Crystal Clear

We use clear, transparent glass for many things, from window glass and fine crystal goblets to thermometer tubes. Glassmaking is an ancient art, but *colorless* glass is a relatively recent development.

Since the beginning of civilization, people have known about two types of naturally occurring glass. When lightning strikes sand, the heat can fuse the silica grains into long slender glass tubes that are known as "petrified lightning," or fulgurites. The heat and pressure of a volcanic eruption can fuse sand and rock into a black glass called "obsidian."

As early as about 3000 B.C., some artisans discovered how to make their own forms of glass as glazes on ceramic vessels. The art of glass manufacture reached great heights during the Roman empire, but many of the techniques were lost during the Dark Ages.

Simple fused-silica glass can be made by melting sand alone. This makes fine-quality glass, but it is very difficult to manufacture because the melting point of sand is 1723°C, a temperature higher than most furnaces can reach. Adding a flux of soda ash (sodium carbonate), though, reduces the melting point to only 850°C, a temperature much more easily attainable to early societies. Unfortunately the resulting glasses are relatively water soluble, making them impractical for many uses.

The addition of a small amount of calcium carbonate, from limestone, to the mixture makes the glass insoluble again and suitable for many purposes. These "soda-lime" or "crown" glasses are the most common types produced even today, accounting for about 90% of current glass manufacture.

The basic ingredients of glass—sand, ash, and lime—were readily available to early societies, but many natural impurities affected the transparency and color of the resulting material. The contaminants varied from region to region, allowing each local glassmaker to claim a characteristic product. Crude manufacturing techniques also left streaks and bubbles in the glass, further decreasing its clarity.

Glassmaking underwent a tremendous resurgence in Venice in the 13th century, possibly because of revived contact with the Eastern Roman Empire. Not until later, though, did Venetian artisans rediscover how to make transparent and colorless glass. They discovered how to eliminate unwanted colors and contaminants from a glass melt by adding counter-colorizers. The resulting grayish glass, somewhat less transparent than the colored material, proved acceptable if the finished article remained thin—the loss of transparency was less noticeable than the unwanted tint. This cristallo, named because of its resemblance to natural rock crystal, proved to be the greatest export product of the Venetian glassmaking industry.

Cristallo was an extremely ductile material, which cooled quickly and could be blown very thin. The glassmakers' need to work with great speed and dexterity to shape the glass properly influenced the style and shape of Venetian glass objects. For the first half of the 16th century, cristallo glasses remained rather simple, but soon the glass blowers developed great skill and creativity in shaping and decorating their products. They made elaborate toys and wineglasses with intricate decorations; they used tools with diamond points to engrave designs into the clear surface.

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Venetian glass was superior to that made in other parts of Europe, but glassmaking, like all crafts in Venice, was regulated by strict guilds and considered a state monopoly. The trade secrets were considered so valuable that all the Venice glassworks were removed to the island of Murano as early as 1291. Workers were forbidden to leave the island so they couldn't sell their knowledge elsewhere. (The move to Murano may also have been motivated by the need to protect the city from fires started from the glassmaking furnaces.)

By the 16th century, though, European kings and nobles openly offered handsome rewards for anyone who knew the secrets of Venetian glass manufacture. Many Venetian glassmakers escaped from the island of Murano and fled elsewhere, setting up their own shops in other parts of Europe with substantial support from local noblemen.

In 1575 the Venetian refugee Giacomo Verzellini was granted a 21-year monopoly in London, provided that he make Venetian-type cristallo. Despite Verzellini's monopoly and others like it, however, England remained dependent on imported glass for the next century.

In 1664 the Worshipful Company of Glass Sellers, a group English glass retailers, incorporated to discover ways to overcome foreign domination in their market, and also to express their dissatisfaction with the quality they received. In 1675 the Worshipful Company commissioned chemist and experimenter George Ravenscroft to investigate new glassmaking techniques using local raw materials. The company hoped to create a glass superior to Venetian cristallo, a glass that more closely resembled rock crystal in clarity and transparency, without the gray or brown muddiness seen in much of the Venetian product.

Ravenscroft first attempted to substitute calcined flints instead of sand, and potash instead of soda ash. His "flint glass" was a failure at first, developing many fine cracks as it aged. Ravenscroft added lead oxide to the flux, however, and this proved to be a tremendous success. Not only did the lead oxide eliminate the formation of fine cracks, it produced a high-quality lustrous glass that was also heavy and durable. "Lead glass" was soft enough to be cut and engraved easily. It had a greater refractive power than common crown glass and a somewhat greater light-dispersion properties than other types of glass.

The Worshipful Company of Glass Sellers then set exacting standards for the production of lead glass as they began to export English glass to foreign markets. In honor of Ravenscroft's work, their earliest glassware bears an engraved raven's head. Ravenscroft's glass is what we generally refer to today as "crystal" or "lead crystal." The term "flint glass" is also sometimes used, though flint is no longer included as a base for its manufacture.

English lead glass quickly superseded conventional Venetian cristallo, and within a short time only a few provincial centers continued to make the less-satisfactory Venetian-style glass. By the 18th century, lead glass had become the favorite in all European markets, and England had become the world's leading glass producer. Makers of lead glass produced chandeliers, bowls, candlesticks, mugs, and cups, but their primary product was wine glasses, whose style evolved and influenced all other manufacturers of tableware.

Crown glasses—made from sand, soda ash, and lime—account for most current glass production. Lead crystal, although more expensive to produce, is easier to melt and fabricate. A high concentration of lead oxide in the flux and a relatively low alkaline content imparts desirable electrical properties to the glass. Lead glass has been widely used in radio and television tubes, in capacitors, and as insulating parts in electric lamps. Lead glass has also been used for prisms and lenses. Telescope makers found that overlapping a lead glass lens with a regular crown glass lens could eliminate most of the chromatic aberration around the telescopic images of bright objects. Lead glass absorbs most ultraviolet light but little visible light, also an advantage in telescope lenses.

The fine crystal in your house, the wedding gift that gathers dust on the high shelf and is taken down only for special occasions, has its own long tradition. But apart from glamorous tableware, brilliant chandeliers and art objects, lead glass has found many other uses in the three centuries since its creation. The science of glasses has branched out enormously, producing many new types for specialized applications. In addition to the basic silica glasses, we now have oxynitride glasses, phosphate glasses, chalcogenide glasses, halide glasses, and others. Materials researchers have developed glassy substances for particular uses, depending on thermal expansion requirements, preparation and softening temperatures, melt viscosities, and chemical compatibilities. No longer are glasses used simply for containers, windows, mirrors, and lenses; current applications have expanded to include fiber optics, thin films, and semiconductor and biological uses. Many applications—and many new types of glassy materials—continue to be developed each year.

KEVIN J. ANDERSON

Editor's Note: For more on today's "science" of glasses, see the *MRS BULLETIN* focus issue on this subject, Vol. XII No. 5, 1987.

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