Photochromic Glasses: Properties and Applications

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Photochromic materials are those which react reversibly to light. Photochromism is
therefore distinguished from the familiar photographic processes, which, because of the
chemical development of the image, are essentially irreversible. Many organic materials,
and a few inorganic ones, show this phenomenon. Their general properties are described,
with particular emphasis on those of a system of photochromic glasses. The behaviour
of these glasses results from reaction of light with silver halide crystals deliberately formed
in the glass during its manufacture. The mechanism of the photolytic reactions is
postulated, and compared with the theory of the photographic process for silver halides.
Reversibility of photochromism in these glasses is explained by prevention of diffusion
of the products of photolysis from the original crystal site within the glass structure, and
their subsequent recombination when the activating light is removed. These glasses show
large ranges in all their photochromic properties resulting from ranges in composition,
and in size and number of the included crystals. The behaviour of typical glasses, in
both sunlight and under artificial sources, is reported in this paper, and some applications
for these glasses are suggested.

1. Introduction

Materials which exhibit the phenomenon of a
change in colour when illuminated have been
known for a long time – both organics and
inorganics [1]. In a recent review of photo-
chromism [2], "phototropy" is the name given
to the general reaction of a spontaneously
reversible change of a single chemical species
between two states having different absorption
spectra, with the change induced at least in one
direction by electromagnetic radiation.

$$A_{\lambda 1} \quad \underset{h\nu}{\overset{\longleftarrow}{\underset{\longrightarrow}{\rule{0pt}{0pt}}}} \quad B_{\lambda 2}$$
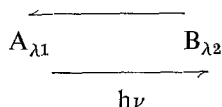
States A and B are both ground electronic
states usually, and are quantum mechanically
stable, although one state may in some cases be
a relatively long-lived, excited electronic state
which does not emit significant amounts of
radiation. It is convenient to establish a dis-
tinction between phototropism and photochrom-
ism, and to define photochromism as the
restrictive case where at least one of the states
absorbs visible light. This definition excludes
fluorescent and phosphorescent materials, which
re-emit light (at characteristic wavelengths)
after irradiation. Note that the reverse reaction
indicated above exists to distinguish photo-
tropic from ordinary and essentially irreversible
photochemical processes.

2. Photochromic Materials

2.1. Organics

Although the first photochromic substance
named in the literature is in a reference dated
1881, it is only in the last decade that study of
photochromic compounds has received in-
creased and serious attention. Much of the
research on these materials has been supported
by Government agencies because of the potential
strategic importance of devices which react
reversibly to light [3]. Reactions in different

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materials fall into half-a-dozen classes, including isomeric and tautomeric transitions, dissociation into ions or into radicals, excited state transitions, and oxidation-reduction reactions. It is possible to group these into three main classes of general interest, depending on how they work [4].

2.1.1. Stereoisomers

One of the chemical bonds in a ring molecule is broken by the energy of the absorbed light, allowing the molecule to unwind to a different geometrical arrangement. The reverse process is a re-forming of the bond. The two states absorb light differently. Spiropyrans and anils are examples of this class.

2.1.2. Dyes

An example of this class is a triphenyl methane dye, which is oxidised by energetic light; the absorption characteristics of the positive ion so-formed are different from those of the original electrically neutral benzene rings.

2.1.3. Triplet States

Molecules of polynuclear aromatic hydrocarbons are excited by irradiation first from the ground state to a singlet state, and then go, via the lowest triplet state, to an excited triplet state. Visible light is absorbed in the triplet-triplet transition.

2.2. Inorganics

To these major classes of organic photochromics must be added several kinds of inorganics: alkaline earth sulphides; zinc sulphide (lithopone, observed in 1881, contains ZnS); titania and alkaline earth titanates; various mercury compounds. Many of these seem to require traces of a heavy metal, or a halogen, to be photochromic.

In all of these, the photochromic response will depend on the intensity and spectral character of the incident light, environmental parameters such as temperature, supporting matrix or solvent, and, in most cases, previous history. This latter is called fatigue – a change in behaviour either with use, or with time in storage.

It is important to note, in discussion of photochromic materials, that, if the reaction is to be truly reversible, the quantum yield will be equal to or less than one. This is to be compared to a yield several orders of magnitude higher (in extreme cases as high as perhaps 10^8) for ordinary silver halide photography, in which energy is added to the system chemically during development. Photochromic processes then are very "slow", in the photographic sense, compared to photographic film. But these light-sensitive materials are unique in that they require no processing to develop a latent image, and are, in varying degrees, reversible and re-usable.

2.3. Glasses

Three classes of photochromic glasses have been reported in the literature. These are interesting if for no other reason than, being inorganic, they have most promise of showing minimum or no fatigue, and therefore of being useful after long periods of storage or of use.

2.3.1. Hackmanite or Hackmanite-Type Glasses [5]

Hackmanite is a naturally occurring mineral of the sodalite group. It has the stoichiometric composition 18 $(Na_2O . Al_2O_3 . 2SiO_2) . 3 NaCl . Na_2SO_4$, and is crystalline, usually opaque white or blue. It can be melted to a glassy state, translucent to reasonably transparent if a flux, such as B_2O_3, is added. Minimum reported haze is 30%. With proper amounts of flux, the material darkens with exposure to ultraviolet light and can be bleached with longer wavelength (visible) light. The natural rate of fading is very slow. Addition of heavier halogens (bromine, iodine) can shift the absorption spectrum (colour) of the resultant glassy material when darkened.

2.3.2. Cerium or Europium Glasses [6]

In suitably purified base glasses, either pure silica or soda-silica glasses, the addition of small amounts of cerium or europium, of the order of 0.01%, produces a photochromic material. Ultraviolet irradiation is absorbed by absorption bands of cerium III or europium II centred in the ultraviolet, transferring photoelectrons to nearby traps which absorb in the visible region, producing an amethyst colour.

Decay times are typically a few seconds. Although the colouring and fading processes may be cycled repeatedly, the absorption band in the visible region (which produces the colour) decreases in intensity with usage. This is interpreted as resulting from photo-oxidation of the europium II to europium III. However, it may

be re-reduced, and the glass therefore re-sensitised, by exposure to short-wavelength ultraviolet light [7].

2.3.3. Silver Halide Glasses

Photochromic glasses which are truly reversible and do not show the large effects of fatigue described above have been reported by Armistead and Stookey [8] of Corning Glass Works. A wide range of base glasses has been found to be suitable – alkali metal borosilicates are perhaps the best from standpoints of both general glass qualities (clarity, durability, ease of melting and forming) and photochromic behaviour. Both the composition and the thermal history of the glass have a large part in determining its resultant photochromic properties.

3. Silver Halide Glasses: Composition and Structure

Some typical compositions for these silver halide photochromic glasses are given in table I [9]. Most of the glasses investigated so far are transparent in the unexposed state, darkening to a grey or reddish grey when illuminated. The glasses designated 6 and 7 in the table have had heavy metals added to increase the index of refraction to that required for ophthalmic use. At high concentrations of the suspended colloid, or following heat treatments which produce large, average particle size, the glasses are translucent or opaque. The upper limit of silver for the transparent glasses is usually about 0.7 wt %. Other metals, in the form of polyvalent oxides, including arsenic and antimony, tin and lead, and copper, increase the sensitivity and the photochromic absorbance.

We can assert with reasonable certainty both from observations on the glass, and by analogy with the known properties of silver halides, that the photochromic behaviour of these glasses results from silver halide crystals within them [10]. The evidence in support of this can be summarised as follows.

(a) Both heavy metals and halides are essential for photochromic behaviour in glasses. Silver is commonly used.

(b) A small amount of copper oxide is an effective sensitiser for the glasses, as it is for bulk silver halides [11].

(c) Phase separation is necessary in order that the glasses be photochromic. (Crystalline silver chloride has been identified by X-ray diffraction in typical glasses.)

(d) The photochromic response of the glasses is affected by their cooling rate, i.e. annealing.

(e) The sensitising optical absorption bands lie in the same wavelength region for the glasses and for crystalline silver halides.

(f) The shapes of the optical absorption curves are similar for the two materials.

(g) The rate of formation of colour centres decreases with decreasing temperature.

(h) Both can be optically bleached, and the rate decreases rapidly with decreasing temperature.

These crystals are formed by precipitation from the homogeneous glassy matrix during initial controlled cooling, or during a subsequent heat treatment (usually desirable for glasses in the lower ranges of silver halide concentration) at a temperature typically between the strain point and the softening point of the glass.

Electron microscopic examination of the

TABLE I Compositions of some typical photochromic silver halide glasses.*

Constituent	Glass 1	Glass 2	Glass 3	Glass 4	Glass 5	Glass 6	Glass 7
SiO_2	60.1	62.8	59.2	59.2	60.1	52.4	51.0
Na_2O	10.0	10.0	10.9	14.9	10.0	1.8	1.7
Al_2O_3	9.5	10.0	9.4	9.4	9.5	6.9	6.8
B_2O_3	20.0	15.9	20.0	16.0	20.0	20.0	19.5
Li_2O	—	—	—	—	—	2.6	2.5
PbO	—	—	—	—	—	4.8	4.7
BaO	—	—	—	—	—	8.2	8.0
ZrO_2	—	—	—	—	—	2.1	4.6
Ag	0.40	0.38	0.50	0.50	0.40	0.31	0.30
Br	0.17	—	—	0.60	0.17	0.23	0.11
Cl	0.10	1.7	0.39	—	0.10	0.66	0.59
F	0.84	2.5	1.45	1.45	0.84	—	—
CuO	—	0.016	0.016	0.015	0.016	0.016	0.016

*Compositions in wt %; halogens are given as wt % additions to that of the base glass.

photochromic glasses show small, dense particles, which are not seen in glasses that, because of either composition or improper heat treatment, are not photochromic. Fig. 1 is a typical photograph of a carbon replication of a fractured surface [12]. The average particle size and number can be determined (with limitations)
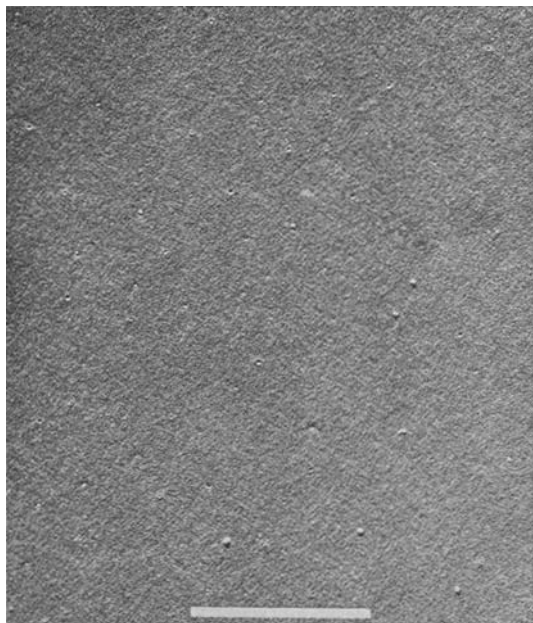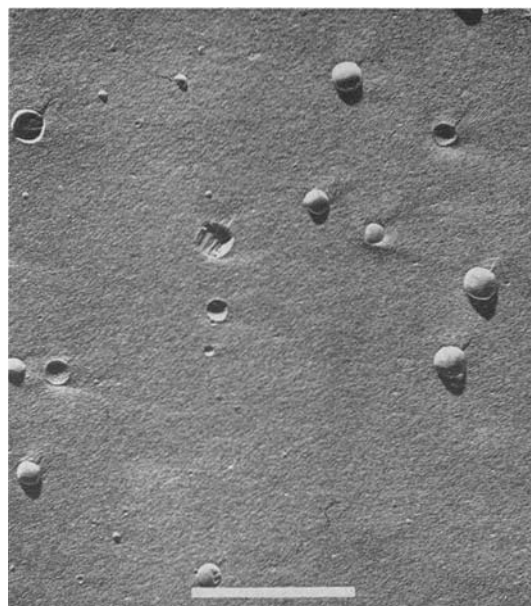

Figure 1 Fractured surface of typical transparent photochromic glass, by carbon replication. Length of white reference bar at bottom of photograph is 1 μm.

by counting from such photographs, or, with more precision, by small-angle X-ray scattering measurements. In general, glasses with particles less than about 50 Å in diameter are not photochromic. As the time or temperature of heat treatment for any one glass is increased, the average number of particles is reduced, and their size is increased, as would be expected from classical nucleation theory. Above about 300 Å, the particles scatter light, and the resultant glass is opal. Fig. 2 is of a glass in which the particles were deliberately grown to relatively large sizes to show their spheroidal character. This glass, with particles which were as large as 0.2 μm in diameter, was translucent.

For particles of average diameter 100 Å, present in concentration say 0.2% in the glass,


Figure 2 Fractured surface of translucent photochromic glass, by carbon replication. Length of white reference bar at bottom of photograph is 1 μm.

there will be about 4.10^{15} particles/cm^3, with average spacing 600 Å between particles.

It is expected, of course, that silver halide crystals will be decomposed by light to form a silver image, as in conventional silver halide photographic film. An essential difference, however, is that in conventional silver halide photography, the incident photons decompose the atoms within the crystal into elemental silver and halogen: the silver may be subsequently chemically developed, and the halogen diffuses away from the original crystal site. The photographic process may then be represented as the irreversible reaction:

$$n\ AgCl \xrightarrow{h\nu} nAg^\bullet + n\ Cl^\bullet$$

$(Ag^\bullet)_n$ the latent image particle
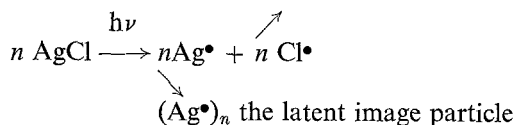
In the silver halide glasses, the halogen is held within the surrounding glass matrix, and is available for recombination with the silver, permitting recovery of the glass to its original, colourless state after the light is removed. The recombination occurs by two independent processes: a natural, thermal recovery, or by interaction with light of longer wavelength (lower energy) than that which darkens the glass

– an optical bleaching. The unique behaviour of these glasses results from the existence of these reverse processes:

$$AgCl \underset{\Delta,h\nu_2}{\overset{h\nu_1}{\rightleftarrows}} Ag^{\bullet} + Cl^{\bullet}$$
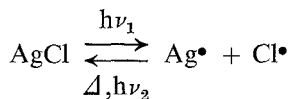
Copper added in small amounts, under reducing conditions, to the glass also permits the following reaction

$$Ag^+ + Cu^+ \underset{\Delta,h\nu_2}{\overset{h\nu_1}{\rightleftarrows}} Ag^{\bullet} + Cu^{++}$$
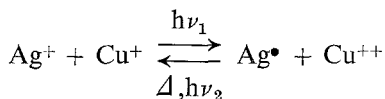
to increase the amount of neutral silver atoms, and therefore acts as a very effective sensitiser [13].

4. Silver Halide Glasses: Photochromic Properties

4.1. General Behaviour

Large, possible ranges and variations in composition, coupled with variations in time, temperature, and schedule of any subsequent heat treatment, give rise to wide latitude in photochromic properties, to greatly different rates of darkening and of recovery, and to similarly large ranges of dependence of reaction rates and equilibrium states on temperature. The glasses are darkened by absorption of high-energy photons, in the near-ultraviolet or shorter-wavelength visible region of the spectrum. The long wavelength limit of the spectral sensitivity for darkening is higher for glasses which contain the heavier halogens. As we would expect from known properties of silver halide crystals, the spectrum of the light which induces darkening (as well as that which is most effective in optical bleaching) is continuous; there appear to be no sharp absorption lines or edges for either process over the wavelength range for which the glass is not itself opaque [14, 15]. Fig. 3 shows the spectral sensitivity for activation of two, different, but representative, glasses. The rate of darkening is primarily dependent on the intensity of the light (in the proper spectral region). In fig. 4 is shown the approach to equilibrium absorbance for a glass illuminated at three different intensities. The rate of natural recovery is primarily determined by glass composition and heat treatment. Recovery in normal room light after irradiation is shown for three different glasses in fig. 5. Recovery (to half maximum absorbance) in the dark at room
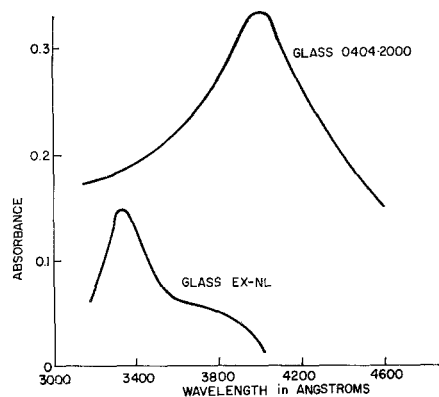

Figure 3 Spectral sensitivity for activation for two glasses of different compositions. The glasses are activated by relatively long-wavelength ultraviolet or, in some compositions, short-wavelength visible light.
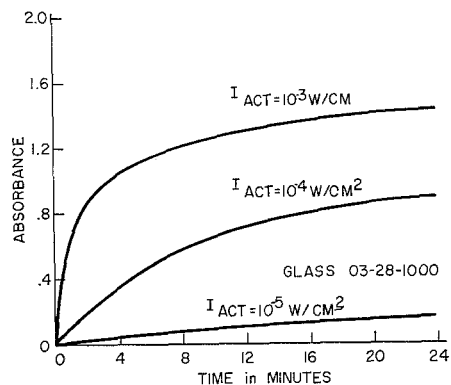

Figure 4 The approach to equilibrium absorbance at different levels of incident energy. Wavelength of the activating light was 4000 Å.

temperature is measured in times from seconds to hundreds of hours. Absorption coefficients at equilibrium range up to about 20 cm^{-1} for the initially transparent glasses, i.e. a resultant transmittance of about 15% for 1 mm thickness.

4.2. Darkening and Fading Phenomena

For these silver halide crystals, the behaviour is determined both by states at their surfaces and in their interior. But the simplifying assumption of a single species and first-order reactions permits generalisations about the behaviour of the glasses [16]. Under illumination, the change of concentration of absorbing colour centres for this case will be given simply by:

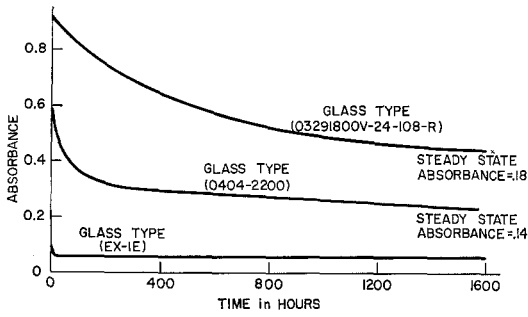$$\frac{dc}{dt} = k_d I_d A - (k_f I_f + k_t)c \qquad (1)$$

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Figure 5 Recovery of three glasses of different fading rates, after activation. The glass labelled EX-IE has relatively a very high thermal-fading constant.

where: c is the concentration of colour centres; k_d, k_f, and k_t are generalised rate constants for darkening, optical bleaching, and thermal fading, respectively; I_d and I_f are the integrated intensities of the light, darkening and fading, over the respective wavelength ranges; and A is the concentration of sensitisable colour centres in the glass. When equilibrium is attained, $dc/dt = 0$, and the equilibrium concentration of colour centres will be:

$$c_s = \frac{k_d I_d A}{k_f I_f + k_t} \qquad (2)$$

The photochromic behaviour of any glass will be determined, therefore, by the relative magnitude of the rate constants describing it; these constants are determined by the composition of the glass, and by the state of the crystals produced from it, i.e. by its heat treatment. If we assume the thermal-fading rate constant(s) to be vanishingly small, then c_s is independent of the light intensity (for constancy of the ratio of darkening to bleaching light intensities); if the total thermal-fading rate is large and becomes the determining rate constant, then c_s is proportional to the intensity. Fig. 6 schematically displays these relationships, at an assumed fixed temperature.

(*Note.* Best attempts to fit curves to carefully measured darkening and fading data lead to the following conclusions [17].

(*a*) The darkening is described by two first-order darkening terms:

$$\frac{d(x_1 + x_2)}{dt} = k_1 I_d (A_1 - x_1) + k_2 I_d (A_2 - x_2)$$

where the x's are related to the concentration of colour centres in such a way that $x_1 + x_2$ is equal to the absorbance, and $A_1 + A_2$ is the
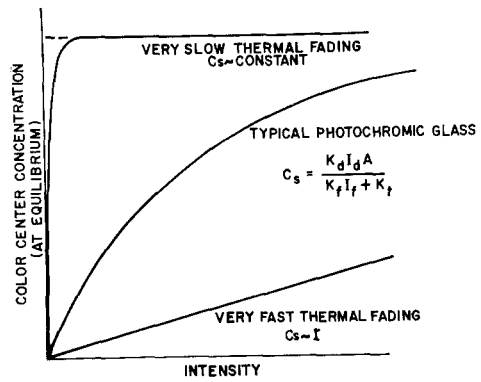

Figure 6 Colour centre concentration at equilibrium versus intensity of illumination. The dependence on intensity is determined by the relative values of the rate constants for darkening and bleaching by light, and for thermal fading.

maximum concentration of colour centres attainable, therefore $A_1 + A_2 = x_1 + x_2$ at $t = \infty$.

(*b*) The thermal fading is best described by [?]

$$\frac{-d(x_1 + x_2)}{dt} = k_3 x_1^2 + k_4 x_2^2$$

(*c*) The optical bleaching is first order:

$$\frac{-d(x_1 + x_2)}{dt} = k_f I_f (x_1 + x_2)$$

These suggest strongly that surface darkening and volume darkening are two separate modes which determine the behaviour of these crystals.)

The photochromic darkening for three glasses, selected to have a wide range of darkening and fading rates, is depicted in fig. 7. The light source
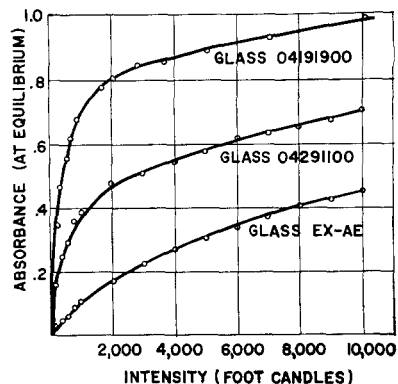

Figure 7 Steady-state optical density versus light intensity, at constant temperature. The thermal-fading rate constant of glass EX-AE is greater than that of glass 04291100. Glass 04191900 is relatively a very slowly fading glass.

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for these measurements was a high-pressure xenon arc. Glass thickness was about 6 mm for these samples. The relative linearity of absorbance with intensity is seen to be much greater for the glass EX-AE which was made to have a high thermal-fading rate, than for the glass 04291100 of intermediate fading rate, and for the slowly clearing glass 04191900. The short-time approach to equilibrium of three selected glasses, under constant illumination at room temperature (23° C), is seen in fig. 8, and fig. 9 shows the behaviour of the same three glasses at 46° C, with the same light source. The light from the arc was turned on at time zero, and off after 120 sec. The glasses were chosen to show differences of fading rates and equilibrium
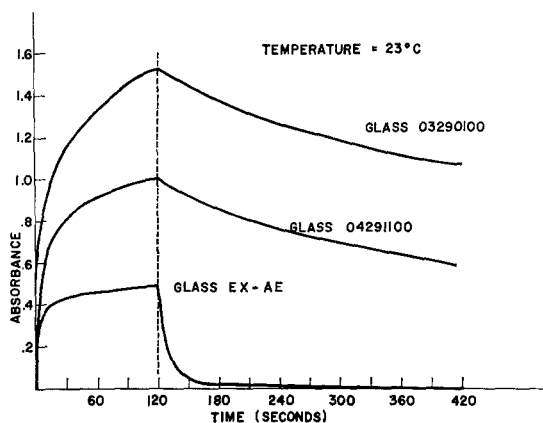
Figure 8 Photochromic darkening and fading in three representative glasses, at room temperature (23° C), with light of constant intensity.
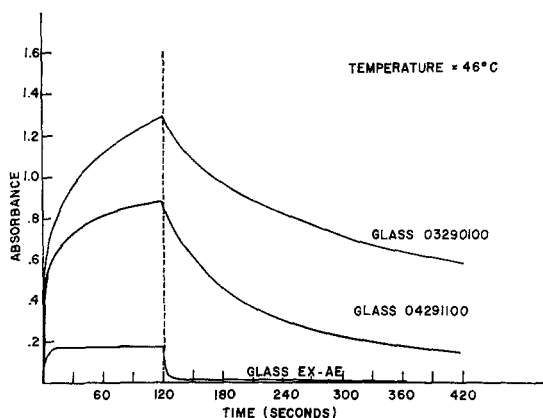
Figure 9 Photochromic darkening and fading in three representative glasses, at 46° C. Comparison with the curves of fig. 8 shows the interdependence of equilibrium absorbances, rates of approach to equilibrium, and temperature.

absorbance. The samples were maintained at the stated, fixed temperature, so that the glass temperature was not appreciably raised by the energy absorbed. The increased effect of change in ambient temperature on a faster-clearing EX-AE is seen in these curves.

4.3. Optical Behaviour

Because the glass reacts differently to light of different wavelengths, a change in transmittance of the glass can be achieved in two ways: by darkening the glass with short-wavelength light, or by bleaching it, after it has been so darkened, with longer-wavelength light. Either of these can be done in any desired geometrical pattern; square arrays of 1 mm diameter dots, made by ultraviolet light irradiation and by bleaching with longer-wavelength light (6000 Å), are shown in fig. 10 [15]. For highest contrast, the glass used would have preferably a relatively high absorbance and relatively long thermal recovery time. (The helium-neon laser, with light at 6328 Å, is also effective in bleaching glass previously exposed to ultraviolet light.) Fig. 11 shows some typical bleaching curves for different activation levels. The bleaching light was at wavelength 6000 Å, with 5×10^{-3} W/cm² applied to the sample.

For quantitative measurement of transmittance differences, it is necessary to know the shape of the optical density versus light energy curves [15]. The familiar D versus $\log E$ curves are used to determined the value of γ defined by:

$$\gamma = \tan\alpha = (D_2 - D_1)/(\log E_2 - \log E_1)$$

where the D's are optical densities and E's are the incident energy (in joules/cm²). This is illustrated in fig. 12. For photochromic glass, this γ-number is characteristic of the material, unlike conventional film, in which it is dependent also on the development process.

Another difference results from the reversible behaviour, and the bleaching by white light. A second γ-number can therefore be defined, analogous to that for darkening, as represented in fig. 13. Some D-log E curves for typical photochromic glasses are shown in fig. 14; γ-numbers taken from the linear parts of these curves are given in table II.

These are results from measurements at room temperature. Thermal fading, occurring continuously, affects the results for both darkening and bleaching, so that the γ-number is a function of temperature.
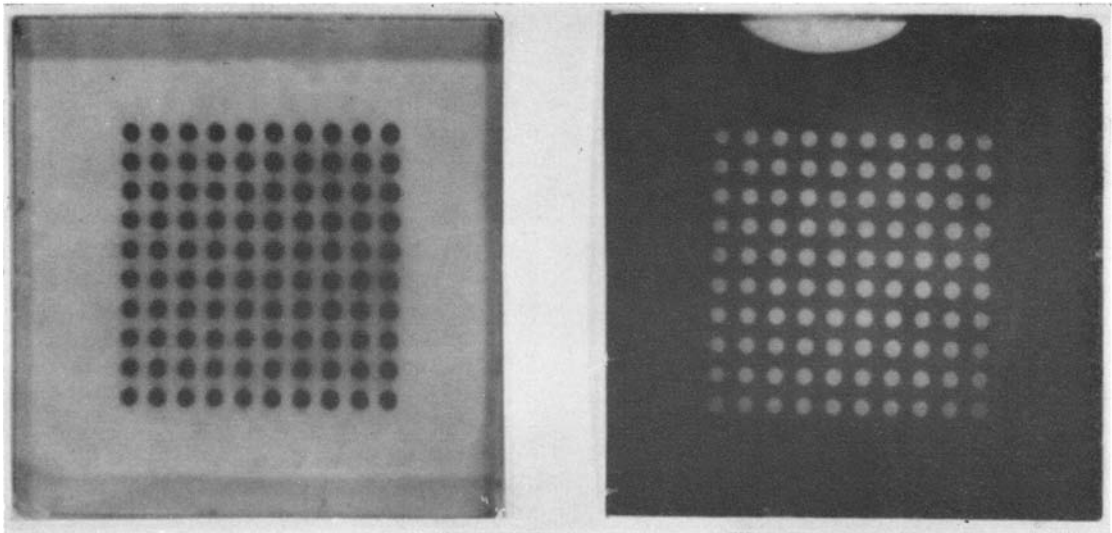
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Figure 10 Digital information as dark spots on previously clear glass, or as bleached spots on previously activated glass. Diameter of spot is 1 mm.

TABLE II Gamma-numbers of activated (γ_{act}) and bleached (γ_{bl}) photochromic glasses.

Type	γ_{act}	γ_{bl}
1	0.59	0.71
2	0.61	0.6
4	0.74	0.64
5	0.27	0.16
6	0.23	0.16
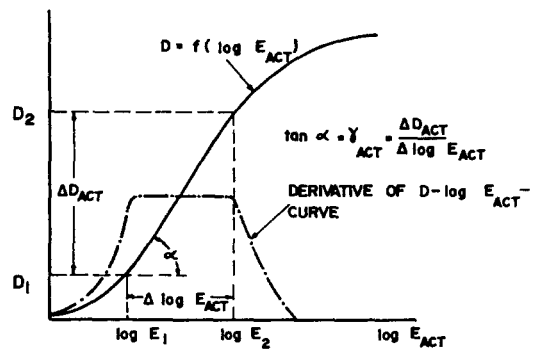
Figure 12 D-log E curve for darkening of photochromic material. The slope of the curve over the central nearly linear region is the γ-number.

It was implied above that, in general, glasses that become the darkest are the slowest to clear. This implies a cycling time slow for display applications involving normal information rates. However, the rate of clearing can be accelerated by external heating as well as by overall exposure to wavelengths longer than those used for darkening.

Fig. 15 shows the recovery times of a glass sample exposed to ambient temperatures of 200 and 300° F (93 and 149° C), compared to that of a control sample that was allowed to recover at room temperature [18].
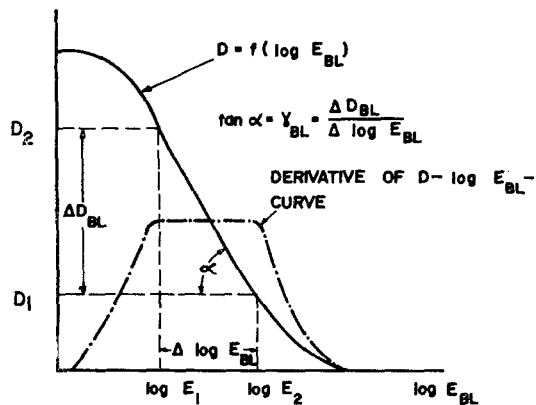

Figure 11 Decrease of absorbance with time by bleaching from different activation levels. The energy of the bleaching light was 5×10^{-3} W/cm², at 6000 Å.

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Figure 13 D-log E curve for bleaching of photochromic material. A γ-number is determined for bleaching, also.

Figure 15 Accelerated fading of photochromic glass by heated ambient air.

More rapid heating can be achieved, as seen in fig. 16, by coating the sample with a transparent, electrically conducting, tin oxide coating. By reducing the thickness of the glass, and hence increasing the heating rate, the glass was made to recover essentially completely in less than 10 sec.
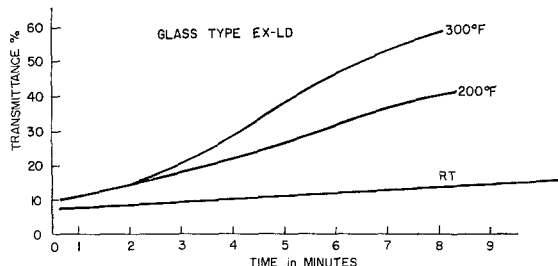
The ultimate resolution obtainable in these glasses may be very high. The crystallite sizes are at most a few hundred Ångstroms: the crystallite separation an order of magnitude larger. This is small compared to that in other photographic materials. High-speed photographic materials of low resolution contain crystal of sizes up to 20 000 Å and low-speed materials of very high resolution have average
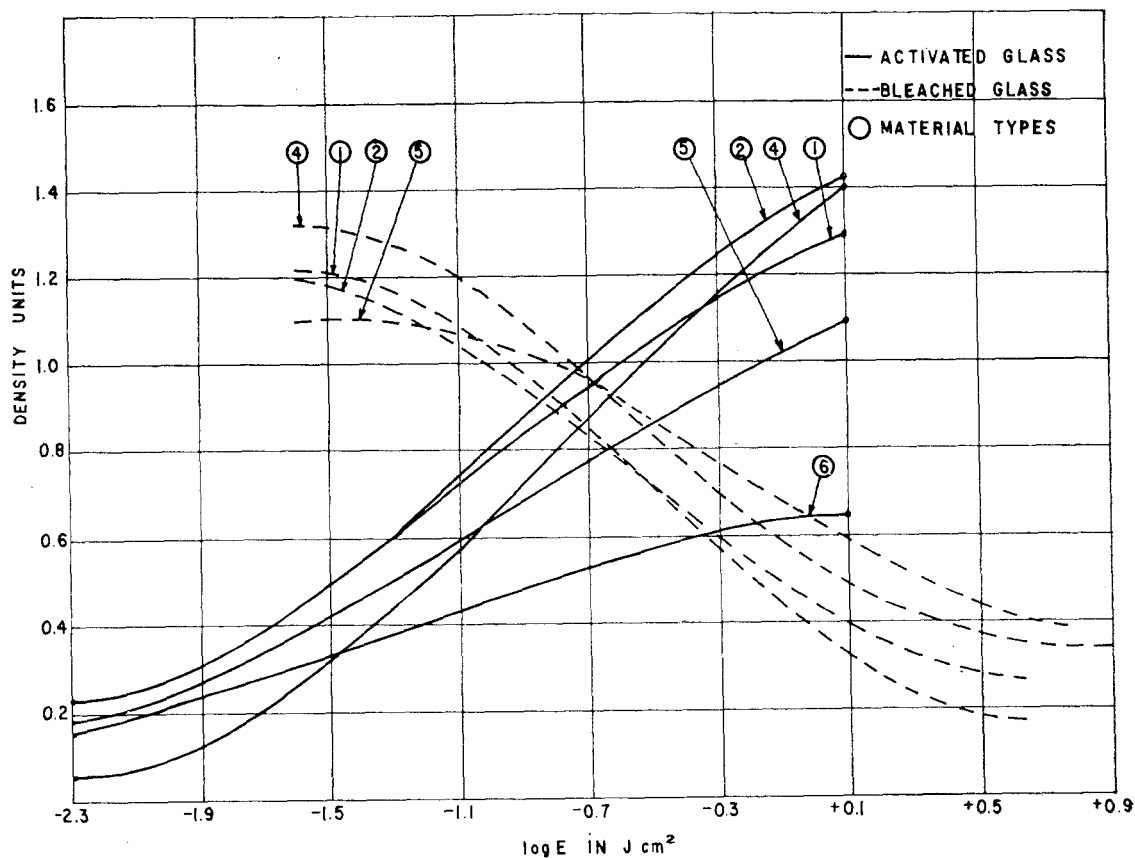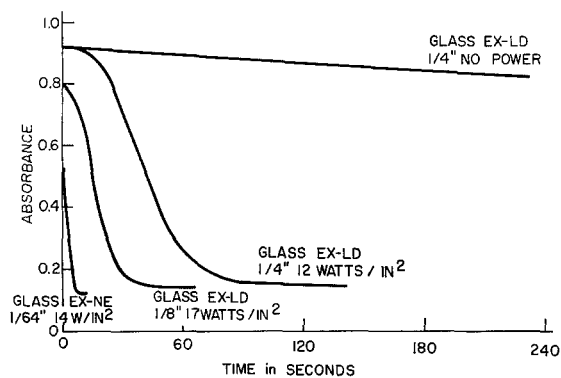

*Figure 14* Measured D-log E curves for both darkening and bleaching for several photochromic glasses.

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Figure 16 Accelerated fading of photochromic glass by heating with conductive coatings on the glass. The glasses reached temperatures of the order of 200° C, for rapid recovery.

crystal sizes of approximately 1000 Å. The usable resolution in optical systems will be determined, probably, by the sharpness of focus of the light used, rather than by any limit of resolution in the glass.

An additional illustration of resolution, and of possible applications of photochromic glasses to photography, is seen in figs. 17 and 18. Fig. 17 is a photographic positive, made in the conventional manner from a film-based negative. Photochromic glass 0.15 cm thick was exposed to ultraviolet light through this negative; the positive, made in this way, was then photographed, and fig. 18 is the positive print made from the resulting negative. It can be seen also in the photograph that a gradient in photochromic density under uniform illumination can be produced within this glass.

4.4. Response to Sunlight

The measurements on these glasses, described above, were made with artificial and controlled sources rich in ultraviolet light. Sunlight, at the surface of the earth, may be considered to be an uncontrolled light source with the amount of ultraviolet light, and the ratio of the ultraviolet to visible light, constantly changing throughout the day, and from day to day with changing
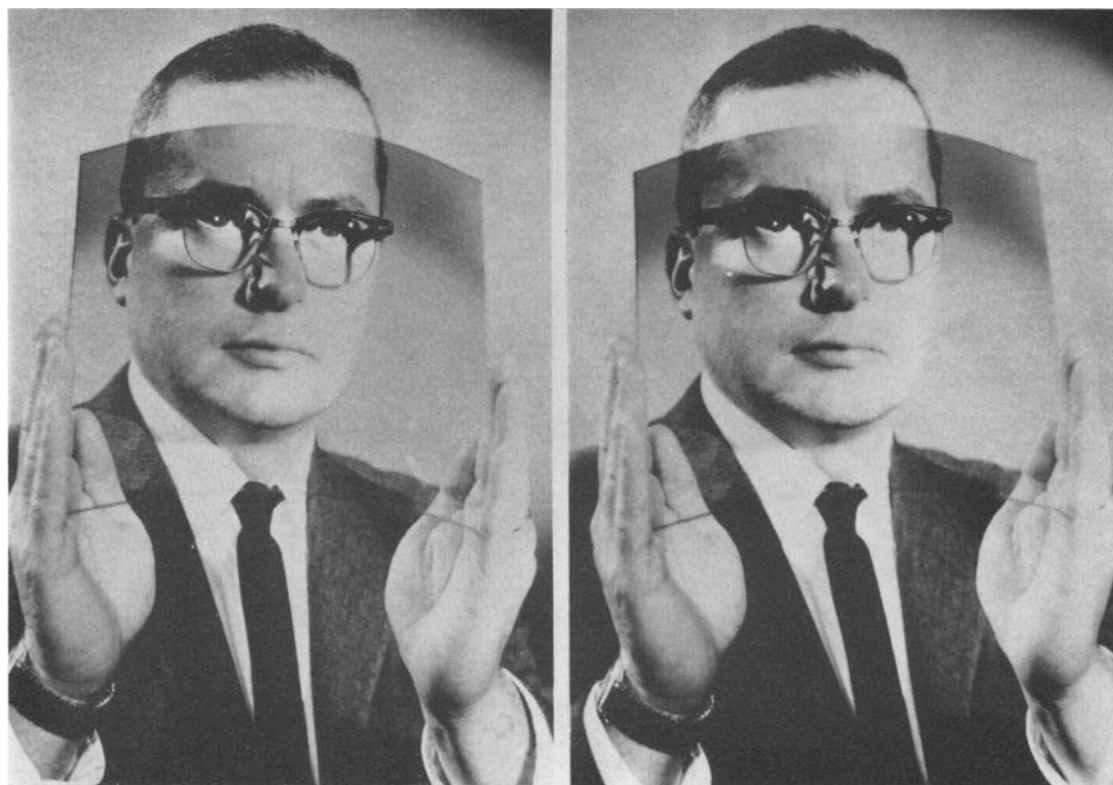
Figures 17 and 18 The use of photochromic glass as a temporary positive in photography. Fig. 18 (right) was made with photochromic glass as an intermediate positive, from the film used to print fig. 17.

weather. The response of glasses to sunlight is of primary interest in many possible uses of these glasses, such as in spectacles, windows in buildings, in automobiles and aircraft. Curves of the transmittance versus wavelength for one selected glass (6 mm thickness) are shown in fig. 19. From the transmittance curve at equilibrium, and the well-known spectral distribution
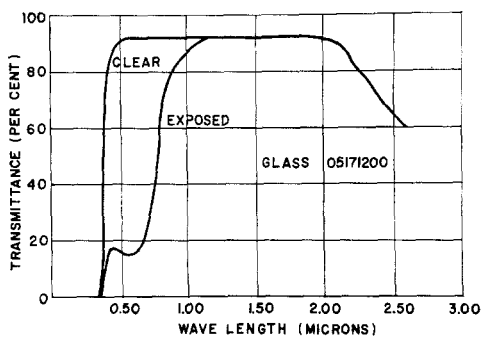

Figure 19 Spectral transmittance of a typical photochromic glass: clear, and exposed. The glass, after exposure, has high absorbance in the visible region of the spectrum, with reduced amounts in the infrared.

of energy of the sun at the surface of the earth [19, 20], the amount of energy absorbed by the darkened glass, and therefore its equilibrium temperature, can be determined [21]. Fig. 20 contains a trace of the spectral distribution of the

energy of the sun at the surface of the earth (air mass 2), and of the spectrum of the amount transmitted by a typical, darkened, photochromic glass.

For most uses in sunlight, we would, by following equation 2, choose glasses in which the thermal-fading rate has been made relatively large; so that: (i) the equilibrium absorbance increases with the intensity to as large values of intensity as possible; (ii) the absorbance decreases as rapidly as possible when the illumination goes to very low values, i.e. at night. But, since the fading rate would be expected to be temperature dependent, this implies a glass composition whose transmittance, to a larger extent, is determined by the temperature of the glass.

A typical glass (06081800) which has a favourable balance of several photochromic parameters for use in buildings shows reduction of transmittance with increasing solar intensity for three mornings of different ambient temperature, as in fig. 21. These curves show the expected increase in equilibrium transmittance with temperature, and also the increase in intensity of illumination at which equilibrium is approached, at the higher temperature.

When the transmittances of these photochromic glasses are recorded over an entire day, they show a characteristic pattern: they begin to
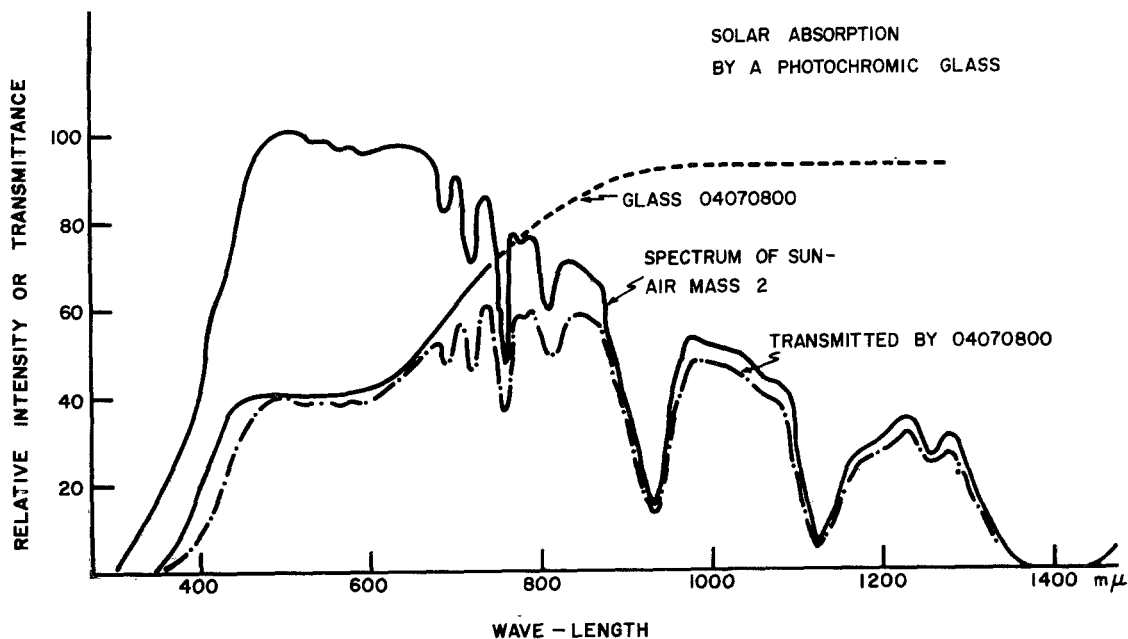

WAVE – LENGTH

Figure 20 Spectral distribution of energy from the sun (air mass 2) transmitted by a photochromic glass. Most of the reduction of energy is below 1 μm wavelength.
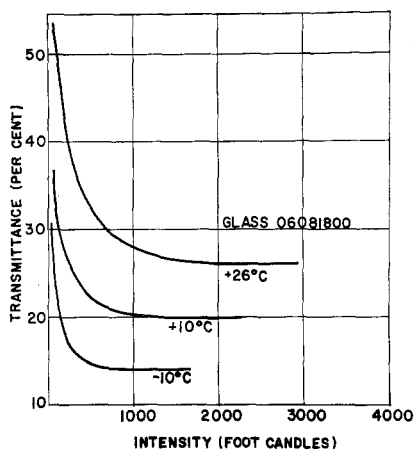
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Figure 21 Transmittance versus increasing intensity, in sunlight at three temperatures.

darken at dawn (actually before sunrise because of the ultraviolet light scattered to the glasses by the atmosphere), continue to darken until saturation is achieved, remain at approximately that transmittance throughout the day, begin to clear before sunset, and continue this clearing at a constantly reducing rate until sunrise the next morning, when the pattern is repeated. Fig. 22 shows smoothed traces of several selected glasses (6 mm thickness). Here, temperature was not externally controlled; the temperature was the equilibrium temperature for these glasses mounted in a vertical, south-facing panel.
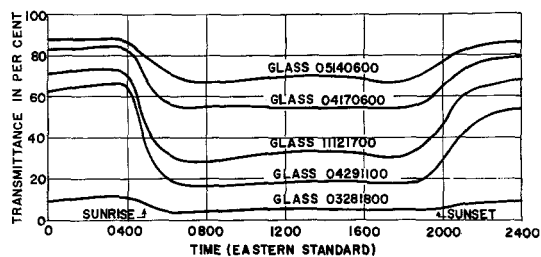

Figure 22 Transmittance of five representative photochromic glasses throughout a summer day (26 June) in Corning. The night of 26 June was cooler than that of 25 June.

Transmittance versus wavelength curves for all these glasses are similar to that of the 05171200 glass shown in fig. 19, so that the glass labelled 03281800 would probably have been warmest. Note that the characteristic shape of all these traces is the same: any one of them can, by translation of the entire curve along the transmittance axis or by stretching or compressing the

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transmittance scale, be reasonably well superposed on any of the others. These curves appear smooth partly as the result of the compensatory dependence of transmittance on intensity and on temperature. That is, as the sunlight intensity increases, the absorbance of the glass increases. But at solar intensities high enough to produce an appreciable temperature increase in the glass, the rate of change of absorbance with intensity is small (cf. fig. 21), and may be cancelled by the decrease in equilibrium absorbance resulting from the increase in the thermal-fading rate of the glass.

It follows, then, that changes in intensity produce changes in transmittance at higher intensity values when the temperature of the glass is controlled. The transmittance of a selected photochromic glass, double-glazed with soda-lime plate glass as a window in an air-conditioned room, versus the intensity of the sunlight for a typical day is shown in fig. 23. On this summer day, the trace of the incident light (here on an arbitrary scale) shows a reasonably bright morning, heavy cloud around 10.00 h, variable cloud and sunshine in early afternoon, and a relatively clear evening. The corresponding trace of transmittance shows darkening of the glass from dawn to about 07.00 h, with clearing after about 17.00 h. The glass clears from about 40 to 52 % transmittance with the heavy cloud at 10.00 h which reduced the illumination, measured normal to the glass, from about 3300 to about 600 foot candles. Response to incident light-intensity change, resulting from a cloud, is also seen just before 13.00 h.

A similar glass, similarly glazed, is seen in fig. 24 to increase in transmittance from 30 to 57 % during a very severe storm, when the external illumination decreased from 2600 to about 50 foot candles. Therefore the light transmitted, when it got relatively very dark outside, was about twice that which a window of fixed transmittance of 30 %, such as a grey light-absorbing window, would have admitted.

4.5. Reversibility

No significant changes in photochromic behaviour have resulted from cycling glass samples with a "black light" source (3600 Å) up to 30000 cycles. Also, there were no apparent solarisation effects causing changes in darkening or fading rates after accelerated ultraviolet exposure equivalent to 20000 h of noonday sunshine. A sample has also been cycled using a
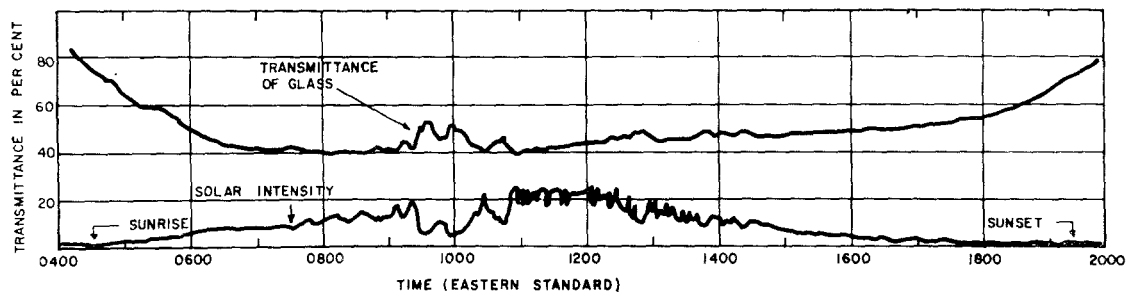
Figure 23 Transmittance of selected photochromic glass, double-glazed with soda-lime glass, throughout a relatively sunny day (9 June) in Corning: lower trace, solar intensity; upper trace, transmittance.
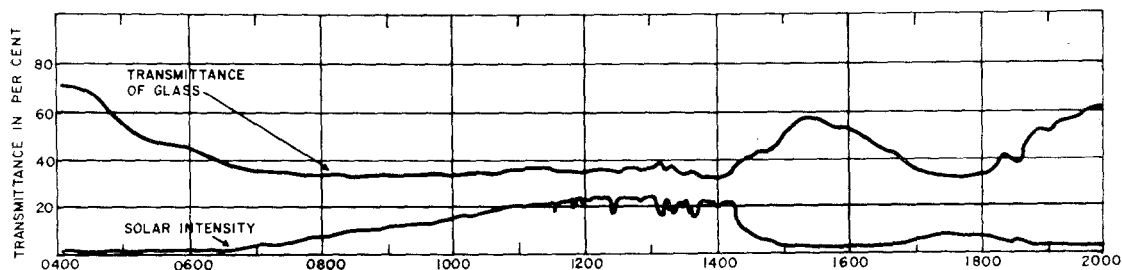
Figure 24 Transmittance of selected photochromic glass, double-glazed with soda-lime glass, on day (2 July) with a severe thunderstorm: lower trace, solar intensity; upper trace, transmittance.

constant output source with switching filters transmitting at wavelengths of 4000 and 6000 Å, i.e. "writing" and erasing, which resulted in 0.3 changes in optical density. To-date, there is no apparent fatiguing after more than 300 000 cycles [15]. The bleaching and darkening times were of the order of 1 min. All these tests are continuing in order to generate more conclusive data.

5. Applications

The properties of the photochromic glasses, discussed above, suggest some possibilities for their use in optical systems which include those of information storage and display, for photography, and for glazing in buildings and in vehicles. Sunglasses made with organic photochromics are now on the market, from several sources; prescription lenses of photochromic glass have now been made commercially available. With development of materials that react fast enough and react to a high-enough optical density, eye protection against nuclear bursts may be possible [22, 23].

Some other possible uses for varied photochromic materials are as dyes, paints, or coatings for radiation control; for bottles and containers for light-sensitive drugs and foods.

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