The Handbook of Glass Manufacture

3rd Edition

Volume II

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A book of reference for the plant executive, technologist and engineer.

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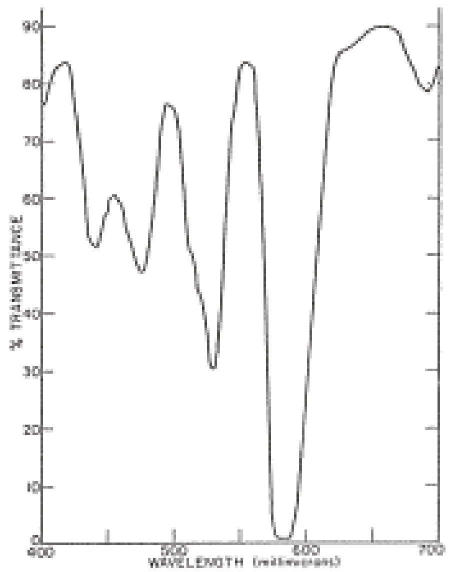

Figure 17. Spectral transmittance of didymium glass (Corning Glass Works Filter #5120).

these ions. Therefore they are less affected by the atomic environment and sharp line spectra (Fig. 17) are obtained. The resulting colors are a very pleasing purple for neodymium (which is used in art ware) and green for praseodymium. We can see that one of the absorption lines of neodymium is right at the wavelength of 589, the D line of the sodium spectra. Neodymium thus can be used when this line is to be suppressed (glass blowers' goggles) or when an instrument is to be calibrated. Neodymium glasses are dichroitic, that is, the color changes with thickness; it is bluish in thin, reddish in thick layers. Praseodymium and mixed neodymium praseodymium (didymium) glasses show similar effects. Neodymium can be used as one of the materials in decolorizers to compensate for yellow tints due to impurities. Its absorption spectrum makes it useful as a laser activator in glass. (See Subsection J(2)).

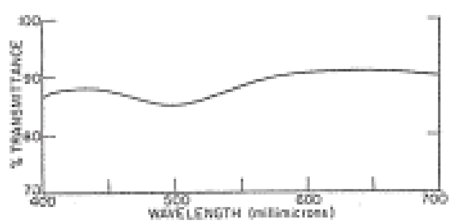

Figure 18. Spectral transmittance curve of selenium pink glass.

(8) Titanium[34] and Cerium[35]. Titanium and cerium in glass absorb primarily in the ultraviolet, and are important in UV absorbing glasses. The absorption band reaching into the visible can cause yellow and brown tints, which can be increased in certain base glasses, and, more so, by combining both ions with each other. A high sodium glass containing TiO_2 is hardly colored. High lead and boron glasses show more color.

Significant changes occur in the presence of other coloring ions. Small amounts of iron and titanium combine to form strong brown colors. Copper titanium glasses are green, manganese titanium glasses deep brown.

The color of cerium glasses is increased by oxidizing conditions as the equilibrium $Ce^{3+} — Ce^{4+}$ is shifted toward Ce^{4+}.

In colorless glasses exposed to high energy radiation cerium prevents the characteristic radiation coloration of glass while more ultraviolet absorption is produced by the radiation instead.

F. Coloration by Sulfur, Selenium and Tellurium

(1) Elemental Sulfur and Selenium. In contrast to the colors produced by the absorption of radiant energy in the electronic shells of the transition elements described under 4.E, there are colors which resemble more those induced by definite compounds or bonds and are obtained by the replace-

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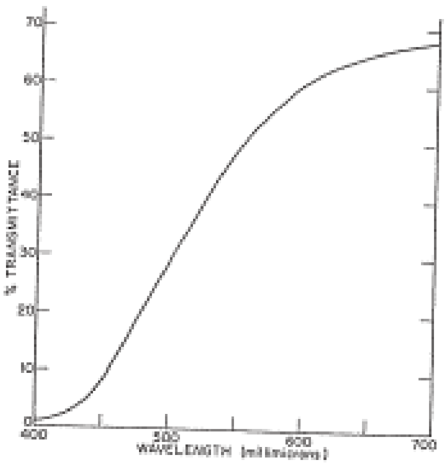

Figure 19. Spectral transmittance of commercial amber glass. (Pittsburgh Plate Glass Co. Amber B).

ment of some oxygen in the glass with the elements of the sixth group (S, Se, Te).

Elemental sulfur is stable only in glasses containing a very high percentage of boric acid. Such glasses are blue. (Dietzel[26])

Elemental selenium, in equilibrium with selenides as well as selenite groups, is believed responsible for selenium pink glass. It is particularly beautiful if potash is used in the base composition. The spectral transmission due to Se is illustrated in Fig. 18.

It is important to prevent reducing conditions which favor the colorless alkali selenide or the equally undesirable brown iron selenide, for the formation of which small iron impurities suffice. Extreme oxidation, however may "burn out" the color due to the formation of colorless selenate groups. These delicate relations are the subject of many studies. (See e.g. Hoefler[37] and Loeffler[38].) Often selenites of sodium, barium or zinc are used as the raw material with reliance upon the proper equilibrium for the presence of enough elemental selenium.

(2) ("Carbon") Amber. Such glasses are most likely colored by iron sulfide and polysulfides of sodium stabilized by reduction with carbonaceous materials such as sugar, starch, and carbon. (See particularly Neuman and Dietzel.[39]) (Transmission see Fig. 19.) It has been definitely established that pure carbon does not tint glasses containing no sulfur and iron impurities. Therefore, the old name of this important bottle color, "carbon" amber, is not adequate. More reddish tints correspond to a higher content in polysulfides. Impurities of iron greatly affect the sulfide amber color, since iron sulfide causes deep brown to black colors.

(3) Cadmium Sulfide. When added to glass, cadmium sulfide appears to be capable of being dissolved in the melt from which a colorless glass may be frozen in as sulfur is randomly distributed in the quenched glass. On reheating, however, or during slow cooling in which characteristic temperature ranges allow rearrangement, sulfur is ordered in a way that cadmium neighborhoods are preferred so that color centers resembling cadmium sulfide are formed and the glass becomes yellow (Weyl[49]).

Exaggeration of this "striking" process can cause crystallization of cadmium sulfide to an extent that the glass can be called devitrified.

The typical absorption of CdS glass is shown in Curve (a) on Fig. 20.

The steep absorption edge is valuable for its use in photographic filters, or for the production of very pure yellows. It appears that in some glasses cadmium sulfide is enriched in one of two separate glass phases. (W. Vogel 1967)[70]. The control of this phase and the use of zinc which is also enriched in this phase giving a colorless sulfide permits the control of filters of steep absorption edge at lower wavelengths than for example (a) in Fig. 20.

(4) Other Sulfides. These are capable of similar reactions, depending upon their solu-