CHEMISTRY CHRONICLES

Eyeing the Glass Past

From antiquity to the present, this unique material has transformed society with its beauty and utility.

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Glass is not really a product so much as a state of matter—a liquid that has obtained such a high degree of viscosity that it appears to exist in a solid state. Vitrium (Latin) and glas (Celtic) not only are the words for glass but are also descriptive of the blue-green color of the typical impure glass formed in antiquity, the color due to the nearly inevitable presence of iron oxides.

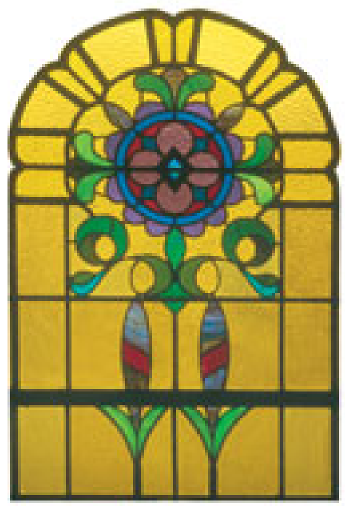
Making Glass

The production of glass requires a combination of chemical recipes and physical treatments (see box, "A Glass Act"), whose increasing sophistication followed the developing civilization in the West. Evidence of the earliest manufactured glass (nontransparent beads) dates from ca. 3500 B.C. in Mesopotamia (current Iraq and Syria), from which it appears to have rapidly spread to Egypt. The oldest piece of Egyptian glass with a datable inscription is a large ball-bead bearing the cartouche of Amenhotep (1551–1527 B.C.).

One of the earliest chemical modifications deliberately made in Egyptian glassmaking was the production of new and deeper colors through the addition of metal oxides to the mix. White opaque glass resulted from tin oxide, and copper additives were used to create turquoise blue, jasper red, and a green color (also obtainable using iron). Such colors became tremendously popular, with color techniques changing little even up to the period of stained glass windows of the High Middle Ages.

Physically, hollow glass objects were first made by pouring molten glass into sand molds and sand cores, with the first glass vases dating back to the 1500s B.C. in Mesopotamia. Glassmakers were then brought to Egypt as prisoners of Thutmosis III (1504–1450 B.C.), as evidenced by glass vases found bearing his name. But the true breakthrough in the production of hollow glass objects came with the development of the glassblowing pipe.

Although of uncertain origin, the most common attribution of this discovery is to Syrian craftsmen ca. 27 B.C. to 14 A.D.



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They created a hollow metal pipe with a mouthpiece at one end that was used to lift gobbets of molten glass that could be blown and turned to create hollow objects. This dramatically changed the quality and speed with which glass could be made.

Roman Glass

The Roman Empire developed glassblowing. The Romans were also responsible for glassblowing into a mold; this made the mass production of identical objects possible, vastly speeding the manufacturing process. Roman glass spread throughout the then-known world, reaching all the way to China via the silk routes.

Another important innovation in the Roman era included the discovery, in Alexandria ca. 100 A.D., that manganese oxide ("glassmaker's soap") interacting with colorizing impurities could be used to produce clear glass on demand. Clear glass also became much prized and allowed for the development of glass windows. And although thin translucent sheets of alabaster or mica were typically used for Roman windows, in Pompeii and Herculaneum, flat panes of glass were used in the windows of the wealthy; one surviving example is a window in the ceiling of a plaza bathhouse.

As recorded by Pliny and Petronius, the Roman emperor Tiberius (who reigned from 14 to 37 A.D.) is responsible for stomping on one particular innovation. Approached by a Roman glassmaker who demonstrated a glass vase that did not smash when thrown to the ground, Tiberius ordered the man killed and his workshop destroyed for fear that such glass would replace the market for silver and gold tableware (thereby greatly diminishing the emperor's wealth). If the story is true, one chemical explanation for the hardness of this glass would be the glassmaker's addition of boric acid or borax to the recipe for glass.

After the fall of the Roman Empire, glass manufacturing did not change dramatically until the early Middle Ages, when glassmaking in Europe significantly diverged—based on chemistry. In the south (as exemplified by Venice), high-quality imported soda ash continued to be used, but in the north, lack of access to these imports led to the substitution of potash derived from the burning of trees. This disparity helped Venice become the quality glassmaking center of the Western world.

By the late 13th century, Venice transferred its glassmaking industry to the island of Murano, both to protect the city from fire and to protect its glassmaking secrets (including the production of fine clear glass using magnesium oxide) from being stolen by other city-states or foreign governments.

Mirror, Mirror . . .

In their book *Glass: A World History*, Alan Macfarlane and Gerry Martin advance an intriguing thesis about glass in human history—that the development of the metal-backed glass mirror was responsible for the Renaissance. Scholars have long held the mirror as being critically responsible for the development of perspective in Renaissance art, but the authors carry the mirror's role much further, tying it to the new concept of individuality, "unique to the West and to the period from about the 14th century" that was the philosophical crux of the Renaissance mentality.

According to the authors, both the timing and the location are right for this assumption—not only were Italy and The Netherlands foci of Renaissance development, they were also two of the most advanced regions of mirror-making and use. The proliferation of mirrors, autobiographical self-portraits of mirror-holding artists such as Rembrandt, and mirrors as décor in Europe stand in contrast to the strikingly different treatment of mirrors in Japan, where they were made of steel and treated as sacred objects for contemplation or practical objects for adjusting one's grooming rather than as decorations and vanity "looking glasses". The metal mirrors reflected back only 20% of the light and added a color tinge. According to the authors, "The Western glass mirror showed what appeared to be real . . . representing three-dimensional space on a flat surface and encouraging the eye to see foreground and background." In contrast, the nonglass mirrors of other cultures "encouraged imagination and stimulated thought," enhancing their mystical rather than real-world significance.

Coupled to these results claimed for the mirror, the invention of spectacles in the 13th century also appeared to have far-reaching effects on the intellectual tide in Europe compared with other cultures, because these glass aids "increased the intellectual life of professional workers by 15 years or more." This had profound implications for both scholarship and crafts.

Revolutions Through Glass

In the 1590s, glass telescope and microscope lenses appeared in The Netherlands. Their importance to the history of science cannot be overestimated. Within the next hundred or so years, natural philosophers from Leeuwenhoek to Galileo to Newton transformed Western understanding of astronomy, physics, and biology through the use of these glass-based instruments. Skilled technicians creating sturdy glass globes enabled the study of vacuums and gases; hence Boyle's laws, the discovery of oxygen, and the study of air and weather using barometers. Historians of science have argued that such glass artifacts are the true, technological source of the scientific revolution and not some arcane quality of Western thought compared to Eastern mysticism.

By 1665, plate glass windows and mirrors were considered to be the height of both technology and culture, symbols of wealth and power. Hence their prominent use by Jean-Baptiste Colbert in creating the majestic effects at the Palace of Versailles to highlight the glory of the Sun King, Louis XIV.

A Glass Act

Glass is manufactured using three key components: formers, fluxes, and stabilizers. Formers can be any chemical compound that can be melted and cooled into a glassy state. Silica (sand) provides the most common former, but anhydrous boric acid and anhydrous phosphoric acid are other examples. Because sand requires such a high temperature to melt (1850 °C), fluxes are added to lower the melting temperature (to 1300 °C). Typical fluxes include soda ash, potash, and lithium carbonate. This decreased temperature comes at a price; for example, it can make the resultant glass chemically unstable to water or contaminated with structurally destabilizing crystals. Thus, stabilizers are added to restore or increase structural integrity. Typical stabilizers include limestone, alumina, barium or strontium carbonate, and zinc oxide.

In 1679, the brilliantly hued "ruby glass", which used gold chloride as a colorant, was developed. Also in the 1670s, George Ravenscroft, an Englishman, patented lead crystal. He discovered it in his attempts to find a substitute for Murano glass; replacing potash with higher proportions of lead oxide resulted in a product that sparkled (because of a high refractive index) and was highly amenable to cutting and engraving. Commercial mass production began in the 1760s.

Developments in the late 18th century made optical (technical) glass readily available in the 1800s for use in precision instruments. A Swiss watchmaker, Pierre-Louis Guinand, achieved the required homogeneity in glass in 1790. He used a process for stirring the molten glass. The procedure was kept as a trade secret, but it was eventually exported to England and became common throughout the 19th century. Such glass is free of physical impurities ("stones" from unmelted particles and gas bubbles). It is also chemically homogeneous (nonhomogeneous regions give rise to variable refractivity).

The other key requirement for the production of optical glass is the need for a wide range of refractive index and dispersion. This led to considerable research in altering the ingredients in glass manufacture. For example, Michael Faraday extensively studied the manufacture of optical glass containing boric oxide. Such studies led to new varieties of optical glass. Equally critical were refinements in the grinding and polishing of such lenses—which demanded significant improvements in machining and the understanding of refractive properties. Two of the modern giants of optical glass instrumentation were born in the 19th century: the Carl Zeiss Co. (1846) in Germany and the Bausch & Lomb Optical Co. (1874) in the United States.

Transparent Success

By the end of the 19th century, Michael Owens, an American engineer, launched a critical stage in the mass production of glass with his invention of the automatic bottle-blowing machine. The device, marketed as the Owens Libbey Suction Blow machine, revolutionized countless industries, from food to pharmaceuticals, by increasing the availability of glass bottles for general use and driving down costs.

The 20th century gave birth in 1912 to heat-resistant glass through the appropriate incorporation of borax into the mix, with the first commercial glass ovenware (Pyrex) offered in 1915. This, of course, also revolutionized the use of glass in scientific research. And throughout the rest of the century, developments in glass, from new means of tempering to fiber optics, continued to transform everyday life, making modern civilization, in the most literal fashion, an edifice built upon sand.

Further Reading

Chronology of glass; www.glassonline.com/history.html.

Corning Museum of Glass; www.cmog.org.

Macfarlane, A.; Martin, G. *Glass: A World History;* University of Chicago Press: Chicago, 2002.

Morey, G.W. *The Properties of Glass;* Reinhold Publishing Corp.: New York, 1954. ◆