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Photochromic Silicate Glasses Sensitized by Silver Halides

Their characteristic of changing color reversibly, in combination with other properties, suggests many uses.

W. H. Armistead and S. D. Stookey

The phenomenon of photochromism—change of color on exposure to light—has been studied by many observers. The proceedings of a symposium on this subject were published in the December 1962 issue of the *Journal of Physical Chemistry* (*1*), and Brown and Shaw, in a recent review (*2*), list hundreds of photochromic organic and inorganic substances. There are many potential uses for photochromic substances, provided the special requirements for these uses can be met. True reversibility of the color change—that is, freedom from fatigue with repeated light-and-dark cycling—is a basic requirement for most of these uses. Very few photochromic substances fulfill this requirement.

The action of ultraviolet light or other high-energy radiation is known to cause color changes in many glasses. In most cases the changes are very slow and are irreversible at room temperature. Recently A. Cohen and H. Smith (*3*) reported photochromic silicate glasses, sensitized by the addition of cerium and europium, which showed rapid darkening and fading. These glasses, however, were reported to fatigue with repeated cycling.

In this article we describe a new type of photochromic material that changes color reversibly and has combinations of properties which make it suitable for a number of practical applications. The photochromic materials of this investigation are silicate glasses containing dispersed crystals of colloidal silver halide, precipitated within the homogeneous melt during cooling or reheating.

In the absence of light, the silver halide glass may be either transparent and essentially colorless or opaque white, depending on the particle size and the concentration of the suspended colloid.

Photochromic behavior has been observed in transparent glasses containing silver halide microcrystals as small as 40 angstroms in diameter, and with concentrations of crystals as low as 500 parts per million by volume, as determined by electron microscopy and by small-angle x-ray scattering.

Chemical Composition

Table 1 gives results of chemical analyses of some photochromic silver halide glasses.

The base glasses are generally alkali metal borosilicates; they are sensitized by silver halide microcrystals precipitated from solution in the glass. The total concentration of silver ranges from 0.2 to 0.7 percent (by weight) in the transparent glasses, and from 0.8 to 1.5 percent in opaque glasses. The concentration of the halogen, consisting of chlorine, bromine, and iodine individually or together, ranges upward from a concentration sufficient to react stoichiometrically with a 0.2-percent concentration of silver to form the halide, or halides, to a total concentration of about 0.4 percent in the transparent glasses, and higher in opaque glasses.

The halogen content of these glasses is expressed in terms of the amount

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(given as a percentage) by which the weight of the halogen-containing glass exceeds the weight of the base glass.

The addition of other "sensitizers" in trace quantities has been found to enhance the sensitivity and increase the photochromic darkening. Among these are polyvalent oxides such as those of arsenic, antimony, tin, and copper. Copper oxide is especially effective and is believed to enter the silver-halide crystals as a cuprous ion. Some analogy with photographic sensitization of silver chloride is indicated by a comparison of our results with recent research results of F. Moser *et al.* (*4*), which show that photolysis of silver chloride is sensitized by a cuprous ion.

While a wide range of glasses of different composition may serve as matrices for the photochromic sensitizers, alkali borosilicates have, in general, been found to be best. Photochromic properties are affected in one way or another by each of the ingredients of the glass. Probably the effects of the base glass depend primarily on factors affecting (i) the solubility of the silver halide particles, (ii) the composition of the precipitated particles (other ions in limited concentrations may dissolve in the particle), (iii) the oxidation state of the silver, and, possibly, (iv) reactions at the particle-glass interface.

Thermal History and Processing

The glass is melted and formed by conventional techniques, the constituents of the desired silver halides being ordinarily added to the batch before melting and going into homogeneous solution in the glass melt. Depending on the concentration of silver halide, either the product may be photochromic after normal annealing and cooling or (at lower concentrations) it may require reheating for minutes or hours at temperatures in the range between the annealing and softening temperatures. This heating results in nucleation and growth of colloidal droplets of molten silver halide to form an emulsion in which the droplets subsequently crystallize as the glass cools below the melting point of the halide.

Table 1. Results of chemical analysis of some photochromic silver halide glasses, designated by number.

Component	Percentage (by weight)				
	1	2	3	4	5
SiO_2	60.1	60.3	59.5	59.8	62.8
Na_2O	10.0	10.0	10.0	10.0	10.9
Al_2O_3	9.5	9.5	9.5	9.5	10.0
B_2O_3	20.0	20.0	20.0	20.0	15.9
Ag	0.40	0.24	0.58	0.70	0.38
Br	.17	.26		.09	
Cl	.10		.31	.16	1.7
F	.84	.80	.94	.85	2.5
CuO					0.016

If the heating is excessive or if the concentration of silver halide is too high, the glass may be translucent or opaque because of growth of the crystals to a size that scatters light. Such glasses are photochromic but are less useful, generally, than the transparent glasses.

Photochromic Properties

General. Depending on composition and prior heat treatment, a wide range of photochromic properties is obtainable: various reaction rates of darkening and fading; a wide spectrum of sensitivity to darkening radiation; a range of optical densities in the darkened state; various temperature coefficients of reaction rates, and so on. Three processes occur simultaneously during illumination: darkening, or creation of color centers by light; optical bleaching; and thermal bleaching. The steady-state coloration, maintained if light intensity and temperature remain constant, is the resultant of these competing processes. The darkening rates, and the optical components of fading rates, follow curves approximating those typical of first-order reactions. Further study of thermal components of fading rates is needed for a better understanding of the reaction kinetics (*5*). It appears that more than one kind of color center is formed.

The typical behavior is illustrated in Fig. 1. The color, after darkening, is generally a neutral gray or gray-brown with a broad absorption band extending through the near-ultraviolet and the entire visible spectrum to the near-infrared.

Spectral sensitivity. The wavelengths that induce darkening occur over a wide area of the spectrum—from the near-ultraviolet through the visible spectrum to about 6500 angstroms, again depending on the chemical composition. Glasses containing silver chloride are sensitive to wavelengths

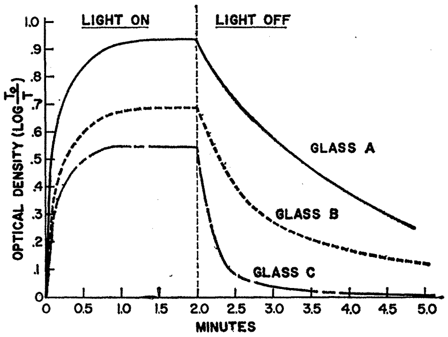

Fig. 1. Photochromic darkening and clearing of three glasses. Illumination with light of constant intensity causes photochromic glasses to darken to a steady-state optical density. Removal of the light causes the glasses to clear. Darker glasses generally clear more slowly than lighter ones.

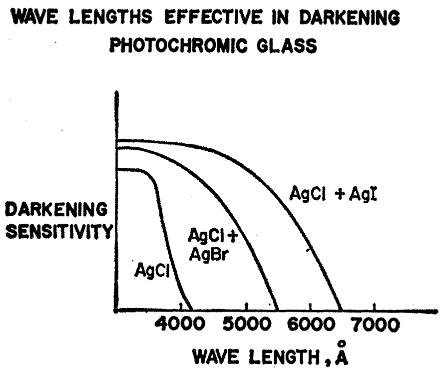

Fig. 2. Wavelengths effective in darkening photochromic glass, plotted against sensitivity. The curves show the approximate wavelengths at which light ceases to have a darkening effect on copper-sensitized glasses. Note that bromine and iodine produce sensitization to light of longer wavelengths.

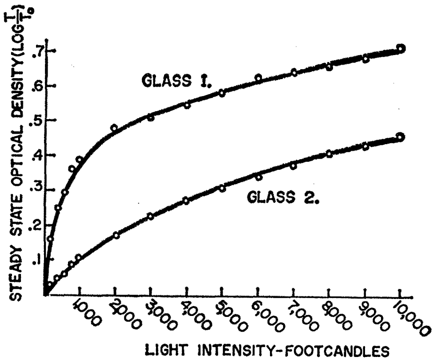

Fig. 3. Steady-state optical density at 20°C plotted against intensity. The steady-state optical density increases with increasing light intensity. Glass No. 2 darkens less than glass No. 1, and in glass No. 2 the increase in darkening is more nearly proportional to the increase in intensity because the fading-rate constant is higher.

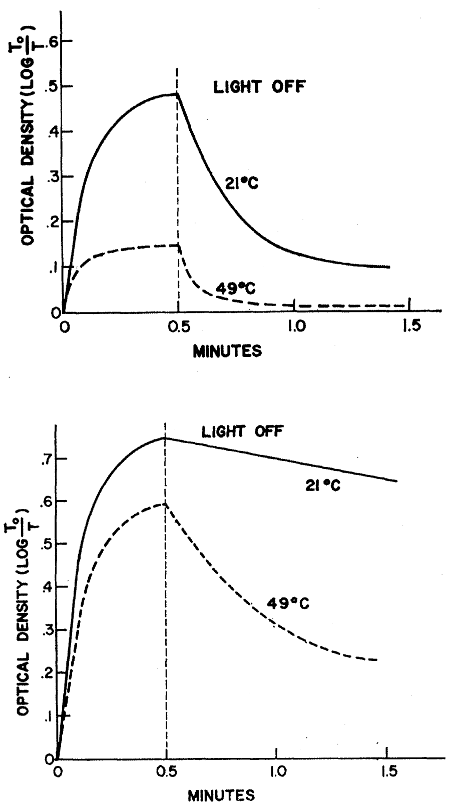

Fig. 4. Effect of temperature on rates of darkening and clearing in (top) fast-clearing glass and (bottom) more slowly clearing glass. The darkening is more sensitive to temperature in the fast-clearing glass.

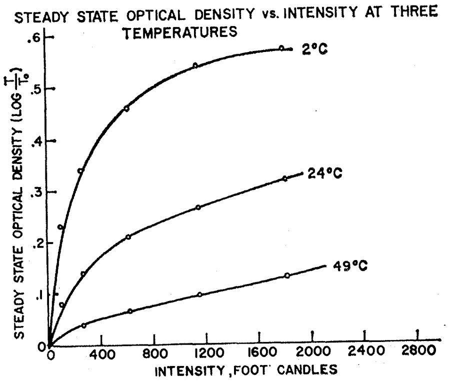

Fig. 5. Effect of temperature on the relation between the steady-state optical density and the intensity.

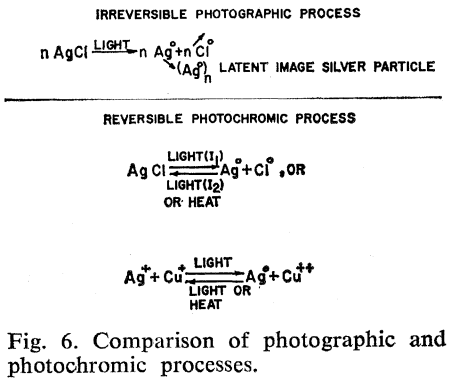

Fig. 6. Comparison of photographic and photochromic processes.

of, roughly, from 3000 to 4000 angstroms; those containing silver chloride plus silver bromide, or silver bromide alone, to wavelengths of from 3000 to about 5500 angstroms; those containing silver chloride plus silver iodide, to wavelengths of from 3000 to about 6500 angstroms (see Fig. 2).

The silver-chloride glasses that are sensitive only to ultraviolet light darken readily in outdoor sunlight but not indoors (unless they are exposed to an ultraviolet lamp).

In the special case of the silver-chloride glasses that are darkened only by ultraviolet light, exposure to longer-wave radiation in the visible and near-infrared regions in the broad absorption band of the darkened "color centers" results in accelerated fading; in other words, such glasses fade more rapidly in visible light than in the dark. As a corollary to this phenomenon, glasses of this type become darker when exposed only to ultraviolet radiation than they do when exposed simultaneously to ultraviolet and visible light.

Darkening rates. The darkening generally approaches its maximum intensity in times of the order of 1 minute in sunlight. A single 3-millisecond flash of high-intensity light (1000 electrical joules discharged through a xenon flash lamp) resulted in a decrease in transmittance to 25 percent of the original value in a glass which, when exposed to sunlight, darkened to the same degree in several seconds.

Dark-clearing rate. In the dark, times required for the optical density to decrease by half range from seconds to hours, depending on the composition of the glass, on previous heat treatment, and on the temperature of the glass. At liquid-nitrogen temperatures, bleaching does not occur.

Steady-state darkening as a function of incident-light intensity. The optical transmittance of a transparent photochromic glass before darkening is similar to that of window glass. On exposure to light of a given intensity (temperature being held constant), the optical density measured at a given wavelength in the visible spectrum—and similarly, the total luminous absorptance—approaches a constant steady-state value. The steady-state optical transmittance for glass plates .63 centimeters thick ranges to as low as 1 percent for exposure to normal sunlight.

When we plot curves for steady-state optical density (log T/T_0) versus intensity I of incident light (Fig. 3) for photochromic glasses having different fading rates, a family of curves is obtained which shows a closer approach to direct proportionality of optical density to I as the fading-rate constants of the glasses increase.

SILVER HALIDE CRYSTAL SIZE AND CONCENTRATION IN PHOTOCHROMIC GLASS

CONCENTRATION	8×10^{15} $\frac{\text{CRYSTALS}}{\text{CM}^3 \text{ OF GLASS}}$
CRYSTAL DIAMETER	50 Å
CENTER–CENTER DISTANCE	500 Å

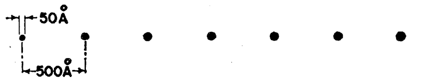

Fig. 7. Typical size and concentration of silver halide crystals in photochromic glass, as determined by electron microscopy and small-angle x-ray scattering.

The logic of this behavior can be seen if one considers the extreme cases. If there were no reverse (clearing) reaction, even a low intensity of incident light would sooner or later convert all the latent "colorable" centers to darkened color centers, so the steady-state optical density would reach its maximum value at a low light intensity and remain constant at all higher intensities. At the other extreme, if the color centers are destroyed almost as fast as they are formed, their concentration at any moment increases proportionally with the intensity of the light that causes their formation.

Temperature-sensitivity. The rate of fading in the dark increases with temperature. Consequently, since the darkening rate is relatively insensitive to temperature, the steady-state optical density of the photochromic glass decreases with increasing temperature for any single intensity of incident light. The glasses with slowest clearing rates at a given temperature are, in general, the least temperature-sensitive (Fig. 4).

Also, as might be expected, the increase in steady-state optical density becomes more nearly proportional to intensity with increasing temperature (Fig. 5).

Reversibility. To be useful over long periods, the photochromic material must not fatigue with time or with number of darkening-and-fading cycles. These silver-halide glasses are believed to be almost unique among photochromic materials in having true reversibility of darkening and in being immune to fatigue. Specimens have been exposed outdoors constantly, day and night, for more than 2 years, and exposed indoors to thousands of cycles of darkening and fading, with no deterioration in performance.

In some cases the environment in which the glass is used may be such that fading is not complete before the next exposure to light. Under these circumstances the glass darkens more rapidly than it would if it had been permitted to fade completely.

Nature of Photochromic Mechanism in Silver-Halide-Sensitized Glass

At present it appears probable that the photochromic process is basically the same as the photolytic dissociation of silver halide into silver and halogen that occurs in silver-halide photography, the difference being that the photographic process is irreversible and leads to the formation of stable silver particles, whereas the photochromic process in glass is reversible (Fig. 6). This reversibility implies that there is no loss of reaction products from the reaction zone, and that the silver and halogen can return to their original states when light is removed. Possibly the photochromic reaction involves only photoelectrons, without atomic diffusion. For maintaining reversibility, glass is uniquely valuable because of its impermeability, chemical inertness, and rigidity. These characteristics prevent loss of the reaction products by diffusion and exclude atmospheric oxygen and moisture, which might cause side reactions. Possibly, also, the mechanical strain impressed on the silver-halide crystals by the surrounding glass during cooling affects the photochromic properties.

The primary photolytic reaction can be represented by

$$\mathrm{Ag^+ + Cl^- \underset{}{\overset{h\nu}{\rightleftarrows}} Ag^0 + Cl^0}. \qquad (1)$$

An electron is freed from the $\mathrm{Cl^-}$ and caught by the $\mathrm{Ag^+}$ ion. The silver atoms, or very small aggregates of atoms, are almost certainly the color centers. In the case of copper-sensitized photochromism, the additional reaction can be written

$$\mathrm{Ag^+ + Cu^+ \overset{h\nu}{\rightleftarrows} Ag^0 + Cu^{++}}. \qquad (2)$$

An electron is freed from the $\mathrm{Cu^+}$ and trapped by the $\mathrm{Ag^+}$ ion. Here the cupric ion as well as the silver contributes to the absorption of visible light. These reaction products are metastable and can return to the original state, or, if they are permitted to diffuse or react with other species, they can make the reaction irreversible. For example, extensive aggregation of $\mathrm{Ag^0}$ would form stable colloid particles of silver, and if the $\mathrm{Cl^0}$ were permitted to diffuse as it does in ordinary photographic films, its loss as chlorine would also prevent restoration of the original state.

One type of experiment which tends to confirm this model is one in which the glass is irradiated with ultraviolet light at high temperatures, above 400°C, where some diffusion of ions and atoms might be expected. Prolonged exposure to such radiation results in a permanent colored image containing colloidal silver. The reversible photochromic coloration, determined on subsequent exposure at room temperature, decreases in intensity with increase of the exposure time at 400°C, and finally disappears. This is taken as evidence that diffusion and precipitation of the photolytic silver occur at the high temperature, thereby producing an irreversible photolysis of silver halide.

The kinetics of darkening and of thermal and optical bleaching are being investigated by some of our co-workers, who employ the changes in optical absorptance as the indicator for the associated changes in the concentrations of the colored reaction products. The results are complicated by the experimental difficulties of maintaining conditions in which Beer's law is valid. In a three-dimensional plate of glass, the induced coloration varies through the thickness of the glass because the actinic light is partially absorbed. In addition, the very broad absorption bands for both the actinic radiation and the darkened color centers make interpretation more difficult than would be the case for narrow bands.

There are fundamental differences between the photochromic glasses described here and the earlier photosensitive gold- and silver-containing glasses (*6*)—differences in the initial state of the silver (that is, before irradiation) and in the nature and stability of the chemical species formed by radiation. In the photosensitive glasses, silver ions are dissolved in the glass rather than in silver halide crystals. Photoelectrons are trapped at sites (probably silver ions) so stable that even heat treatment at high temperatures does not release them but results in a permanent precipitate of photolytic colloidal silver. In the new

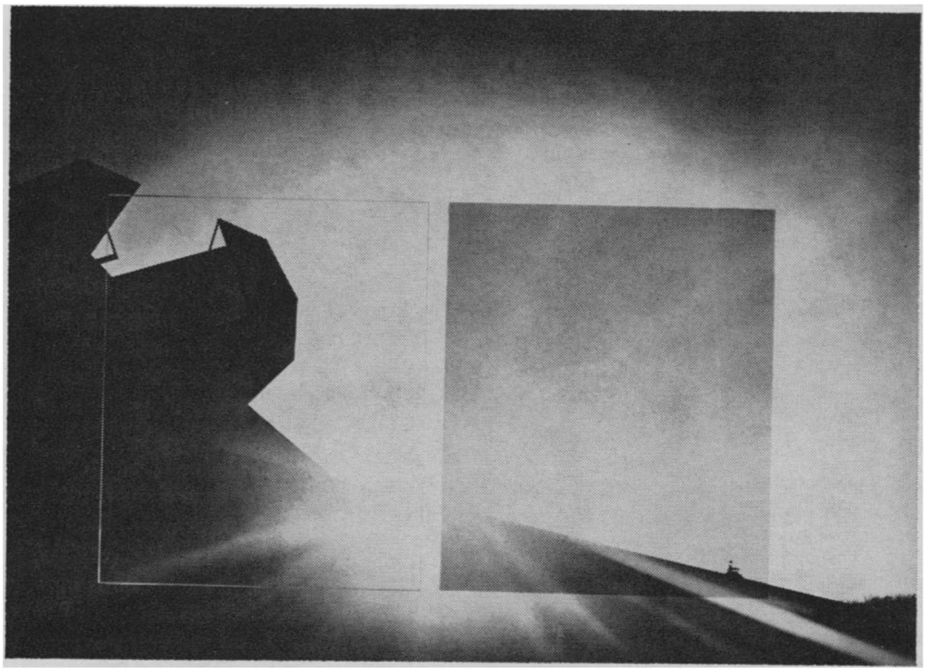

Fig. 8. At Corning a glass has been invented that changes color when exposed to light. (Left) A soda-lime glass, such as used in window panes, remains clear in the sun's rays; (right) the photochromic glass darkens in the sun and will clear again when the sun goes down. In the background, a giant ventilator above a glass melting unit.

photochromic glasses, on the other hand, the species formed by irradiation at room temperature is completely unstable, and subsequent heat treatment precipitates no colloidal silver.

All of the photochromic properties of a given glass, including the wavelengths to which it responds, fading rates, and so on, vary between wide limits, depending on its thermal history.

The thermal history, beginning with the initial cooling of the glass melt, controls a number of critical factors that determine photochromic behavior, including not only the size and number of microcrystals but also the chemical composition and the atomic arrangement within each crystal (*7*). There is a complex interplay between nucleation and growth of the molten salt droplets; between relative solubilities of various ions in the glass, in the molten salt, and in the crystal; and between rates of diffusion of ions between glass and salt. In addition, interfacial phenomena may be important, since these particles are so small that they consist essentially of surface.

Research is in progress on the correlation of these phenomena with photochromic behavior. The problems of analysis are difficult, since the particles we are investigating are so small and occur in such low concentrations that they are exceedingly difficult to detect and are inbedded in a large mass of glass (Fig. 7).

Potential Applications

The most obvious potential uses for photochromic glasses in which darkening is reversible appear to be uses as material for windows, sunglasses, and other objects where dynamic control of sunlight is desired. Perhaps such glasses can be adapted for use in devices employing optical memory, in self-erasing display devices, and as "light-valves" in many types of new optical systems or in other systems in which variations of the amount of light can be used as a control or a monitoring device. Research has been going on for several years in the Corning laboratory on the complex interactions between the photochromic behavior of hundreds of glasses and environmental factors such as sunlight intensity, temperature, and atmospheric haze, with the objective of perfecting glasses for specific uses of these types (Fig. 8) (*8*).

Several years of research on photochromic silicate glasses sensitized by silver halide have led to the conclusion that these glasses possess combinations of properties (reversible photochromism, chemical durability, and transparency, or opacity, if desired) which make them potentially useful for light-control devices where long operating life is required. The small size of the silver halide crystals and the rigid, impervious, chemically inert nature of the glass matrix appear to be vital requirements for maintaining reversibility. These characteristics prevent loss of the colored photolytic products by side reactions with moisture or gases, or by diffusion.

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News and Comment

NSF: New Program Aims to Speed Process for Transforming Good Institutions into Excellent Ones

A major departure from the general postwar pattern of federal support for science education is about to get under way in the form of the National Science Foundation's science development program. Although the funds involved are, at least at this point, relatively small, the scientific, educational, and political implications are quite large—so large, in fact, that it is probably safe to say that the success or failure of this program is going to have a far-reaching influence on the evolution of higher education in the United States.

Briefly, the object of the science development program is to speed up the complex process whereby good institutions become excellent ones. Heretofore, federal agencies, including NSF, have indirectly contributed to this process through support of research projects at particular institutions. The rationale for project support was that the federal government was seeking research results—and, accordingly, research competence was considered the principal criterion for allocating funds. The rich got richer through this process, but for a long time it provided the granting agencies with an effective defense against political pressures for spreading the wealth on a geographical, rather than a quality, basis. Those pressures have been building up over the past few years, partly because of the cries of the have-nots, but also because of the need for new educational facilities to meet the federal government's technical and scientific aspirations. The result is that NSF, with a good deal of caution and with Congress looking on carefully, is about to embark on an effort specifically aimed at promoting institutional excellence, rather than at supporting particular research groups or projects.

Although the science development program is still in its formative stages, with the first grant yet to be made, one thing is clear: it obviously is not intended for the rich (the NSF announcement states that "institutions already recognized as being outstanding in science should continue to depend on ex-