

Effects of Various Manufacturing Conditions on Darkening and Fading of Photochromic Glasses

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Effects of melting time, heat-treatment time, and γ -ray irradiation before heat treatment on darkening and fading of a photochromic glass were investigated. It was found that the degree of darkening was determined principally by the amount of AgCl crystal particles precipitated in the glass and the absorption coefficient of the particles. The latter showed the maximum when the particle diameter was about 400 Å. The fading rate was high for the specimens which exhibited the strong absorbance after the completion of U. V. illumination.

I. INTRODUCTION

In the previous study,^{1,2)} the authors have investigated the effects of furnace atmospheres on the loss of Ag and Cl from the photochromic glasses during melting. In the present study, effects of melting time, heat-treatment temperature, heat-treatment time and γ -ray irradiation treatment *etc.* on darkening of a photochromic glass have been investigated. Especially, effects of the particle size of the AgCl crystals precipitated in the glass on darkening and fading of the glass have been investigated in detail. The fact that darkening of the photochromic glass can be enhanced by γ -ray irradiation before or during its heat treatment was already found by O'Leary.³⁾

II. EXPERIMENTAL

II.1 Preparation of Glass

The batch composition of the glass used in this experiment is shown in Table 1. As the raw materials, quartz sand for manufacturing optical glasses and reagent grade oxides and chlorides were used. AgCl, BaCl₂ and Cu₂O were premixed with a part of quartz sand for dilution. The batches each yielding about a 80 g. glass were melted in a platinum crucible in an electric resistance furnace at about 1450°C for various times under the normal atmospheric condition. The melts were stirred every one and a half hour to homogenize glass. The melts were then poured on a steel plate and cut into slabs, 5 × 8 × 50 mm. The contents of Ag and Cl remaining in the glass were determined by X-ray fluorescence analyses by the method reported previously.¹⁾ It was found that even for the slabs cut from a piece of glass plate their Ag and Cl contents scattered a little; the dispersion were <5 wt.% for the Ag content and 5 to 10 wt.% for the Cl content. The transition and softening temperatures of the glass obtained from its thermal expansion curve were 520° and 590°C, respectively.

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Table 1 Batch Composition

SiO ₂	40.0 g	BaCO ₃	3.65 g
H ₃ BO ₃	27.1	PbO	3.66
Al(OH) ₃	8.01	ZrO ₂	1.60
Li ₂ CO ₃	4.90	Cu ₂ O	0.011
Na ₂ CO ₃	2.34	AgCl	0.45
BaCl ₂	4.63		
		Total	96.35 g

II.2 Heat Treatment of Glass

The specimens were put in the furnace previously heated to a given temperature between 500° to 650°C, kept these for various times, 0 to 48 hours, taken out from the furnace and allowed to cool in air. Some of the specimens were irradiated by γ rays (6×10^6 röntgen) before the heat treatment.

II.3 Measurement of Darkening and Fading

The heat-treated specimens were ground and polished to size, 2 ± 0.1 mm in thickness, 7 mm in width and 40 mm in length. They were placed at a distance of 5 cm from a fluorescence lamp of 12 watt and illuminated by a U.V. light of 3650Å in wavelength for 15 min.. The 15 min. illumination was found to be enough for all the specimen to darken to their saturated values. The absorbance of the darkened specimens ($\log I_0/I_a$, where I_0 is the initial intensity of the light and I_a is the intensity of the light transmitted through the darkened specimen.) was measured at $22 \pm 0.5^\circ\text{C}$ by a spectrophotometer using a 5000Å light every 2 min. after the completion of U.V. illumination. Except specially noted, the darkness was expressed by the absorbance measured 2 min. after the completion of U.V. illumination.

II.4 Determination of Particle Size and Content of AgCl Crystal in Glass

The mean particle size of AgCl crystals precipitated in glass was measured from the degree of broadening of the X-ray diffraction peak profile due to 200 reflection of the AgCl crystal. The content of AgCl in glass was measured by comparing the area of its specified X-ray peak with that of the standard samples which were prepared by mixing 0.1 to 0.5 wt.% of chemical pure AgCl powders with the powdered base glasses free from AgCl. Since the contents of AgCl crystals in the specimens were generally very low (< 0.5 wt.%), the X-ray radiation power was increased and furthermore the X-ray intensity was measured at an interval of 0.1° from $2\theta = 31.5^\circ$ to 33.0° using a scintillation counter and a pulse height analyser. The mean particle size of the crystal, D , was calculated using the formula,

$$D = \frac{K\lambda}{\beta \cos \theta}$$

where β is the pure diffraction breadth (the half-width of the peak) of the specimen, which can be obtained by subtracting from the experimentally observed breadth, B , of a diffraction line the instrumental breadth, b , ($\beta = B - b$), using the correction curve of β/B vs b/B^4 . λ is the wavelength of X rays and K is the shape factor. In the present experi-

ment, 0.9 was used as the value of K . Hammel *et al.* used the above method for measuring the mean particle size of Ag-halide crystals precipitated in a photochromic glass.⁵⁾

III. RESULTS

III.1 Electronmicroscopic Observation

Figure 1 is a typical electronmicrograph taken of the fractured surface of the specimen melted at 1450°C for 9 hours and then heat-treated at 600°C for 48 hours after γ -ray irradiation. Its Ag and Cl contents were 0.26 and 0.23 wt.% respectively. The mean particle size of AgCl crystals determined from the micrograph was about 400 ± 20 Å, which was almost the same as that determined by the X-ray method (380 ± 10 Å).



Fig. 1. Electronmicrograph of fractured surface of glass (Ag 0.26, Cl 0.23 wt.%) heated at 600°C for 48 hours after γ -ray irradiation.

III.2 Effects of Melting Time on Darkening of Glass

In previous report, the relations between the glass melting time and the contents of the Ag and Cl remained in the glass were investigated. The result is reproduced in Fig. 2 (a). Figure 2(b) shows the relation between the melting time and the darkening of the glass, *i.e.*, the absorbance of the glass specimens, 2 mm thick. Before the measurements of absorbance, all of the glasses were heat-treated at 550°C for 48 hours. Dotted lines in Fig. 2(b) represent the relations of the absorbances of the glasses before and after U.V. illumination with the melting time. A solid line between these dotted lines represents their difference. The relations of the melting time with the content and the mean particle size of the AgCl crystals precipitated in the glass are also shown in Fig. 2(c) and (d). The relation between the melting time and the number of AgCl crystals in unit volume of the glass, calculated from the content and the mean particle size of the crystals, is shown in Fig. 2(e).

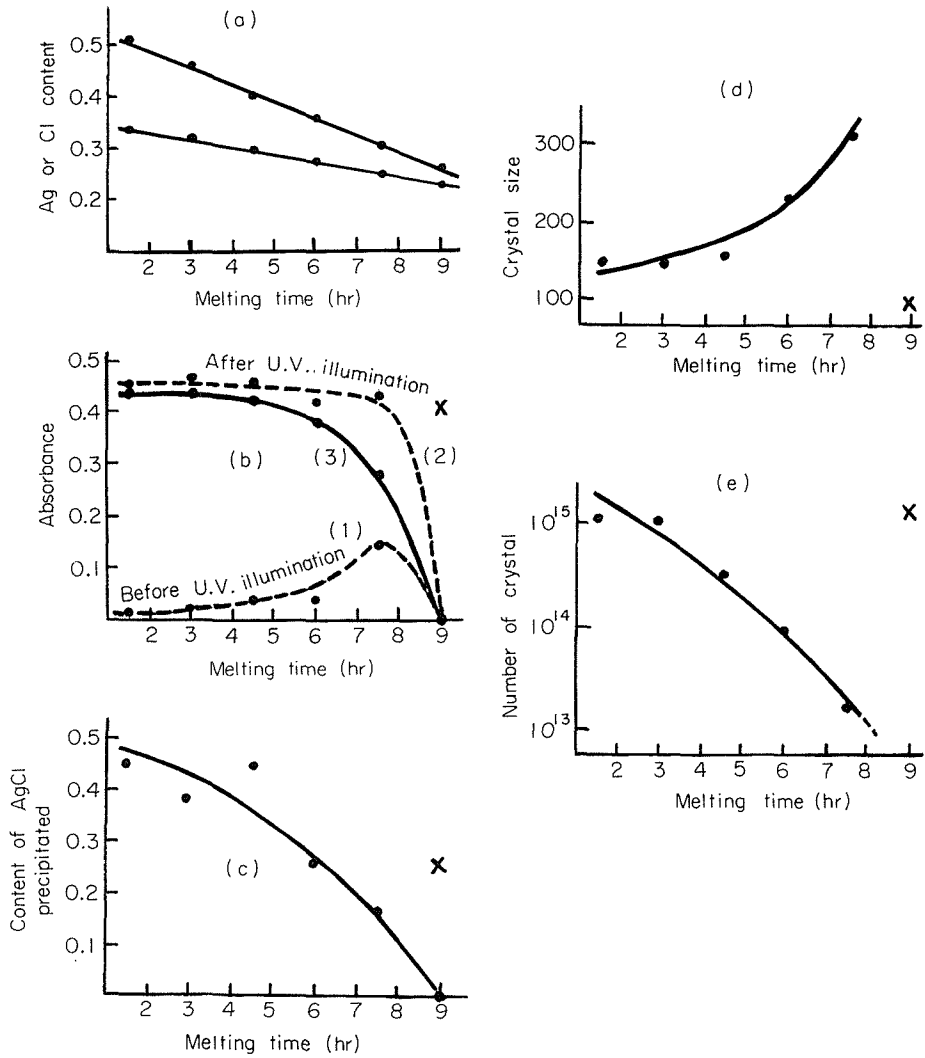


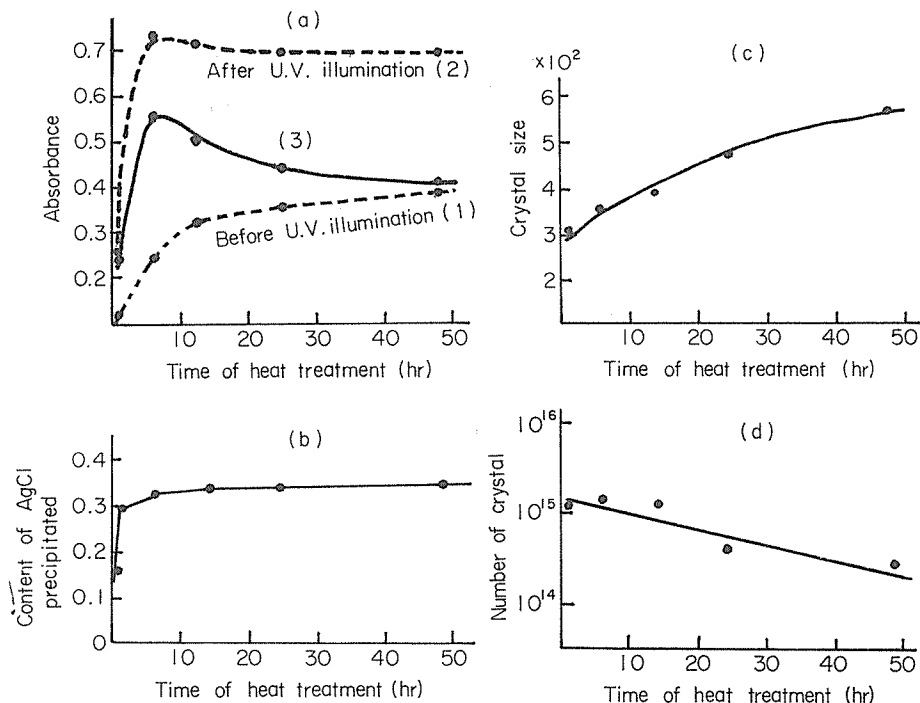
Fig. 2. Properties of photochromic glass in relation to melting time. The glasses were melted at 1450°C for various times and then heat-treated at 550°C for 48 hours.

- (a) Contents of Ag and Cl remained in glasses (wt.%)
- (b) Absorbance of glasses ($\log \frac{I_0}{I}$)
- (c) Total contents of AgCl crystal particles precipitated in glasses (wt.%)
- (d) Diameter of AgCl crystal particles precipitated in glasses (Å)
- (e) Number of AgCl crystal particles precipitated in glasses (per CC glass)

The signs, x, denote the results for glasses irradiated by γ rays before heat treatment.

III.3 Effects of Heat-treatment Time on Darkening of Glass

The glass specimens whose Ag and Cl contents were the same as those used in the experiment described in the foregoing paragraph were heat-treated at 600°C for 2 to 48 hours. The relations of the heat-treatment time with the darkening of the glasses as well as with the content, the mean particle size and the number of the AgCl crystals precipitated in the glasses are shown respectively in Fig. 3(a), (b), (c) and (d). Dotted lines in Fig. 3(a) represent the relations of the absorbances of the glasses before and after U.V. illumination with the melting time. A solid line between these dotted lines represents their difference.

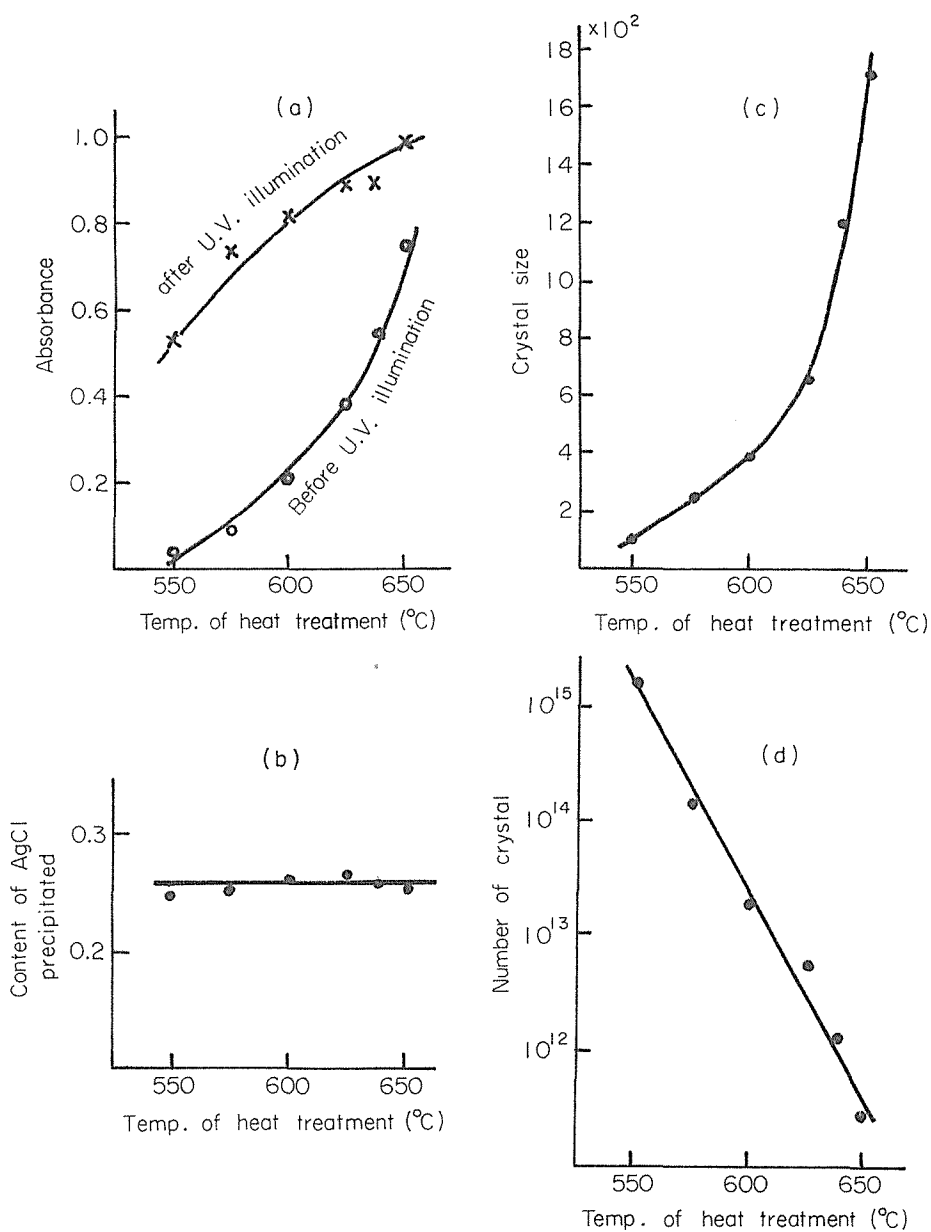


- (a) Absorbance of glasses ($\log \frac{I_0}{I}$)
 (b) Total contents of AgCl crystal particles precipitated in glasses (wt.%)
 (c) Diameter of AgCl crystal particles precipitated in glasses (A)
 (d) Number of AgCl crystal particles precipitated in glasses (per CC glass)

Fig. 3. Properties of photochromic glass in relation to heat-treatment time. The glasses were melted at 1450°C for 6 hours (Ag 0.33, Cl 0.40 wt.%) and then heat-treated at 600°C for 2~48 hours.

III.4 Effects of γ -ray Irradiation

The glass specimen, melted for 9 hours (Ag 0.26, Cl 0.23 wt.%) (see Fig. 2(a)) and then heat-treated at 550°C for 48 hours, showed little darkening on U.V. illumination. However, when γ rays were irradiated to the same glass before the heat treatment, it showed a remarkable darkening. The signs, x, in Fig. 2(b), (c), (d) and (e) present the data for the glasses, each irradiated with γ rays before the heat treatment.



- (a) Absorbance of glasses ($\log \frac{I_0}{I}$)
- (b) Contents of AgCl crystal particles precipitated in glasses (wt.%)
- (c) Diameter of AgCl crystal particles precipitated in glasses (Å)
- (d) Number of AgCl crystal particles precipitated in glasses (per CC glass)

Fig. 4. Properties of photochromic glass in relation to heat-treatment temperature. The glasses were melted at 1450°C for 9 hours and heat-treated at various temperatures between 550° and 650°C after γ -ray irradiation.

III.5 Relation of Darkening and Fading Versus Mean Particle Size of AgCl Crystals Precipitated

The glass specimens, melted for 9 hours (Ag 0.26, Cl 0.23 wt.%) (see Fig. 2(a)) were irradiated with γ rays and then heat-treated respectively, at 550°, 575°, 600°, 625°, 635° and 650°C, all for 48 hours. Figure 4(a), (b), (c) and (d) show the relations of the temperature of heat treatment with the darkening of the specimens, the content, the mean particle size and the number of the AgCl crystals precipitated in the specimens. From these results it can be seen that, in all the specimens, the contents of the AgCl crystals precipitated are the same but their mean particle sizes are different, increasing with increasing temperature of their heat treatment. A relation of the darkening of the specimens with the mean particle size of the AgCl crystals precipitated, was obtained from Fig. 4(a) and (c), which is shown in Fig. 5.

Figure 6 shows fading processes of the glass specimens having the AgCl crystal particles of different sizes. The abscissa represents the time elapsed after the completion of the U.V. illumination and the ordinate represents the difference between the absorbances before and various times after the completion of U.V. illumination. Figure 7 was obtained by shifting all the curves shown in Fig. 6 so that their initial values on the ordinate become equal to zero.

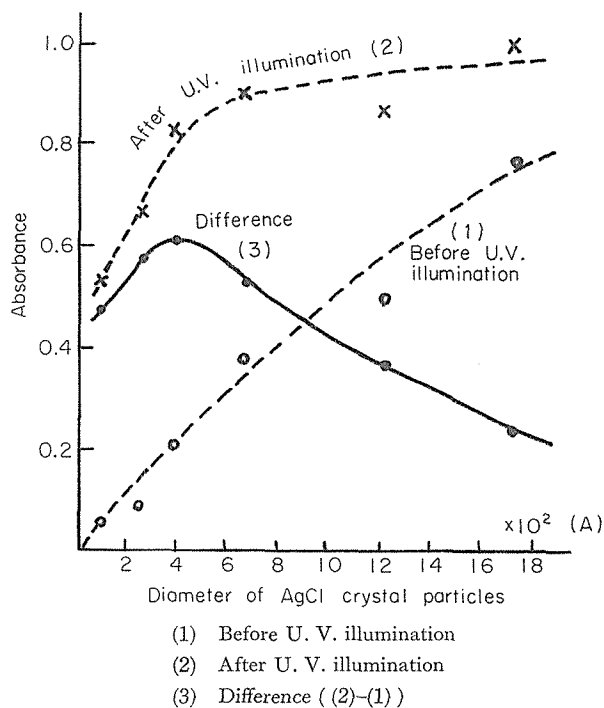


Fig. 5. Absorbance of glasses before and after U. V. illumination versus particle size of AgCl crystals. The total amounts of AgCl crystals in glasses are all the same (ref. Fig. 4(b)).

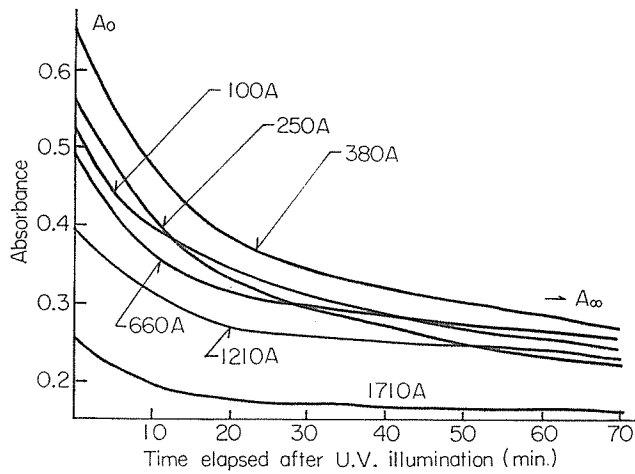


Fig. 6. Fading of glasses containing AgCl crystal particles of different sizes. The total amounts of AgCl crystals in glasses are all the same (ref. Fig. 4(b)).

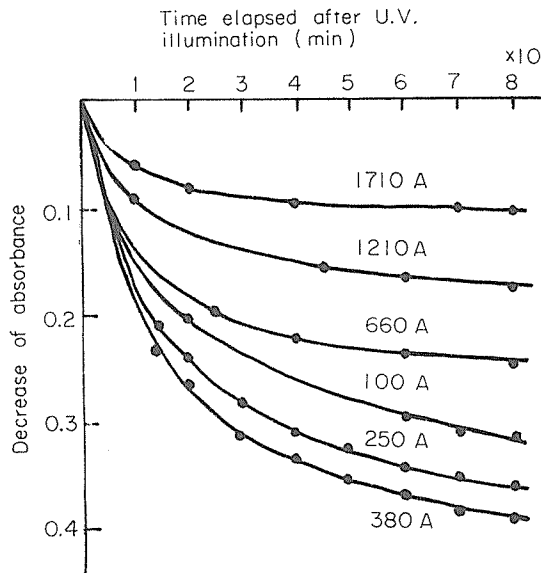


Fig. 7. Decrease of absorbance of glasses containing AgCl crystal particles of different sizes.

IV. DISCUSSIONS

IV.1 Changes in Amount of AgCl Crystals Precipitated in the Heat-treated Glass with Melting Time of Parent Glass

The amount of AgCl crystals precipitated in the glass decreased greatly with increasing the time of glass melting, and after melting for 9 hours it reached almost zero,

although the contents of Ag and Cl in the parent glass were both still fairly high (Fig. 2 (a), (c)). The lowering of the amount of the precipitated AgCl crystals to zero, however, does not mean that the concentration of AgCl in the parent glass from which a AgCl-rich phase was separated lowered below its saturation value at the temperature of heat treatment. This is apparent from the fact that a fairly large amount of the AgCl crystals as indicated by the sign, x in Fig. 2(c) precipitated even in the glass melted for 9 hours if it was irradiated with γ rays before heat treatment. Therefore, it would be reasonable to consider that the lowering of the amount of precipitated AgCl crystals was caused by the lowering of the nucleation rate of the AgCl-rich phase in the parent glass. The marked effect of γ -ray irradiation in increasing the amount of the AgCl crystals as well as the marked decrease of the number of the AgCl crystal particles with increase in melting time (Fig. 2(e)), both observed in the present experiment, appear to support the above approach. The effect of γ -ray irradiation in accelerating nucleation in glasses is generally found. The reason why the nucleation rate of the AgCl-rich phase decreased with increasing melting time is not yet clear but probably it resulted from the decrease in degree of supersaturation of AgCl in the glass caused by the prolonged melting.

IV.2 Intensity of Light Transmitted through Photochromic Glass

As light is transmitted through a photochromic glass plate, a certain fraction is lost by reflection, scattering and absorption; reflection occurs at both sides of the plate and scattering and absorption are caused by AgCl crystal particles in the glass. A change in intensity of the light is given by

$$\frac{I}{I_0} = (1-R)^2 \exp(-KN\pi r^2 X) \exp\left(-\frac{4}{3}\pi r^3 NaX\right) \quad (1)$$

or

$$\log \frac{I_0}{I} = -2 \log(1-R) + \frac{1}{2.3} \left(KN\pi r^2 + \frac{4}{3}\pi r^3 Na \right) X \quad (2)$$

where I_0 is the initial intensity, I is the transmitted intensity, R is the reflectivity, X is the thickness of the glass plate, K is a scattering factor, N is the number of the AgCl crystal particles per unit volume of the glass, r is the particle radius, a is the absorption coefficient of the AgCl crystal. If the volume fraction of the AgCl crystal particles present is V_p ,

$$V_p = \frac{4}{3}\pi r^3 N \quad (3)$$

$$\frac{I}{I_0} = (1-R)^2 \exp\left(-\left(\frac{3}{4}\frac{K}{r} + a\right)V_p X\right) \quad (4)$$

$$\log \frac{I_0}{I} = -2 \log(1-R) + \frac{1}{2.3} \left(\frac{3}{4}\frac{K}{r} + a \right) V_p X \quad (5)$$

IV.3 Darkening of Photochromic Glass Irradiated with γ rays before Heat Treatment

The series of glasses irradiated with γ rays before heat treatment contained the AgCl

crystal particles of a constant volume (Fig. 4(b)). If the thickness of the glass specimens are the same, the following equation holds for these glasses.

$$\log \frac{I_0}{I} = a + b \left(\frac{3}{4} \frac{K}{r} + a \right) \quad (6)$$

where a and b are constants, respectively. Before U.V. illumination,

$$a \doteq 0 \quad (7)$$

Therefore, a great increase in absorbance with increase in diameter of the AgCl crystal particles as observed for the glasses before U.V. illumination (Fig. 5) is interpreted to be principally due to a great increase in K value with increase in the crystal particle size. For the absorbance of the glasses after U.V. illumination, $a > 0$ in equation (6). Therefore, the difference in absorbances between the glasses before and after U.V. illumination is given by

$$\log \frac{I_b}{I_a} = ba \quad (8)$$

where I_b and I_a is the transmitted intensities of the light before and after U.V. illumination, respectively. Therefore, the curve (3) in Fig. 5 indicates that the absorption coefficient of the AgCl crystal particles in the glasses after U.V. illumination increases with increasing the size of the AgCl particle, goes through the maximum at about 400 Å and then decreases gradually.

IV.4 Darkening of Photochromic Glasses not Irradiated with γ rays before Heat Treatment

For each series of the glasses not irradiated with γ rays, total amount of AgCl crystal particles precipitated in the glasses were not constant (Fig. 2 (c) and 3 (b)). Therefore, the difference in absorbances between the glasses before and after U. V. illumination must be expressed by an equation including the volume fraction of the particles, V_p , *i. e.*,

$$\log \frac{I_b}{I_a} = caV_p \quad (9)$$

where c is a constant.

(a) Glasses Melted for Various Times (Fig. 2)

As noted previously, for this series of glasses, the content of the AgCl crystals precipitated, namely, V_p in equation (9), fell almost to zero as the melting time was extended to 9 hours (Fig. 2 (c)). Therefore, the fact that the difference in absorbances of the glasses before and after U. V. illumination ($\log I_b/I_a$) decreased with increasing melting time (Fig. 2 (b)) is principally attributed to the decrease in the V_p value in equation (9). It has also been noted in paragraph 4.3, that the absorption coefficient, a , of the AgCl crystal particles increased with increasing mean diameter at least up to 400 Å. For this series of glasses the diameters of the particles ranged from 140 to 320 Å (Fig. 2 (d)). The fact that the decrease in difference between the absorbances before and after U. V. illumination with increase in melting time was slow (Fig. 2 (b), curve (3)) at least up to about

7 hours melting, compared to the decrease in content of the AgCl crystals (Fig. 2 (c)), would suggest that the effect of particle size in increasing the value of absorption coefficient of the AgCl particles noted above checks the sharp decrease of the difference in absorbance of the glass due to the sharp decrease in the V_p value with increase in melting time.

(b) Glasses Heat-treated for Various Time (Fig. 3)

In this series of glasses the content of AgCl crystal particles first increased greatly with increase in heat-treatment time, but after about 10 hours heat treatment it reached almost its saturation value (Fig. 3 (b)). On the other hand, the difference in absorbances of the glasses between before and after U. V. illumination ($\log I_b/I_a$) first increased greatly with increasing time of heat treatment, and then decreased slowly after going through the maximum (Fig. 3 (a), curve (3)). The first increase of the difference in absorbance with increase in heat-treatment time is considered to be principally due to the great increase in the content of AgCl crystal particles, namely, to the great increase in the V_p value in equation (9). The decrease in the difference after going through its maximum is attributed to the decrease of the absorption coefficient of the AgCl crystal particles, namely, to the decrease of the α value in equation (9). It has been mentioned previously that the absorption coefficient of AgCl crystal particles decreased as their mean diameter increased after their absorption coefficient went through its maximum.

In the above discussions, the problem why the absorption coefficient of the AgCl crystal show a maximum at a certain grain size has not been referred to. Further investigations are necessary.

IV.5 Effects of Particl Size of AgCl Crystals on Fading Rate of Glass

All the curves shown in Fig. 6 were found to be fitted into an equation

$$d(A - A_\infty)/dt = -k(A - A_\infty)^n \tag{10}$$

or

$$\ln(A - A_\infty) = -a \ln(t + t_0) + b \tag{11}$$

where $(A - A_\infty)$ is the difference between the absorbances at the time, t , and that at the infinite time, t_∞ , after the completion of U. V. illumination, k is a constant, n is reaction orders, $a = 1/n - 1$, $b = 1/n - 1 \ln(1/n - 1)k$, and t_0 depends α , b and the initial value of A , A_0 . The above formula represents n th order reaction processes.⁶⁾ The values of n , k , $A_0 - A_\infty$, $(A_0 - A_\infty)^n$ and $k(A_0 - A_\infty)^n$ obtained are listed in Table 2. Figure 8 shows

Table 2 Analysis of fading rate as a function of the size of AgCl crystals dispersed in glass

Size (A)	n	k	$A_0 - A_\infty$	$(A_0 - A_\infty)^n$	$k(A_0 - A_\infty)^n$
100	1.75	0.158	0.340	0.151	0.0238
250	1.65	0.150	0.365	0.190	0.0285
380	1.63	0.147	0.410	0.234	0.0344
660	1.62	0.259	0.245	0.102	0.0264
1210	1.62	0.314	0.170	0.056	0.0176
1710	1.62	0.451	0.100	0.024	0.0108

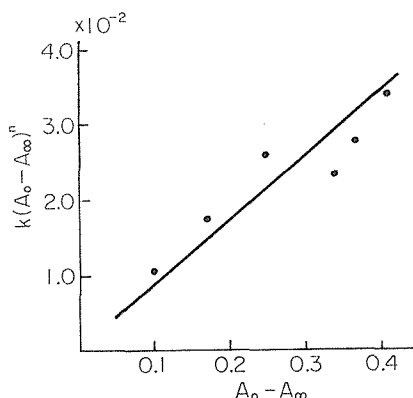


Fig. 8. Relation between initial fading rate and absorbance for glasses containing AgCl crystals of different sizes.

a relation between the initial fading rate, $k(A_0 - A_\infty)^n$ and the difference in absorbance, $(A_0 - A_\infty)$ for the specimens having AgCl crystal particles of different sizes, which indicates that the fading becomes faster for the specimens which darken stronger upon U. V. illumination.

V. SUMMARY

Effects of melting time, heat-treatment time and γ -ray irradiation before heat treatment on darkening of a photochromic glass were investigated. The batch composition of the glass investigated was; SiO₂ 40.0, H₃BO₃ 27.1, Al(OH)₃ 8.01, Li₂CO₃ 4.90, Na₂CO₃ 2.34, BaCO₃ 3.65, BaCl₂ 4.63, PbO 3.66, ZrO₂ 1.60, Cu₂O 0.011, AgCl 0.45, Total 96.35 g. The melting was made at 1450°C for 1.5 to 9 hours and the heat treatment was made at various temperatures 550° to 650°C, for 2 to 48 hours.

1) The content of AgCl crystal particles precipitated in the glass decreased almost in proportion to the increase in time of glass melting. This decrease was much faster than the decrease in content of AgCl dissolved in the parent glass. At a certain time of glass melting, *e. g.*, 9 hours in the present experiment, the content of the AgCl crystal particles precipitated fell into zero, although the contents of AgCl dissolved in the glass were still kept fairly high. The difference between the absorbances of the glass specimen before and after U. V. illumination, *i. e.*, $\log I_b/I_a$ where I_b and I_a are the intensities of the light transmitted through the specimen before and after U. V. illumination, respectively, was found to be determined principally by the content of the AgCl crystal particles precipitated in the glass, although the decrease in the difference in absorbance, $\log I_b/I_a$, with increase in the time of glass melting was checked to a certain extent by the increase in absorption coefficient of the AgCl crystal particles precipitated in the glass which resulted from the growth of the particles from 140 Å to 320 Å in diameter.

2) The difference in absorbance of the specimen, $\log I_b/I_a$, first increased rapidly, went through its maximum and then decreased gradually with increasing the time of heat treatment. The first rapid rise in the difference in absorbance, $\log I_b/I_a$, was attributed

to the rapid increase of the content of the AgCl crystal particles precipitated in the glass and its second gradual fall was attributed to the decrease in absorption coefficient of the the AgCl crystal particles which resulted from the growth of the particles from 370 Å to 550 Å.

3) A series of glasses heat-treated after γ -ray irradiation contained AgCl crystal particles of a constant volume. For this series, the relation between the difference in absorbance, $\log I_b/I_a$, and the diameter of the AgCl crystal particles was obtained; the value of $\log I_b/I_a$ increased as the diameter of the particles increased from 100 Å to 380 Å, but after went through its maximum it decreased as the diameter of the particles increased from 380 to 1710 Å. This change was attributed to the change in absorption coefficient of the AgCl crystal particles with the change in diameter of the particles.

4) The fading rate was high for the specimens which exhibited strong darkening on U. V. illumination.

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