Variable Transmission Silicate Glasses Sensitive to Sunlight

Abstract. The process of variable transmission in silicate glasses has been accomplished by optically pumping color centers by electron transfer from europium (II) or cerium (III) which absorb sunlight at higher energies than the color center. Absorbed energy quickly pumps the visible color center band to a maximum. Upon removal of activating light, the visible color spontaneously decays.

For some years we have studied color centers in quartz and simple glasses. This work has led to the discovery of glasses which immediately darken in sunlight and quickly recover their transmission in shadow. This effect involves the optical pumping of a color center absorption band centered at 5700 Å. Glasses of a large variety of compositions, including many commercial formulations, can be used.

The optical pumping by sunlight is accomplished by producing a suitably purified glass containing the proper amount of cerium (III) or europium (II). The glass must be prepared under controlled reducing conditions. The absorption bands centered at 3150 Å for cerium (III) or 3325 Å for europium (II) absorb sunlight (or other suitable light such as the 3660-Å line of mercury) and apparently transfer photoelectrons to nearby traps. The traps form the color centers which absorb light in the visible spectrum, giving an amethyst color to the glass. The color centers are metastable and decay in a few seconds; however, in presence of activating light, the color centers reach an equilibrium and exhibit a high absorption which is maintained for long periods under illumination. On removal of the activating light, the color in the glass disappears almost completely in a few seconds. The coloring and fading processes may be cycled repeatedly. After long usage, there is a decrease in intensity of the absorption band which may be completely restored, however, by exposure to 2537-Å light (*1*).

The behavior of a soda-silica glass having the approximate composition $Na_2O \cdot 2 \cdot 5SiO_2$ and containing 100 parts of europium per million (added as a solution to the glass batch) is given in Fig. 1 as an example. Curve 1 is the absorption spectrum of a specimen before any treatment with sensitizing light. The absorption band centered at 3325 Å is due to europium (II). After a 13-minute exposure to a Mineralight source of 3660-Å light, curve 2, showing the development of the broad absorption band centered at 5700 Å, is obtained.

Curve 3 shows the complete decay of the color center band in this particular glass after 20 hours' exposure to 3660-Å light. The europium (II) band has decreased from an extinction coefficient of 1.84 to 1.49, while the ultraviolet cutoff has moved to longer wavelengths. This is interpreted as photooxidation of the europium (II), in the vicinity of the color center traps, to europium (III). Curve 4 shows the spectrum of the glass after treatment of the exhausted glass with 2537-Å light. The band at 3325 Å is now more intense than in the original sample. It appears that some of the europium (III) known to be present in the original sample has been photo-reduced by 2537-Å light as well as an undetermined fraction of the europium previously oxidized by 3660-Å light. In any event, the sample should now exhibit a heightened sensitivity to 3660-Å light. Exposure of the resensitized glass to 3660-Å light for 8 minutes is shown in curve 5. The glass now colors more intensely than originally, since more photoelectrons are available for trapping. The effect of sunlight is similar to that of 3660-Å light. However, glasses sensitive to 3660-Å light and insensitive to sunlight have also been synthesized.

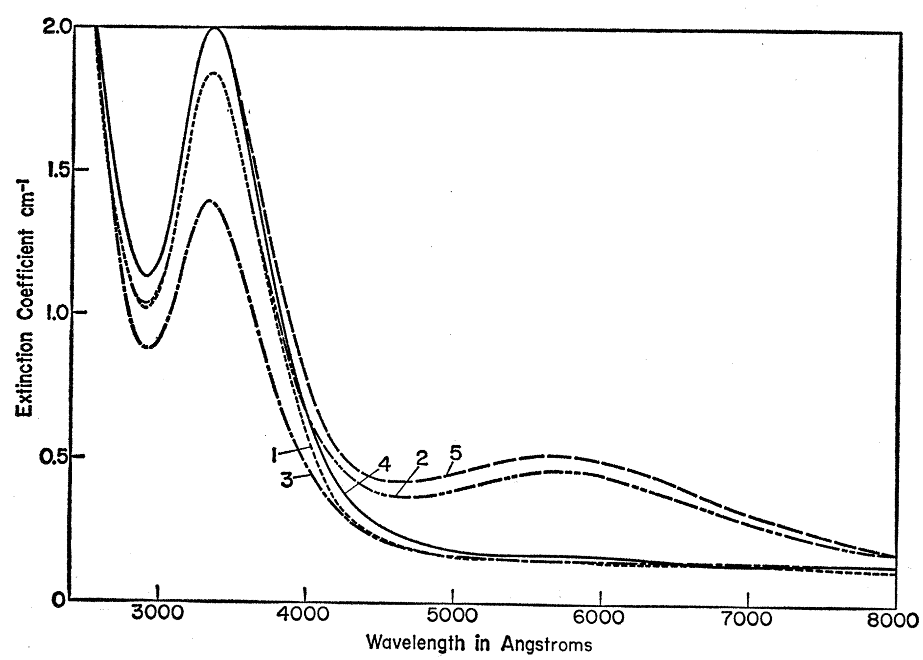

Fig. 1 Absorption spectral curves of a soda-silica glass containing traces of europium, illustrating the magnitude of visible light absorption by the glass. Extinction coefficient is used here as the optical density divided by the thickness in centimeters.

Although the color center band involved may be produced in many glasses free of poisoning impurities such as iron and titanium by 2537-Å light, the color center is activated by sunlight only in the presence of additives that absorb energy in the region of solar emission. In outer space, the absorption band should be produced without the presence of the activators. Since the europium (II) band is centered at lower energy than the cerium (III) band, it gives the more sensitive pumping action with sunlight.

Processes of this type that interact with laser mechanisms in the glass structure may be possible (*2*). This discovery makes possible the development of a variety of new products such as glass window curtains and variable-intensity windshields as well as ophthalmic and space devices (*3*).

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References and Notes

1. This effect of 2537-Å light was discovered by E. Lowell Swarts of the Glass Research Center, Pittsburgh Plate Glass Company.
2. A paper describing the detailed mechanisms involved in this process is in preparation.
3. This work was supported by the Pittsburgh Plate Glass Company.

11 September 1962