THE CHEMISTRY OF PURPLE GLASS

by Rick Baldwin, Brunswick, Ohio

As newer collectors become involved in the hobbies of collecting glass bottles and insulators, curiosity develops about how different colors are achieved...particularly with respect to purple and amethyst glass. Questions about purple-colored glass collectibles are routinely posted to social media sites, primarily because of the influx of "irradiated" or "artificially-altered" purple-colored items into these hobbies over the past several decades. New collectors are increasingly wary about purchasing such colored items, especially if there are big prices associated with such, as they do not have the experience in differentiating between "legitimate" and "altered" items. Seasoned collectors can also have significant difficulty, as there are so many variables in the glass-making process that can influence the specific tint, shade, depth-of-color, etc. of the final product, whether color-altered or not. Besides being increasingly available at flea markets and on internet sales and auction sites, color-altered items are routinely observed on sales tables at bottle and insulator shows, despite attempts by show hosts to deter such. As we try to bring new and younger collectors into our "aging" hobbies, it would be self-defeating to turn them away due to their uncertainties in what they may be purchasing for their collection!

The following article elucidating the chemistry associated with purple glass was written by the author and previously published in a major insulator hobby periodical. Although this article focuses on glass insulators, the technical content is applicable to any purple and/or "decolorized" bottles, insulators or other early glass collectibles.

Decolorizing Glass With Manganese

by Rick Baldwin

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To the insulator collector colored glass has special appeal, and the challenge of acquiring the wide variety of purple and sun-colored amethyst (SCA) insulators which are known to exist can be attributed to almost every major insulator manufacturer. The shades, tints and color variations which exist are numerous, ranging from the pink, rose and burgundy tints of western glass to the deep purples which are common to Brookfield, Hemingray, Australian and Canadian glass. Threadless and other early telegraph insulators have also been found in amethyst and scarce puce shades.

Colored glass is usually made by adding an oxide of transition metal to the glass mixture, but the final color produced will depend upon the interactions between

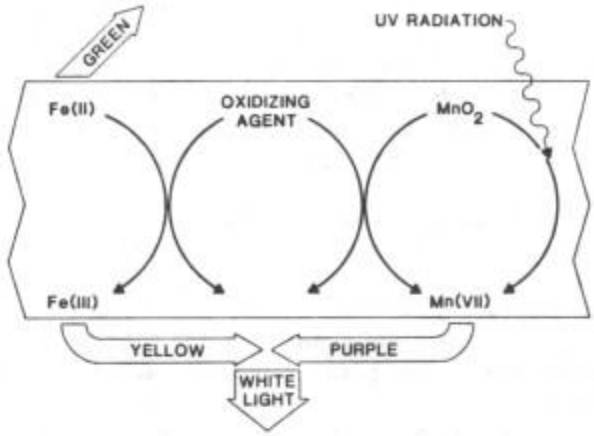
the valence or oxidation state of the metal,
the compositions of the base glass, and
the heat treatment to which the glass is subjected.

The chemistry associated with the transition element manganese is primarily responsible for the purple and amethyst colorations found in glass.

Soda-lime glass, which is the common base composition for bottles and insulators, almost always contains iron oxide as an impurity, and a small percentage of iron in the glass will give it a green coloration. Around 1880, a demand for clear glass for food preservation containers forced manufacturers to perfect techniques of decolorizing aqua-colored glass. Manganese was commonly employed as a decolorizing agent, until approximately 1915, at which time World War I cut off the main source (Germany) of this element. During the period 1915 to 1930, selenium, which imparts a straw, pink, or "honey" tint to glass, was used as a decolorizer.

The initial step in decolorizing glass was to add oxidizing agents (such as potassium nitrate and red lead) to the melt. The iron impurities would thus be oxidized to the +3 state Fe(III), which imparted a much weaker yellow color to the glass than the bluish-green color of Fe(II). Adding manganese dioxide ($MnO2$) to the melt would aide in oxidizing the iron, and the manganese would also be oxidized to a chemical state (e.g. MN(VII)) having a characteristic lavender color which would neutralize the yellow-green color due to the iron impurities.

Substances exhibit color because they can absorb selected wavelength or energy ranges from white light and transmit others. Due to its discrete electronic structure, the highest oxidation state of manganese, Mn(VII), will absorb electromagnetic radiation in the green region of the visible spectrum. The energies on either side of this region, which correspond to blue and red light, will be transmitted (or reflected) and blend to produce the color sensation of purple or magenta to the human eye. The purple color of the Mn(VII) ion and the yellow-green color of the iron impurities are complimentary that is, when mixed in equal proportions, they produce white light or the sensation of no color at all. During the decolorizing process, if the manganese content of the glass melt was too high and the purple color was too evident, a reducing agent (such as a piece of charred wood or a potato) would be added to reduce the excess manganese back to a lower (colorless) oxidation state.



Deep purple-colored glass would be produced if the concentration of manganese in the melt was high and if strongly oxidizing conditions were present. It is conceivable that purple insulators were purposely produced for their beauty or for identifying or distinguishing different lines. The final color obtained with manganese present in the glass mixture (pinkish-purple to violet) would depend on such factors as

whether lead or barium was a constituent in the glass mixture base,
the presence of soda or potash as the alkaline constituent,
the reducing or oxidizing conditions of the furnace, and
the heat and duration of the "found."

Nickel oxide could also be used as an additive to impart stable purple shades to glass, depending upon the composition of the base glass: a brownish-violet color would result with soda-lime glass, a redish-violet color with potash-lime glass, and a deep purple color with lead silicate glass.
"Black glass" is usually made by adding MnO2 to the melt, either alone or along with oxides of nickel and chromium. A beautiful puce color is obtained when purple and amber coloring agents are blended together. Sun-colored amethyst glass results from the exposure of manganese-containing decolorized glass to the ultraviolet (UV) rays of the sun. Any manganese still present in the reduced chemical state will absorb UV-radiation, which is sufficient in energy to oxidize it to the purple-colored chemical state. The extent of purple coloration in the glass is due to the length of exposure to the UV-radiation. Glass cannot be effectively sun-colored through a glass window because the window glass will absorb much of the sun's ultraviolet rays.
It is possible to artificially sun-color glass by exposing the glass to an intense UV-light source or to other sources of ionizing radiation. A Germicidal Lamp in a "purpling box" is often employed to accelerate the sun-coloring process.
In conclusion, every collector knows that the color which the eye perceives an object to have may differ when the object is viewed under different lighting conditions. Natural sunlight produces a fairly uniform distribution of visible light. However, light from other sources have different spectral energy distributions -- e.g., incandescent illumination contains more red light than green light. The actual color that is perceived is a "blend" at each wavelength of the spectral reflectance or transmission of the object, the spectral sensitivity of the eye, and the spectral energy distribution of the light source. If any one of these contributing factors is changed, then the color of the object may appear different.