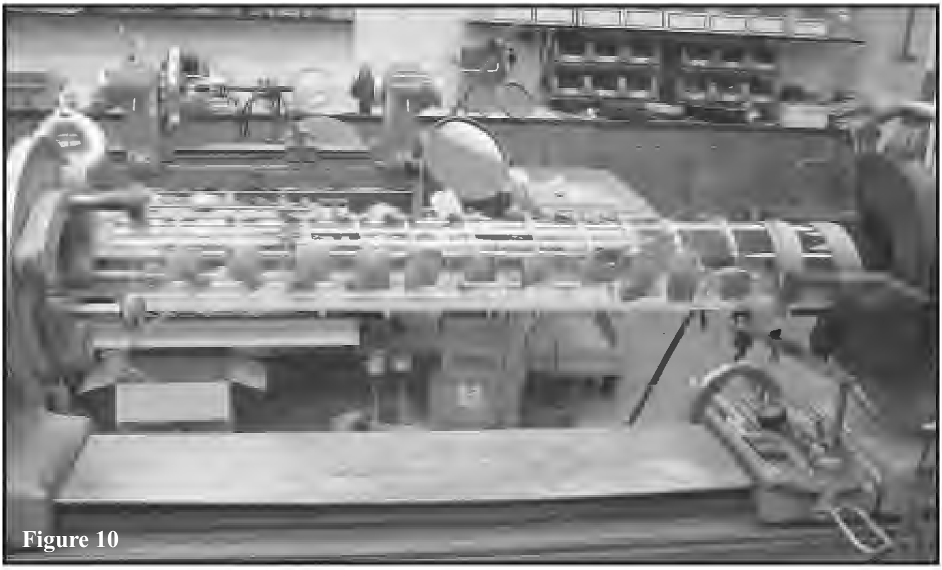

Figure 10

Figure 11

Figure 11 shows the coil on the 150 mm in the annealing oven. Starting at one end, nichrome wire was used to pull together two sections of the coil at a time. It was then run through an annealing cycle. I pushed the oven temperature up to 590ºC which was enough to relax the coil into the desired dimensions. The next day another two sections were adjusted. The coil went through twelve oven cycles before I was satisfied with the result.

Moving on to the second aspect of this paper, the definition of elasticity is very simple. Elasticity is a branch of physics which studies the properties of elastic materials. A material is said to be elastic if it deforms under stress (e.g., external forces) but then returns to its original shape when the stress is removed. Units of elasticity are measured using Young's Modulus.[1]

After adjusting the coil in the oven and removing it from the 150 mm, the ends were prepared for tubing connections. At this point I determined that a crude test of elasticity was called for.

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[1] Young's Modulus. (n.d.) In *Encyclopedia Britannica Online*. Retrieved May 30, 2008, from http://www.britannica.com/EBchecked/topic/654186/youngs-modulus.

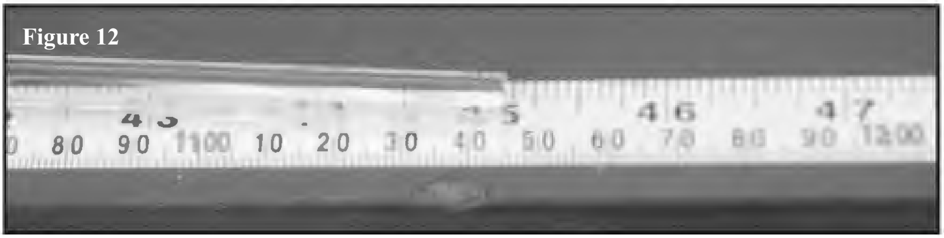
Figure 12

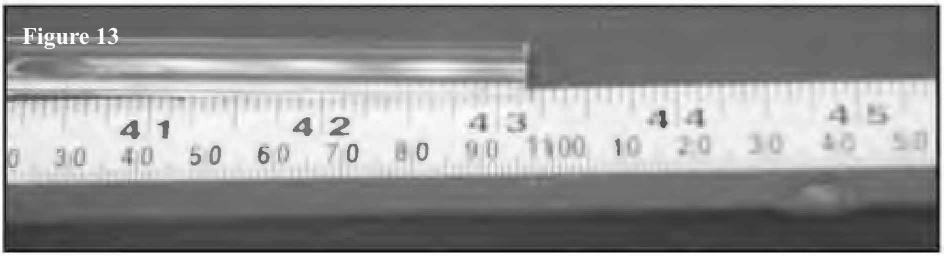
Figure 13

Figures 12 & 13 show the coil being compressed. The length went from the 45” mark on a ruler to the 43.75” mark, resulting in a 4.86% reduction in length.

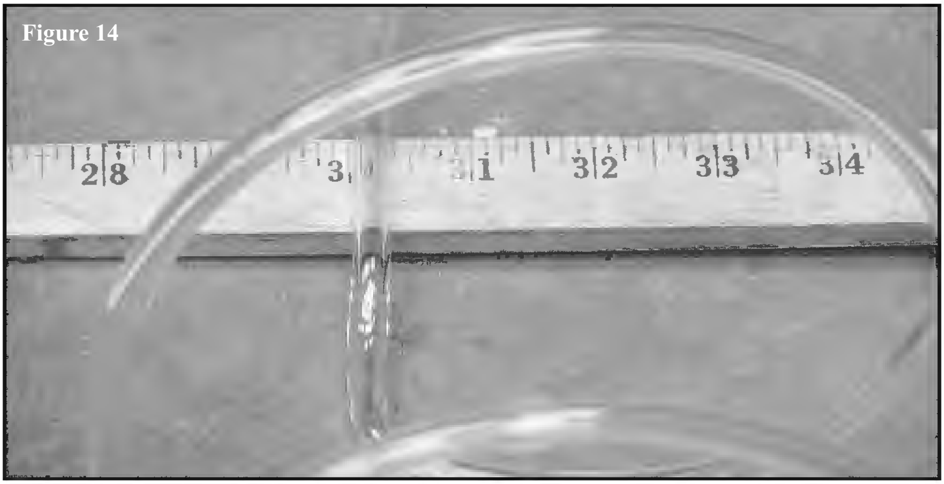
Figure 14

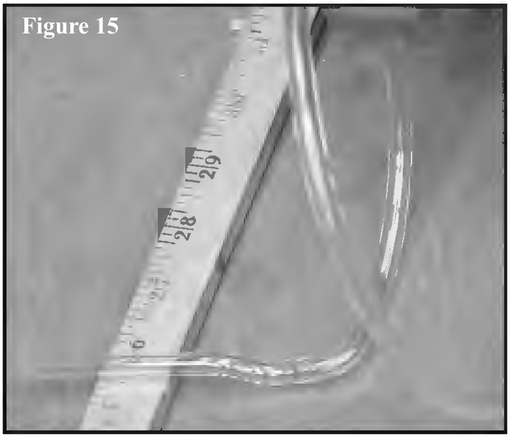
Figure 15

Figures 14 & 15 show a lateral test of the coil’s flexibility. The 3.5” lateral movement results in a 14º movement off center.

The graphic in Figure 16 demonstrates the elasticity of the complete coil.

A mechanical test of the coil flexibility would certainly have been more accurate in determining the extent of the coil’s elasticity. Taking glass to the limit means only one thing though, making another.

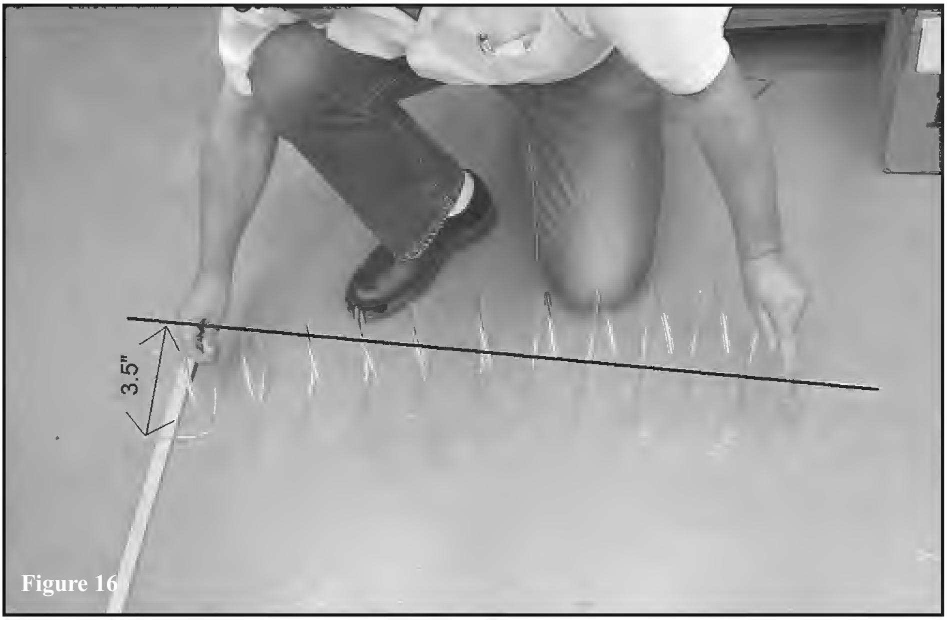

Figure 16

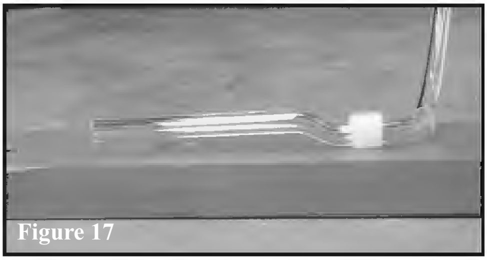

Figure 17

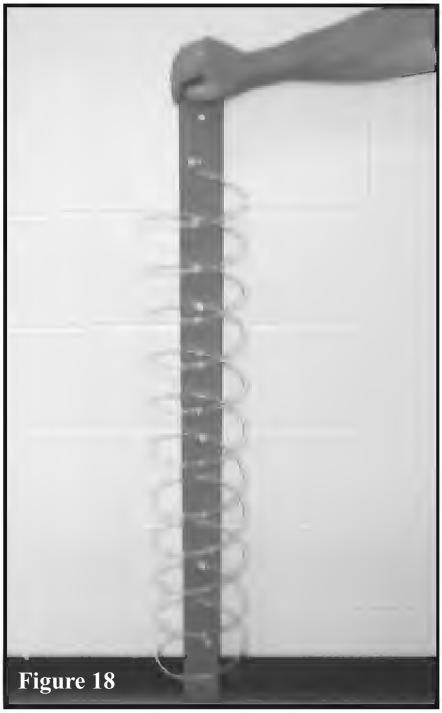

Figure 18

Knowing that flexible tubing was to be attached, the ends were moved up and off the surface of the mounting board using a small "S" bend. (Figure 17)

Figure 18 shows the completed and mounted coil. Five plastic electrical cable clamps were used to fasten the coil to the mounting board. These clamps offer a great amount of movement though the piece is secure. I have always believed that less is better when it concerns clamping glass.

CONCLUSION

I would like to thank the Chemistry Department at MSU for allowing me to put this project together and to present it you. Also many thanks to Mat Puskar, my student assistant of 4 ½ years, for his input and ability to work with me.

Characterization and Discussion of Vitreous Silica Bloom

by

Anatoly Kishinevski[a]

ABSTRACT

Vitreous silica bloom is a classic challenge in the world of scientific glassblowing. This paper gives a brief description of the matter and explains some simple analysis techniques performed to gain a better understanding of the microstructure and appearance of bloom.

INTRODUCTION

Silicon dioxide (SiO_2) also known as silica is one of the most abundant naturally occurring materials on the planet. Silica can be found throughout nature in at least six different crystalline arrangements including quartz, cristobalite, tridymite, coesite, stishovite, and moganite. There is a synthetic crystalline phase of silica known as keatite. It has not yet been discovered in nature, however someday it may be. For now keatite only exists when produced in a laboratory under extremely high pressures and temperatures.

The most common silica polymorph is α-quartz and is readily found in nearly every climate on earth. Besides existing naturally as a crystalline material, silica can also be found as a naturally occurring glass known as lechatelierite which forms when lightning strikes a sandy region. The intense energy of lightning instantly fuses the sand together and creates a long branch-like structure of vitreous silica that extends into the ground. Despite their delicate nature, several lechatelierites have been carefully removed from the ground intact. A prime example of one can be seen at the Boston Museum of Science.

Vitreous and crystalline silica plays many important roles in our world of technology. It is commonly used as a substrate material for many thin film applications and it is also used for electrical applications in which its piezoelectric behavior is utilized in the manufacturing of accurate timekeeping devices.

Quartz crystals in the form of sand are also used as a key ingredient in the manufacturing of commercial glass products including windows, bottles, etc. For these applications, the quartz crystals are melted at high temperatures with other oxide materials resulting in a homogenous blend. The combination of the quartz with other oxides allows the melting temperature of the material to be low enough to be economical from a manufacturing standpoint.

Through several intense processes, quartz crystals can also be melted independent of all other chemicals and be formed into an amorphous structure by itself. Scientific glassblowers often refer to this product as quartz glass, which is a misnomer to some degree. By using the name "quartz glass," it is being implied that the material is crystalline and glassy concurrently, when in reality it is purely a vitreous material. Technically it makes the most sense to refer to quartz glass as vitreous silica, amorphous silica, or fused silica.

In our world of science and technology, vitreous silica plays many important roles. Having an extremely high service temperature, as high as 1200°C (2200°F) and near zero coeffi-

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cient of expansion, vitreous silica is a material capable of enduring very abrupt changes in temperature without breaking from thermal shock. Vitreous silica also plays a critical role in the optical fiber industry and in the semiconductor industry where it exists in such a pure state that it is quite possible that nothing exists that is purer. Without the presence of vitreous silica, the world we know today may have developed into a very different place.

Due to its critical presence in the world in which we live, it is often necessary to assemble vitreous silica in many different shapes and types of apparatus. More often than not, the process of manipulating the material is dependent on a skilled scientific glassblower whose gift is that of being able to melt glassy materials in a controlled and precise manner to yield a product of unique integrity.

The process of working vitreous silica in a flame is similar to that of welding. It takes a tremendous amount of localized heat, generates a blinding light, and the glass has a very short working range. Vitreous silica is not a liquid until 2200°C (4000°F) and at that point is similar in viscosity to honey at room temperature.

During the process of working vitreous silica, the intense heating of the material causes some of the silica to volatilize. A signifigant amount of the silica vapor condenses on neighboring cooler glass. This silica vapor deposit, as can be seen in Figure 1, appears as a white powdery layer and is referred to in industry as bloom.

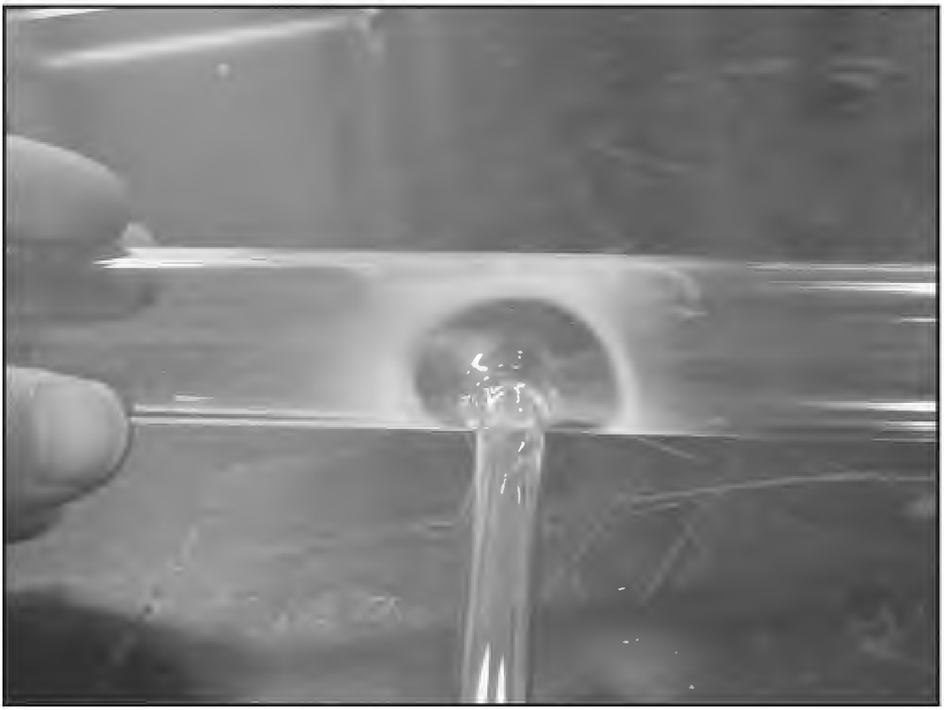

Figure 1. *A completed vitreous silica side seal with the classic bloom formation.*

Most often it is desirable to remove the bloom from a finished piece of glassware. This may be due to a desire to make the glassware look clean. Sometimes it is also important to remove bloom for practical reasons such as if the vitreous silica apparatus is being used for an optically sensitive application where uninterrupted transmission is necessary.

The removal of bloom is usually accomplished by rinsing the glassware in some type of hydrogen fluoride solution such as hydrofluoric acid or ammonium-bifluoride. The glassware is submerged in the solution for a period of time. When the glass is removed from the solution, the bloom will no longer exist. The solutions are very effective at etching the bloom from the glass.

For shops that do not use acid to remove bloom, often a flame is used to simply “brush” the bloom away. This is accomplished by using a hot flame directed in the right way so that the bloom is re-volatilized and simply evaporates away with the heat and exhaust of the flame.

The last method for removing bloom is to simply wipe it away with a cloth or brush of some type. The bloom is only removable in this manner if it was formed on a small of piece of glassware that was not heated sufficiently to cause the bloom to adhere to the surface of the glass. The bloom on the outer perimeter of a seal can often be simply wiped off to some degree.

Figure 2. *Shown here are pieces of vitreous silica with bloom. The sizes of the samples range from 0.5-2cm^2.*

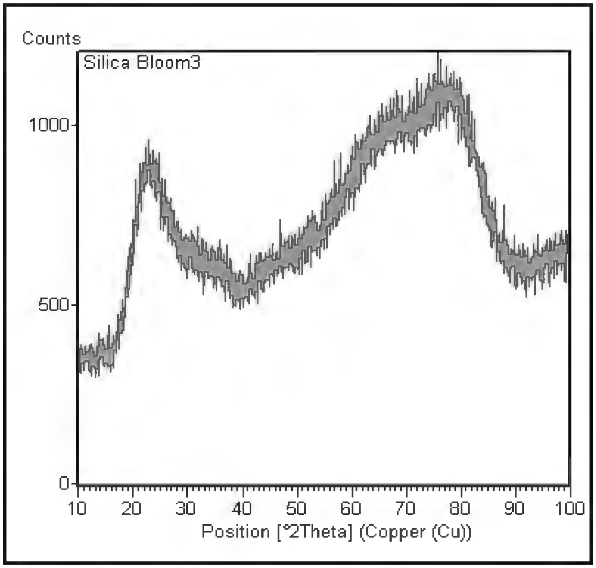

Figure 3. *The analysis of several samples of vitreous silica bloom resulted in x-ray spectra as shown in this Figure. The lack of narrow defined peaks indicates that no crystalline material was present in the sample.*

Hoping to get a better understanding of the microstructure of bloom and what type of interface existed between the bloom and the bulk of the material, several characterization methods were used to closely examine the material.

The first method used to analyze bloom was x-ray diffraction. Pieces of vitreous silica with varying degrees and thicknesses of bloom were prepared by crushing a completed vitreous silica seal and retrieving select pieces for analysis. The samples used can be seen in Figure 2.

The technique works by measuring the diffraction pattern of x-rays off the surface of the sample material. Every crystalline material has its own signature diffraction pattern and can be used to determine very precisely if crystals exist and if so what kind of crystals they are along with their approximate size.

Upon completing an x-ray analysis of the bloom, no indication of the presence of crystals was observed. As can be seen in Figure 3, there are no resolvable peaks present in the spectra collected from the bloom samples. Several samples were run and all yielded similar results. The broad peaks seen in the spectra are often referred to as amorphous peaks and are characteristic of a material with no crystalline structure. Thus a preliminary conclusion was drawn that bloom is amorphous in nature.

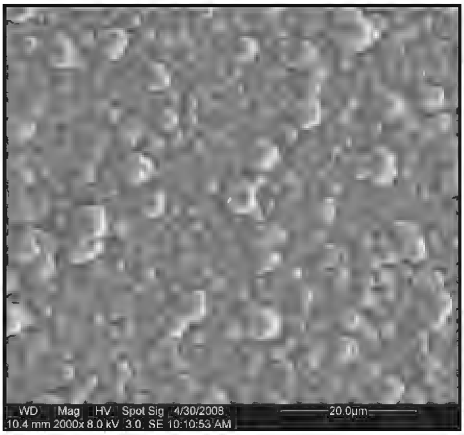

Figure 4. *Vitreous silica bloom at high magnification.*

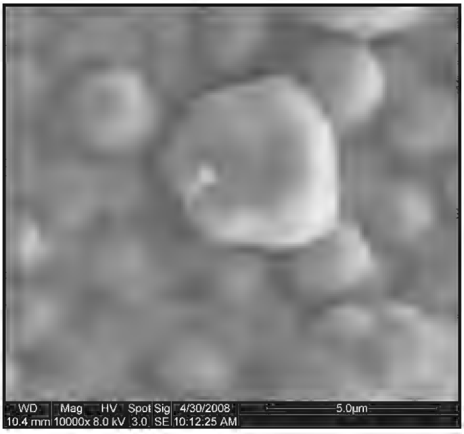

Figure 5. *Vitreous silica bloom at very high magnification. The resolution attempted for this image approached the limits of the scanning electron microscope being used, thus a slightly blurry image resulted.*

Scanning electron microscopy was also used to see with very high magnification what form bloom took. (Figures 4-6) Magnification used ranged from 2000-80,000X. What was observed resembled little puffy balls of partially popped popcorn kernels that appeared to sit on the surface of the glass.

CONCLUSION

Upon inspection of the microscope images of the bloom, there were no definite signs of crystalline material present. It was also apparent that the bloom coating was only very lightly adhered to the surface as one can see from the spherical shapes the particles assume.

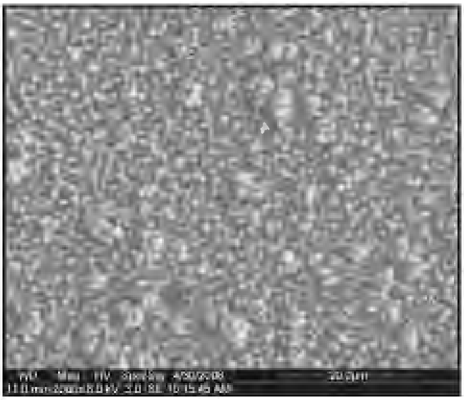

Figure 6. *This image is of the thickest area of bloom. At this point in the coating, the bloom was thick enough that some could be wiped off with a finger tip.*

Taking the results of both the x-ray diffraction and electron microscopy into consideration, it is believed to be sensible to conclude that bloom is non-crystalline in nature.

Reversible Color Generating Redox Reaction Involving Silver Oxide and Germanium Dioxide in a Thermachromic Sodium Borosilicate Glass

by

Jesse Kohl[a] and Matthew J. Dejneka[b]

ABSTRACT

A previously undocumented reversible color generating redox reaction found to be occurring in a $33x10^{-7}$ *1/ºC -expansion borosilicate art glass was investigated by electron microprobe analysis (EMPA), transmission electron microscopy (TEM), and UV/VIS spectroscopy. It was determined that color was generated by the reduction of ionic silver to form color generating metallic silver nanospheres that ranged in size from 5-40 nm. Germanium was discovered to be the constituent that facilitated the reversibility of this reaction by acting as a redox couple for the silver.*

INTRODUCTION

Silver has been a common art glass colorant since ancient times. It is traditionally introduced to glass as a nitrate or a carbonate, which is subsequently reduced upon heat treatment to form color generating metallic silver nanospheres.[1] These nanospheres give rise to an absorption band centered at 410 nm on the basis of the Mie theory.[2, 3] The chemical reduction of ionic silver is facilitated by the presence of an internal redox couple within the glass. Iron, manganese, tin, and antimony have been identified as potential redox couples for silver in such color generating reactions.[4]

An unexplored redox reaction involving silver has been discovered in a series of commercially available thermachromic sodium borosilicate art glasses. The lampworker Suellen Fowler developed the base formula for these colors in the early 1970's.[5] This type of glass is referred to as "amber/purple," referring to the differing appearance when viewed in transmitted versus reflected light respectively. This dichroism exhibited by these glasses is referred to as the Lycurgus Effect.[4] When these glasses are molten, they are completely colorless and transparent. If rapidly cooled, they will remain colorless. Upon slow cooling or heat treatment at or slightly above the annealing temperature, the glass will begin to develop color. The body of the glass strikes to a deep honey/amber brown color which can be observed in transmitted light. Simultaneously, as the body of the glass develops color, the surface of the glass takes on an alternate hue that can only be viewed in reflected light. This surface phenomenon can range in color from a royal purple to a lustrous metallic sheen depending on the duration and temperature of the heat treatment.

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[1] W. A. Weyl, *Coloured Glasses*, United Kingdom: Society of Glass Technology, 1951.

[2] M. Anotello, G.W. Arnold, G. Battaglin, R. Bertoncello, E. Cattaruzza, P. Colombo, G. Mattei, F. Trivillin, *J. Mater. Chem.* 8 (1998): 457.

[3] G. Mie, *Ann. Phys.* 25 (1908): 377.

[4] R. H. Brill, *Comptes Rendus; VII^e Congrès International du Verre, Bruxelles, 28 juin-3 juillet,* 1965, Section B (Paper no. 219), 219.1-219.11.

[5] S. F. Fowler, Personal Interview, 19 January, 2007.

Aside from the range of color that the amber/purple glasses can produce, when a colored sample of amber/purple glass is reheated above 1230ºC, the color is eradicated. Subsequently, this colorless glass can again be heat-treated to redevelop the color. This cycle of color generation, eradication, and regeneration can be carried out over thirty times. In addition, the generation and eradication of color is independent of furnace atmosphere and can be carried out under an inert (nitrogen) environment. Thus the glass is very useful for making multicolor glassware from a single low expansion glass. Fowler noted that only when germanium dioxide was added in conjunction with the silver was this reversibility of the color generating reaction possible.[6]

To elucidate the role of germanium dioxide in this color generating reaction, a multifaceted analytical study was made. The first step in this exploration was to confirm that silver was undergoing a redox reaction in which colorless silver ions were being reduced to form color generating silver metal nanospheres. This was first done by conducting a UV/VIS analysis of the amber/purple glasses heat treated at different durations of time. (TEM) was then used to quantitatively determine the color generating specie. By conducting TEM analysis on a colorless sample of amber/purple glass as well as on a heat-treated sample, further evidence of the presumed redox reaction was collected. To further understand the color generation taking place on the surface of these glasses, electron microprobe analysis (EMPA) was carried out. By examining an EMPA generated cross section view of the amber/purple glass and mapping where the silver nanospheres are deposited in relation to the germanium, a clearer understanding of the color generating redox reaction can be derived.

To clarify and more effectively establish the role of germanium dioxide and its interaction with silver, several small-scale batches were made. These batches were primarily composed of vitrified germanium dioxide doped with silver (I) oxide and some with metallic silver. Observations made during the quenching and subsequent re-melting of these glasses aided in establishing a relationship between silver and germanium.

EXPERIMENTAL

Samples

Samples of Northstar Glassworks NS-13 Amber/Purple and NS-26 Double Amber/Purple made between 2001 and 2003 were obtained (see Table 1 for glass composition). Northstar Glassworks created the samples by melting Schott glass cullet code 8340 with powdered silver (I) oxide and germanium dioxide with an electric oven (see Table 2 for cullet composition).

Table 1. Glass	Mol% Ag_2O	Mol% GeO_2	Mol% Cullet
NS-13	**0.033**	**0.52**	**99.4**
NS-26	**.157**	**9.91**	**89.9**

Table 2. Cullet Composition:	SiO_2	Al_2O_3	Na_2O	NaCl	B_2O_3
Mole Percent	82.2	1.32	4.23	0.570	11.63

Sample Preparation

Water quenched samples of Amber/Purple glass were prepared by melting small quantities of NS-13 Amber/Purple in a Rapid Temp electric furnace in a quartz crucible at 1300ºC for ten minutes. Once the glass was completely colorless and transparent, it was removed from the furnace and the quartz crucible was plunged into de-ionized water. Several additional samples of NS-13 were prepared with the same heat treatment but allowed to cool in air.

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[6] S. F. Fowler, Personal Interview, 19 January, 2007.

Heat treatments of NS-13 Amber/Purple glass were conducted in a Rapid Temp electric furnace at 565ºC. The samples were heat treated for times ranging from fifteen minutes to 180 minutes in fifteen-minute increments in ambient atmosphere. Additional heat treatments of NS-13 Amber/Purple and NS-26 Double Amber/Purple were conducted in a Thermolyne 54500 High Temperature Tube Furnace that was fitted with a fused quartz tube and was pumped with a steady flow of forming gas (4% hydrogen/96% nitrogen.) The gas was flowed at 15 ml/min at atmospheric pressure through a Matheson Rotometer Model 840 BV with a 601 tube.

Small Scale Batch Preparation

Five small-scale batches were prepared and melted in 50cc quartz crucibles (see Table 3 for batch formulas). Finely powdered (300 mesh) germanium dioxide of 99.99% purity from PIDC was used as the major constituent of these glasses. Powdered (300 mesh) silver (I) oxide 99.99% purity was supplied by Cascade Silver. Melt time ranged from 12 hours to 36 hours at 1300ºC. The variation in melt time was not critical to the experiment. Based on visual inspection, the minimum melt time to allow the glass to homogenize and become free of bubbles was eight to ten hours. A lengthier melt time did not have any effect on the quality or the reactivity of the glass.

Table 3. Batch Number	Mol % GeO_2	Mol % 8340cullet	Mol % Ag_2O	Mol % Ag Metal	Quench Method
1	95.6	0	4.6	0	Air
2	95.6	0	4.6	0	Water
3	85.7	0	0	14.7	Water
4	0	90.8	0	9.18	Air
5	93.1	0	0	6.9	Air

The air-cooling of batch 1 was carefully observed. These observations were made by removing the crucible from the furnace and allowing the glass to cool in air until it ceased to emit an orange glow. Once the glass had ceased glowing, it was placed back into the furnace and allowed to re-vitrify for a thirty-minute period. It was then removed and the cooling process was again observed. In total, this air-cooling and re-vitrifying was carried out three times. These observations were made to view bursts of light that emanated from droplets of metallic silver that agglomerated on the bottom of the crucible upon cooling.

Additional Experiments

Fifteen grams of powdered 99.99% pure silver (I) oxide from Cascade Silver was weighed and placed in a shallow crucible. The crucible was placed in a Rapid Temp electric furnace that was preheated and held at 1240ºC. The crucible was removed after fifteen seconds. This process was then repeated with powdered silver nitrate, also from Cascade Silver.

Sample Analysis

Seven samples of NS-13 heat treated for different durations of time were prepared for UV/VIS analysis by cutting 6 mm diameter discs of 2 mm thickness (see Table 4). The discs were polished with 1 micron alumina slurry to achieve a suitable surface for spec-

Table 4 Sample	1	2	3	4	5	6	7
Treatment Procedure:	Water quenched	Un-heat treated as from the factory	Heat-treated at 565ºC for 15 min	Heat-treated at 565ºC for 30 min	Heat-treated at 565ºC for 45 min	Heat-treated at 565ºC for 60 min	Heat-treated at 565ºC for 75 min

troscopic analysis. The samples were analyzed using a PERKIN ELMER UV/VIS/NIR spectrometer Lambda 900 from 200 to 800 nm with 2 nm bandpass, 60 nm/min scan rate with a 1 nm data interval.

Two additional samples of glass were made for TEM analysis. The first sample analyzed was water quenched NS-13 glass (see sample preparation section). The second sample consisted of NS-13 Amber/Purple glass that was heat-treated at 565ºC for three hours (see sample preparation section.) The glass TEM specimens were prepared by mechanically polishing and dimpling to a thickness of about 10 μm. The final thinning of the sample to electron transparency was carried out using an Ar ion mill. The acceleration voltage of ion beam was 6 kV with final thinning at 3 kV. In order to have a large thin area of the specimen for the observation of small particles, the incident angle of the ion beams was about 7º. The specimens were coated with a thin C layer in vacuum chamber before TEM observation.

The TEM examinations were performed with a JEM-2000FX transmission electron microscope equipped with Evex ultra-thin window X-ray detector. The operation voltage was 200 kV. To evaluate the nature of the particles found in the glass matrix, as shown in Figure 2, the electron diffraction patterns and EDX data were taken from the particles. Because of the small size of these particles, the smallest convergent lens aperture and a small spot size of the beam were chosen in the investigation.

EMPA analysis was conducted on a sample of NS-26 Double Amber/Purple that was heated at 900ºC for one hour in a tube furnace under forming gas (see sample preparation section).

RESULTS AND DISCUSSION

The NS-13 Amber/Purple UV/VIS spectra in Figure 1 show a 410 nm absorption peak that grew and broadened with time. This absorption peak matches that generated by spherical colloidal Ag particles of 2 to 20 nm, indicating that the color generation in the body of the Amber/Purple glass is due to the formation of metallic silver nanospheres.[2, 7] The absorption data shows that the longer the glass is heat-treated, the larger the absorption and hence the greater the quantity of metallic silver nanospheres generated. The broadening of the peak is due to a coarsening of the colloid size distribution.[2] It is thought that interactions between larger colloidal silver nanospheres

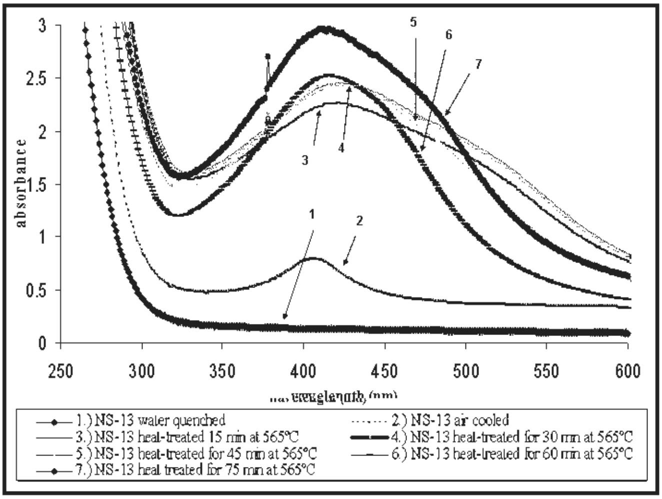

Figure 1. *NS-13 UV/VIS Analysis*

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[7] A. Abdolvand, *Modification of Optical and Structural Properties of Glass Containing Silver Nanoparticles Via DC Electric Field and Moderately Elevated Temperatures*. Martin-Luther-Universitat Halle-Wittenberg, 2006.

ranging from 70-90 nm contribute to the absorption bands centered at 450 to 530 nm.[2] This analysis also indicated that in the colorless water quenched sample, no absorption bands from metallic silver were present.

Figure 2 shows a Transmission Electron Micrograph of a heat treated sample of NS-13 Amber/Purple. The bright/dark spots are spherical Ag metal colloids ranging in size from 2-15 nm. This was confirmed by the electron diffraction patterns which showed that the particles are crystals. The EDX data taken from the particles and from the area outside the particles indicate that the crystal particles in the glass matrix are Ag metal particles.

Figure 2. *TEM image of Water Quenched NS-13 Amber/Purple glass*

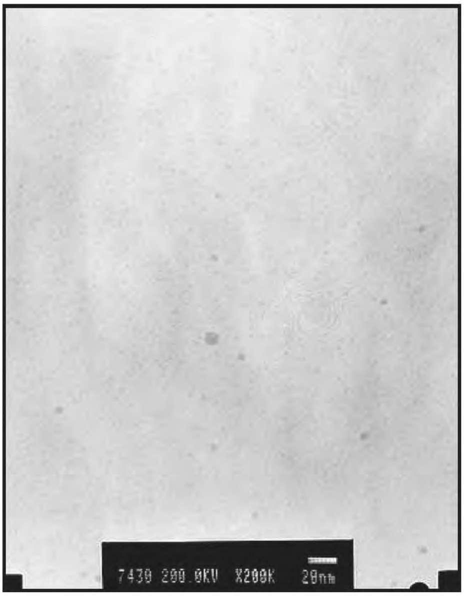

Figure 3. *TEM image NS-13 Amber/Purple glass heat treated at 565ºC for three hours*

In the water quenched sample of NS-13 Amber/Purple, no metallic silver nanospheres were detected (see Figure 3). This suggests that virtually all of the silver is in the colorless ionic state when the glass is at or above 1230ºC or quenched in water from a temperature exceeding 1230ºC.

By heat-treating samples of both NS-13 Amber/Purple and NS-26 Double Amber/Purple in a tube furnace under reducing conditions, a colored precipitate developed on the surface of the glass. The resultant color, viewable only in reflected light, was dictated by the thickness of the surface precipitate. The longer the heat treatment, the thicker the surface precipitate became with the color going from a purple to silvery opaque sheen as the heat treatment increased from ten to sixty minutes at 900ºC. It was observed that the rate at which the surface precipitate formed was largely dependent on temperature. EMPA determined that the surface precipitate was made up of large deposits of finely divided metallic silver

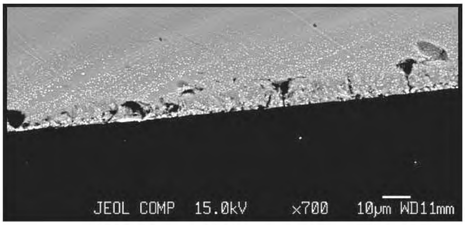

Figure 4. *EMPA generated cross-section view of NS-26 Double Amber/Purple glass that was heated at 900°C for one hour in a tube furnace under forming gas (4% hydrogen/96% nitrogen)*

spheres that ranged in size from 50 to 450 nm (see Figure 4).

EMPA also revealed that the glass was poorly homogenized and that there were large germanium rich veins and pockets that ran throughout the glass. In addition, nearly all of the metallic silver was found to reside along the outer edges of the germanium rich regions. This can be observed by the EMPA generated image in Figure 5 which shows a large oval shaped pocket of pure germanium surrounded by nanospheres of metallic silver. No metallic silver was found within the germanium rich pockets or at any great distance from a germanium rich region. This poor mixing is thought to be due to the method and low temperature (1230ºC) at which these glasses were produced. The manufacturing process involved adding powdered silver (I) oxide and germanium dioxide (300 mesh) to a pre-weighed amount of coarsely ground cullet. The mixture was gently tumbled to distribute the powdered oxides throughout the cullet. It was subsequently charged into a cylindrically shaped crucible and heated in ambient air with an electric pot furnace. It is important to note that each individual piece of cullet was roughly 2 x 4 x 0.1 cm in size. Thus, it is believed that as the melt progresses, the finely powdered oxides become trapped between the 'sheets' of cullet. Furthermore, the high viscosity of the glass (due to the low melt temperature 1230ºC) and the geometry of the crucible prevent little if any convective mixing from taking place. Therefore, once the small quantities of silver and germanium become encapsulated by the cullet, these pockets remain in suspension within the glass matrix.

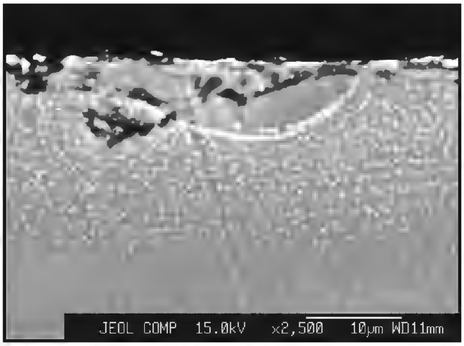

Figure 5. *EMPA generated surface view of NS-26 Double Amber/Purple glass that was heated at 900°C for one hour in a tube furnace under forming gas (4% hydrogen/96% nitrogen)*

Based on the understanding that an internal redox couple is present, and taking into account the close proximity of the silver and germanium, it indicates that germanium is acting as a redox couple for the silver. To explore the possibility that germanium acts as redox couple, it is critical to observe the initial oxidation state shift of silver as the cullet mixture is charged into the furnace. When powdered silver (I) oxide was heated for fifteen seconds at 1230ºC, it is thermally reduced to silver metal. This experiment confirms that fifteen seconds after the Amber/Purple batch is charged into the furnace predominately metallic silver is present. This has been corroborated by observing the amber/purple glass batches in the initial stages of melting in which visible droplets of metallic silver can be seen. Only later in the melt does the silver and germanium reach their thermodynamically favorable oxidation states. However, it is possible that the germanium does buffer the silver (I) oxide and prevent it from reducing to metal.

After an amber/purple glass is melted for 8 to 10 hours at 1230ºC, it is colorless and transparent. This indicates that over the fining period the metallic silver that formed in the initial fifteen seconds of melting due to thermal reduction is oxidized to the colorless (+1) state. To test if the cullet alone has any ability to oxidize metallic silver, a small-scale batch composed solely of 8340 cullet and metallic silver was prepared. Even after a prolonged melt the metallic silver was not oxidized and remained as a large metallic deposit in the bottom of the crucible. Upon the water quenching of this glass, color was only observed directly around the large metallic silver deposit. The balance of the glass was colorless. This indicates that the base glass (without GeO2) has no ability to oxidize metallic silver to Ag ions which are soluble in glass

To determine if germanium has the ability to oxidize metallic silver, several small batches composed of germanium dioxide doped with small granules of metallic silver were prepared. It was observed that after only one hour in the furnace, all the metallic silver had disappeared and the glass was completely colorless and transparent. When the glass was removed from the furnace, it developed a uniform yellow/amber color as it cooled and several large metallic silver deposits agglomerated at the bottom of the crucible. Just as the glass ceased to emit an orange glow, each of the metallic silver deposits emitted a burst of light. This light emission has been previously observed by several research groups.[8, 9] It has been suggested that the light emission is a release of binding energy gained from the agglomeration of smaller silver metal clusters to form larger ones.[8] However, no explanation has been offered as to why the light emission occurs after the clusters coalesce. Riebling suggests that the light emission is due to the shearing of the metal deposits from the glass matrix as they freeze.[8]

When the crucible containing the silver and germanium was placed back into the furnace and heated for thirty minutes, the metallic silver deposits that had formed upon cooling in air disappeared. The glass was again completely colorless and transparent. This reversibility, identical to that demonstrated by the amber/purple glasses, indicates that the Ge^{4+} is the specie that facilitates this reversibility by acting as a redox couple for the silver. As expected, this phenomenon was also observed when silver (I) oxide was substituted as the starting material in place of the metallic silver. Several of the small-scale batches were quenched in water. This captured the glass in the colorless state, indicating that the virtually all the silver was in the colorless (1) state.

Knowing that there are only two stable oxidation states of germanium (II, and IV), the summary of the redox reactions taking place in the amber/purple glasses can be written as follows:[10]

- When the mixture of cullet and powdered silver (I) oxide and germanium dioxde is charged into the furnace the following reaction immediately takes place ("Δ" denotes heating at 1230ºC):

$$Ag_2O \rightarrow\Delta\rightarrow 2\ Ag\ (0) + \frac{1}{2}\ O_2$$

- Over an 8-10 hour fining period, the following reaction below takes place:

$$2\ Ag\ (0) \rightarrow 2\ Ag\ (I) + 2\ e\text{-},$$
$$2e\text{-} + Ge\ (IV) \rightarrow Ge\ (II)\ \textit{(Colorless state)}$$

Once the oxidation of silver by the germanium has taken place, the glass is completely colorless and transparent while it remains at or above 1230ºC. The method of cooling subsequently determines the reaction pathway and in turn, the resultant color. Figure 6 maps the various reaction pathways through which the glass can cycle.

The proposed reaction pathway was further corroborated by examination of the amber/purple glasses in short wave (254 nm) ultra violet light. It is known that Ge (II) emits a blue fluorescence under short wave UV light.[11] The water-quenched samples of amber/

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[8] E.F. Riebling, *J. Mat. Sci.* 6 (1971): 1204.

[9] I. Rabin, W. Schulze, G. Ertl, *J. Chemical Physics.* 8 (1998): 5137.

[10] J. M. Yuen, *Appl. Opt.* 21 (1982): 136.

[11] V. B. Neustruev, *J. Phy.: Condens. Matter*. 6 (1994): 6901.

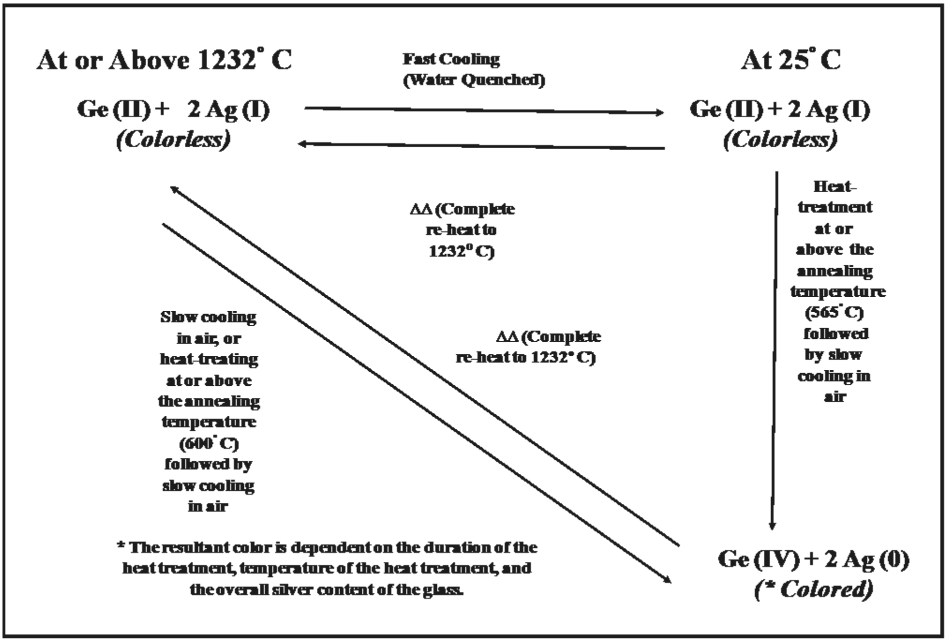

Figure 6. *Overall color generating reaction scheme*

purple glass exhibited an identical blue fluorescence. The heat treated samples of amber/purple glass that exhibited color had virtually no fluorescence. This confirms the presence of the alternate (+2) oxidation state of germanium in the amber/purple glass and proves that germanium shifts oxidation state in conjunction with the silver.

CONCLUSIONS

In this study, a unique reversible redox reaction between silver and germanium was documented and mapped. It was confirmed that the color generation in both the body and the surface of the glass was due to the formation of nanospheres of silver metal. It was found that heat-treating the glass at or above its annealing temperature gave rise to the formation of the color generating metallic silver nanospheres. The color, generated by heat treatment, could be erased by re-vitrifying the glass. This indicated that the metallic silver formed during the initial heat treatment, was subsequently oxidized back to the colorless +1 state during re-melting. Because this color generating redox reaction was found to be easily reversible (upwards of thirty times), a mechanism that facilitated the flow of electrons to and from the silver was concluded to be present. In the glasses studied, it was determined that germanium oxides are the species that not only accepts electrons from the silver at high temperatures but also can donate electrons back to the silver ions at lower temperatures, causing the precipitation of colloidal metallic Ag.

ACKNOWLEDGEMENTS

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Calculating Pressure at Elevated Temperatures More Information for Glassblowers

by

James R. Hodgson[a]

ABSTRACT

Running chemical reactions in a closed glass vessel brings an element of risk. With an understanding of some basic physical properties and with a knowledge of their limitations, online calculators can provide a means of better assessing the potential hazards involved in such experiments.

INTRODUCTION

If you are a scientific glassblower working in a research setting, you are probably already aware that designing, fabricating and repairing glass apparatus is only a portion of your responsibility. Often you are expected to be a source of information on everything involving glass or utilizing glass in its operation. It is not necessary to know everything, but knowing where to locate the desired information increases the value of the glass shop.

REACTIONS AT ELEVATED TEMPERATURE AND PRESSURE

Reactions in sealed glass ampoules are not uncommon in chemistry or chemical engineering. In chemistry, some Diels-Alder reactions are run at temperatures above the boiling point of the solvents used. An example would be a reaction using diethyl ether as the solvent heated to 90 degrees centigrade (the boiling point of diethyl ether is 34.6 degrees centigrade). It would be prudent for the chemist running the reaction to have at least a rough idea of the internal pressures which will be generated, especially if they are going to use a sealed glass ampoule from the glassblower to run the reaction.

THE IDEAL GAS LAW

If you ever took a high school or college chemistry course, you are probably familiar with the Ideal Gas Law and the corresponding Ideal Gas Equation.

$PV = nRT$ where
P = Pressure
V = Volume
n = Moles of gas
R = Gas Constant
T = Temperature in Kelvin

It seems like it should be easy to calculate the predicted pressure since the volume, V, and moles of gas, *n*, are constant, but unfortunately the Ideal Gas Equation can only be applied to gases. The simple examples in the freshman texts do not adequately address the problem of having a liquid in thermal equilibrium with its vapor thrown into the mix. However, by looking at the Ideal Gas Equation, we can easily see that as the temperature increases the pressure will also increase if the volume is held constant.

PHASE DIAGRAMS

Phase diagrams, a graphic representation of equilibrium conditions for the various states of a substance at different temperatures and pressures, are a useful tool in visualizing the

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problem, but they are not easily available for the many different possibilities which may arise.

VAPOR PRESSURE EQUATIONS

Vapor pressure equations used by chemists and chemical engineers may provide an answer. Chemists often use the Clausius-Clapeyron equation to estimate the vapor pressure in thermal equilibrium with a pure liquid.

$\ln \frac{P_2}{P_1} \approx -\frac{\Delta H_m}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$ where

ΔH is the heat of vaporization
R is the gas constant
P is the pressure
T is the associated temperature

The Clausius-Clapeyron equation works fairly well but is not very accurate near the critical point.

Chemical Engineers more frequently use the Antoine equation.

$\log_{10} P_{vp} = A - \frac{B}{T+C}$ where

A, B and C are Antoine Coefficients
T is the temperature
P is the desired vapor pressure

The Antoine equation also works fairly well if the temperature of interest is in the temperature range for the given coefficients.

ONLINE CALCULATORS

Fortunately, the number crunching and fear of logarithms does not need to hinder these useful tools. There are many online calculators for the Antoine equation.

The *Yaws' Handbook of Thermodynamic and Physical Properties of Chemical Compounds* at www.knovel.com is very useful, if you have access. It has an online calculator listing the Antoine coefficients and temperature ranges for almost 5,000 organic compounds. By selecting your compound of choice, a pressure vs temperature graph is generated with the units you choose over the specified temperature range.

The *NIST Chemistry Webbook* at http://webbook.nist.gov/chemistry/ is also a powerful tool and anyone with access to a computer can access this resource. Not only does it contain Antoine coefficients, it also lists many other pieces of physical data and their sources.

Another nice calculator is located at www.ruf.rice.edu/~aiche/calc/calculator.html.

USING YOUR KNOWLEDGE

Once you have determined the potential pressure at your experimental temperature, it is relatively simple to use a pressure nomogram or formula to determine the necessary details (wall thickness for selected diameters) for a glass vessel to contain that pressure.

CAVEATS

Unfortunately, nothing is as simple as it seems. The equations and calculators discussed above are meant for pure substances under limited conditions. In real life chemistry, it is rare that only one pure substance would be used. This does not even take into account the chemical reaction itself and whether or not it generates heat and other materials with vapor pressures. The calculators from Yaws' and NIST list the temperature ranges for which the Antoine constants are valid, but the calculator from Rice allows any temperature value to be input, which can lead to absurd results.

CONCLUSION

In the end, the equations and calculators are only a rough estimating tool, a starting point. Coming closer to a better answer in complex chemical situations is the real-life work of chemists and chemical engineers. Books are devoted to the subject with chapter titles like "Fluid Phase Equilibria in Multicomponent Systems" and terms like "fugacity coefficient" or "Poynting factor." Be cautious of plugging numbers into calculators without knowing the science and limitations behind them, and take heed of the words of Harry Callahan, "A man's got to know his limitations"

ACKNOWLEDGMENTS

I would like to express my appreciation to Kansas State University and the Department of Chemistry for their support of the scientific glassblowing facility and their continuing encouragement in my professional endeavors.

Seven pictures have been deleted from the printed text due to copyright. For further information, please contact the author directly.

Stress Management

by

Ariel J. Rom[a]

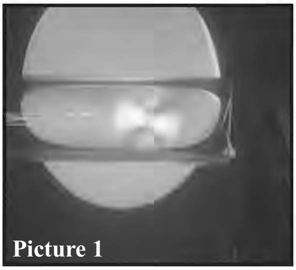
ABSTRACT

Build a polariscope, understand how stress develops, and reduce and/or alleviate stress in borosilicate and other types of glass in the most efficient manner.

Craftsmen and artisans who work in the medium of glass are familiar with the unfortunate fact that glass can break in many different ways. Therefore, it is of the utmost importance to understand the glass before working with it. The concentration here is on strain, stress (compressive and tensile), compatibility and the coefficient of expansion, and the annealing process. Overall, one of the most important things to remember is to listen to your gut. If you are feeling a little tense, odds are, the glass is too.

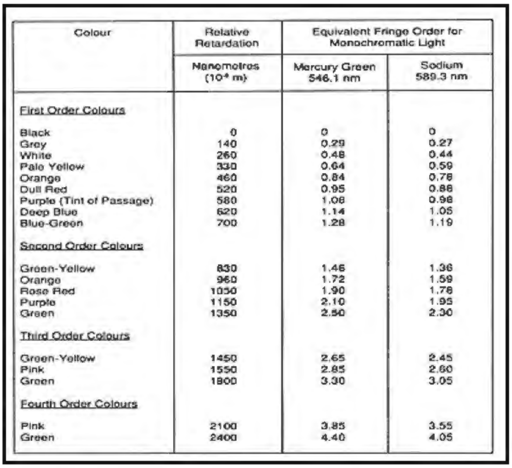
STRAIN

Strain is defined as the measure of the dimensional change that occurs as a result of external forces, or differential thermal contraction during production of the apparatus and as the product cools down unevenly. Strain is the result of the various systems of stress within the glass. Stress is defined as the internal force per unit area. One of the best things to do when dealing with residual stress is to visually mark where the strain is coming from and that is done with a polariscope. (Picture 1)



Picture 1

The polariscope highlights the intensity of the light as plane polarized waves will be traveling at different velocities through the stressed parts of the glass. It allows the glassblower to visually measure the strain in the glass at that particular time. It is important to remember that stress cannot be seen. The intensity of the light under the polariscope measures the strain which is caused by the force of the residual stress present in the glass. A polariscope is a necessity in every shop, not only to ensure the customer a fully functional apparatus when finished, but also for a better understanding of the stress endured by the glass while making it. If you have an understanding of the glass's inclinations to be stressed in a certain area at any given point, you will find yourself breaking less and being far less frustrated.



Colour	Relative Retardation	Equivalent Fringe Order for Monochromatic Light	
	Nanometres (10^{-9} m)	Mercury Green 546.1 nm	Sodium 589.3 nm
First Order Colours			
Black	0	0	0
Grey	140	0.29	0.27
White	260	0.48	0.44
Pale Yellow	330	0.64	0.59
Orange	460	0.84	0.78
Dull Red	520	0.95	0.88
Purple (Tint of Passage)	580	1.06	0.98
Deep Blue	620	1.14	1.05
Blue-Green	700	1.28	1.19
Second Order Colours			
Green-Yellow	830	1.46	1.36
Orange	960	1.72	1.59
Rose Red	1050	1.90	1.78
Purple	1150	2.10	1.95
Green	1350	2.50	2.30
Third Order Colours			
Green-Yellow	1450	2.65	2.45
Pink	1550	2.85	2.60
Green	1800	3.30	3.05
Fourth Order Colours			
Pink	2100	3.85	3.55
Green	2400	4.40	4.05

Table 1. *Colors produced by the progressive increase of stress in a model placed in a crossed polariscope using white light*

The components necessary to build a polariscope are two polarized sheets and a light. One sheet is turned perpendicular to the other which is backlit

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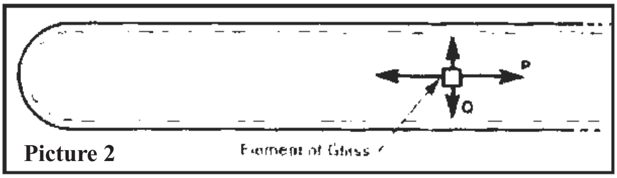
by a light bulb. Polarized sunglass lenses work just as well, but they can be very limiting. As far as light bulb options go, you may use a monochromatic or a white light bulb (chosen based on what kind of analysis you are doing). Monochromatic light sends out a single wavelength and this produces a black and white image with varying intensities of black, white, and grey. Monochromatic light is preferable for quantitative analysis. A white light bulb sends out many wavelengths producing a spectrum of color with varying intensities. White light is preferred qualitatively. There are filters available to achieve the colored effect when using a single wave length light source. (Table 1)

Ideally we would finish up the day's work, anneal the product overnight, and ship it in the morning. However, life is unfortunately not like this; if it was, we would obviously not be reading about stress management right now. So if you have some big time Texas oil corporation breathing down your neck saying they need that condenser shipped this afternoon, take some simple steps to get the job done stress free.

The predominant factor in controlling the level of stress is slow, even heating and cooling cycles to prevent too much temperature deviation throughout the area worked and the surrounding area. During heat transfer, the energy stored in the intermolecular bonds between atoms changes. When the stored energy increases, so does the length of the molecular bond. As a result, solids typically expand while being heated and contract on cooling. For example, it is similar to the behavior of a stringed wooden instrument like a banjo. If I leave my banjo in a cold place it will be quite some time before it will damage the instrument. Conversely, if I bring it in from my snow covered car to my heated living room, the wood will expand causing the neck to bow. However, unlike the elasticity that exists in metal or wood, which will adapt to the force created, glass is a brittle substance, and will break before any noticeable deformations occur.

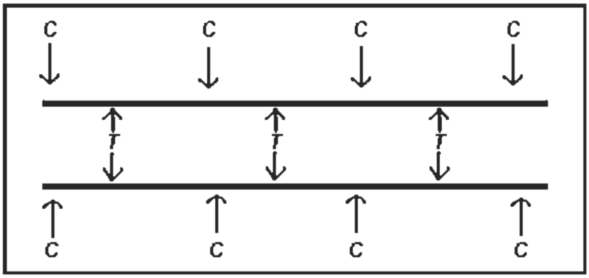
Stress in tubes tends to run perpendicular as shown in the figure at right. (Picture 2)



Picture 2

COMPRESSIVE STRESS

Compressive stress will occur as the glass is heated up. Due to the low thermal conductivity in the glass, as heat is applied to the outer surface, it pushes against the still cool inner surface and this type of stress will develop between the layers. If too high of a heat is applied to the surface of the glass without a proper warm in, it may crack. A slow and even warm in to ensure the entire area being worked is above the strain point will keep the level of stress in the glass minimal. (Picture 3)



Picture 3. *Flat glass showing compression and tension forces. Once annealed, the forces are in balance.*

TENSILE STRESS

"Tensile stress is that type of stress in which the two sections of material on either side of a stress plane tend to pull apart or elongate."[1] It usually occurs as the glass is cooling down and the inner tube continues to shrink after the outer tubing has reached room temperature.

The forces created as the tubes contract at different rates produce the tensile stress. The cooling rate therefore should not be too high and should always be correlated to the glass' thickness. Nevertheless stresses generated during this phase are only temporary and vanish after the temperature equalizes within the glass part.

The thickness of the glass is the key factor in determining your annealing rate. The annealing time increases with the "square" of the thickness. So a 10 mm thick piece of glass will take a hundred times longer to anneal than the 1 mm piece. Keep in mind that larger diameter tubing, flasks, and bell jars may often have inconsistent wall weights, so anneal according to the thickest spot. In my experience, a single bell jar can vary up to six millimeters in thickness (from six to twelve millimeters). By using an ultrasonic thickness tester gauge, you can determine precisely the thickest spot.

COMPATIBILITY

There are thousands of different types of glass available and they all have a unique set of properties. Almost everyone has an antique glass or dish that needs repairing, but make sure to determine exactly what type of glass you are dealing with prior to attempting the repair. The base ingredient in the batch is silica, which has an unusually high melting point. So compounds are added to lower the melting point and then other compounds are necessary to stabilize the glass. Since glass has many unique applications, there are many specialized glass formulas. For example, eye glasses use lanthanum oxide which creates a high refractive index. Boron in glass will alter the thermal and electrical properties. All of the ingredients in a batch will alter the coefficient of expansion (hereinafter referred to as COE) of the glass. The coefficient of expansion is the most important factor when it comes to glass compatibility.

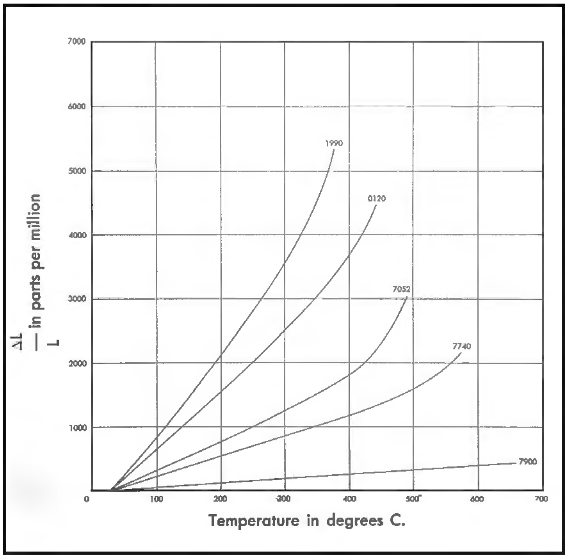


Table 2. Thermal Expansion. *The curves remain linear until 300ºC where they swing upward, indicating a higher rate of expansion as the glass reaches the annealing zone.*

It also must be kept in mind that just by melting, the glass composition is changed, and once overworked, foggy spots known as divitrification may appear. These spots may be fire polished to regain clarity. Though sometimes after being overworked (perhaps being fixed one too many times), they are permanent.

As for defining compatibility with glass, it is difficult. Two different glasses with different COEs may hold together, but are you willing to hold your breath as your piece hits room temperature? Remember that COEs for glass are valid from 20-300ºC. The rate of expansion increases as the temperature rises towards the annealing point.

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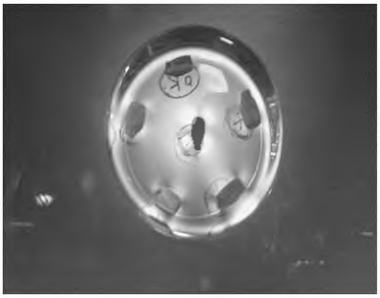
[1] "Tensile Stress," *Nuclear Power Fundamentals*. March 10, 2008. www.tpub.com/context/doe/h1017ul/css/h1017vl56.htm.

There are even times when two samples of the same type of glass are incompatible.



Picture 4. *To ensure glass used is all compatible, studio glass artist, Gordon Smith, encapsulates samples of several colors of the same coefficient of expansion as well. After the paperweight was fully annealed, strain has developed around all but one.*

The stringer test is a great way to determine compatibility. In the stringer test, thoroughly melt two samples together, and pull a fine thread with it. One of two things will happen: the stringer will stay straight, which means it is compatible, or it will bend out of shape upon cooling because there is a difference in the expansion rates.

When dealing with larger apparatus, keep in mind that the more glass being heated, the more expansion will occur. This force can be a menace in an apparatus with a double ring seal as the tubing elongates and contracts. Make sure to properly anneal the first ring seal in order to comfortably complete the second seal. Do not forget, bellows are always an option. One bellow for every 100 mm will give the jacket the flexibility to compensate for the expanding of the inner part of the tube. Many of the processes glassware is used for require extreme heating. So if the bellows are not in place, the apparatus could break during usage.

COEFFICIENT OF EXPANSION OF COMMONLY USED GLASS

Satake (used in Japan's bead making: often melted by a strong Bunsen burner): 113 to 115 x 10^{-7}/K

Soft: 90 to 105 x 10^{-7}/K (expansion rate of 0.0000090 inches for each 1 degree Centigrade)

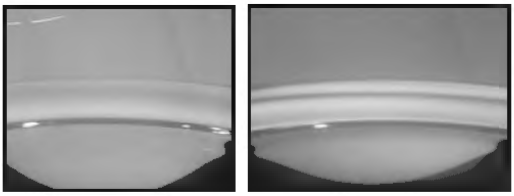
Borosilicate: 33 x 10^{-7}/K

Quartz: 5.9 x 10^{-7}/K

Soft glass expands three times the rate of borosilicate. No wonder those soft glass rods blow up when not properly warmed!

ANNEALING

Glass passes through several phases when it goes from working temperature to room temperature. A slow warm in will ensure the area being worked is above the strain point and will significantly reduce the amount of strain created. Flame annealing and a slow warm out will usually ensure an apparatus' ability to make it to room temperature. Flame annealing is ideal for dispersing the strain, but the object should be annealed in a lehr to alleviate all the residual stress remaining at room temperature.



Pictures 5 and 6. *The first flange was annealed by blasting the fire at an angle hitting both the outer and inner surface of the tube. The second flange was annealed by spinning over a Bunsen burner which only made contact with the outer surface. These pictures were taken under a colored polariscope. The more colored lines in an area represents more stress present.*

As one increases the temperature, a viscous glass lowers its viscosity over a wide temperature range. More viscous glass is stiffer when worked and usually takes more heat to reach a softening point. From the chart in Table 3 it can be seen that the viscosities for strain and annealing points do not change by the type of the glass, only the temperatures are different. When the glass has reached 10^13 Poise, stress is relieved from the glass. When the viscosity surpasses 10^14.5 poise, all residual stress still present will become permanent. Glasses that have a lower viscosity will generally need less time soaking at their annealing temperature but due to a high COE, will need a more precise cooling cycle from the strain point.

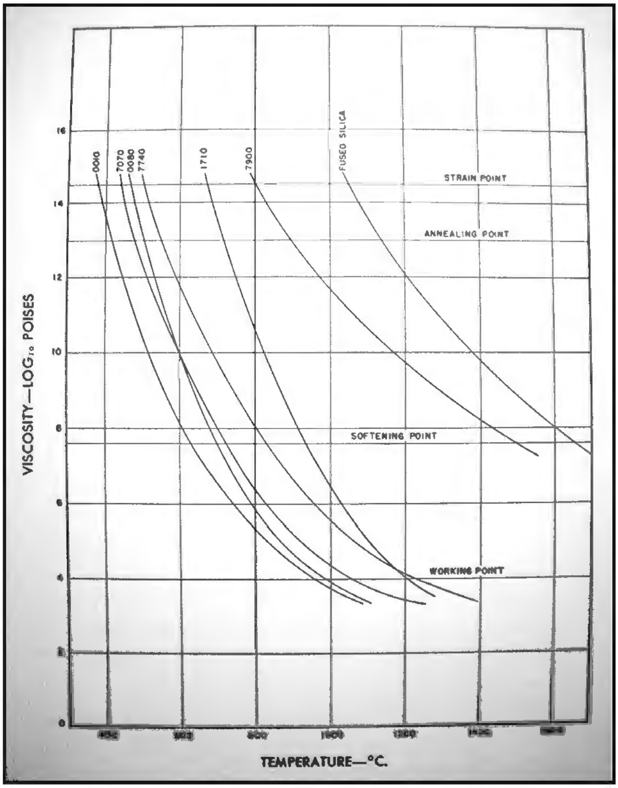


Table 3. *This chart shows viscosity curves for several Corning brand glasses.*

There is a big gap between the strain point and the softening point. In this zone, a higher annealing temperature will relieve the stress faster. Just make sure not to slump your coils in the process. Less viscous glass, such as soda-lime, will slump at a greater rate than its counterpart borosilicate if the annealing temperature is too high. At the upper end of the annealing range, the internal stress is substantially relieved in fifteen minutes. As the temperature approaches the strain point, the rate at which stress is relieved slows down. At the lower end of the annealing cycle, the stress is substantially relieved in four hours. Once the temperature drops below the strain point, the remaining strain is permanent. Temporary strain results as the temperature decreases from the strain point to room temperature. The apparatus may crack if the temperature decreases too fast, but the stress is relieved when it hits room temperature. If residual stress remains in the glass below the strain point, it is more likely to break due to this temporary stress. If annealing an apparatus after it has already cooled down or to make a tricky repair, a more gradual warm up is recommended. The complexity and thickness of said apparatus will determine how long a cooling cycle you will need as previously described when discussing compressive stress.

The good news is stress can even be used to our advantage. For example, just scoring the glass and inducing a controlled line of stress will crack the glass with a perfect edge when done right. Toughened or tempered glass has been processed by controlled thermal or chemical treatments and is designed to break into small pieces by using heat and chemical treatments. It has increased strength compared to normal glass and will usually shatter into small fragments, rather than sharp shards, when broken. This quality is lost when the glass is reheated past a certain point. Some theorize that old time paperweights have an increased strength due to compression stress.

In a world where efficiency has become a priority, we must strive to continue to make the finest product. We must have an understanding of the glass' physical and chemical properties, have the equipment necessary to gauge and test the glass prior to working, and the knowledge to complete the product with efficiency.

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Oxide Free Seals Used at Liquid Helium Temperature

by

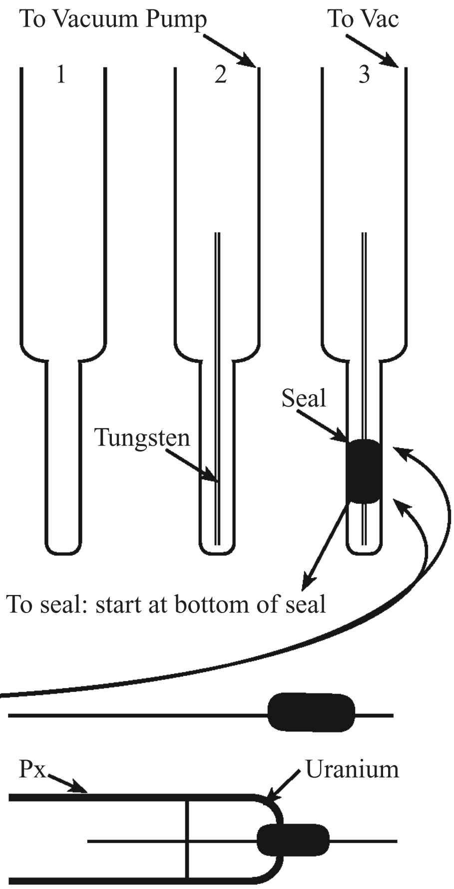
Ralph Albertson[a]

ABSTRACT

A technique for making a glass to tungsten seal which is stable at helium temperature.

While I was working at Columbia University in the late 60's, I was asked by a doctoral student to make three microwave tubes to be used at liquid helium temperature. The reason he wanted three at this temperature was because you lose about 50% of your seals due to the seals not working. He wanted three hoping to get a least one of them to work. I decided to try oxide-free seals. I sealed tungsten to a four-foot length of tubing, placed it in liquid helium while testing it with a Vecco Helium Detector. It was vacuum tight. I made him three oxide-free sealed microwave tubes. He performed his experiment with no loss of tubes.

Prepare Glass (Uranium)



1. Degas tungsten
2. Clean tungsten oxide
3. Clean with distilled water, do not touch clean area with your hands. Do not oxidize tungsten.
4. Crack off carefully
5. Seal to tubing
6. Use mechanical pump
7. I used Sylvania ground seal tungsten

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