BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 848—851 (1973)

Photochromism of Thallium Chloride

Sumio SAKKA and J. D. MACKENZIE*

Department of Industrial Chemistry, Faculty of Engineering, Mie University, Tsu, Mie
**School of Engineering and Applied Science, University of California, Los Angeles, California, USA*

(Received July 26, 1972)

The ultraviolet-induced darkening and subsequent bleaching of crystalline thallium chloride was investigated in order to study the processes occurring in a photochromic glass containing TlCl crystalline particles. Doping with a small amount of copper, silver or indium ion was found to be effective in promoting darkenability of TlCl crystals. Exposure to visible light causes bleaching of UV-induced coloring of TlCl crystals. Almost no fading occurs, however, when TlCl crystalline pieces are kept in darkness at room temperature or higher temperatures up to about 70°C, where very quick fading in color is observed in the case of TlCl crystals embedded in a glassy matrix.

Much attention has been drawn to photochromic silver halide glass[1,2] since its discovery. The glass darkens when it is exposed to UV light and returns reversibly to the original non-colored state when kept in darkness. The active agents inducing such behavior are silver halide crystalline particles embedded in a glassy matrix. The reversibility of color change was explained by the reasoning that silver halide particles do not lose halogens since they are surrounded by impermeable and inert glassy matrix.[1]

Thallium monohalides are supposed to be similar to silver halides in some respects[3] and it is considered that photochromic glasses could be made with the use of thallium halides as active agents. This was actually found to be the case.[4] Experimental results on the photosensitive and photochromic behavior of TlCl crystalline pieces and a comparison with the behavior of TlCl crystals in glass are given in this paper. The photolytic behavior of silver halide crystal has been extensively investigated, because of its importance in the field of photography, but not that of thallium halide crystal. It is known that the presence of impurity Ag or Pb promotes the photosensitivity of TlCl,[5] although, according to Renz,[6] even very pure TlCl becomes dark by prolonged UV irradiation. Optical absorption measurements[7,8] show that TlCl has a few large absorption bands with the absorption edge reaching 400 mμ and a broad visible absorption band peaking at 535 mμ before and after UV irradiation, respectively. The crystal shows selective bleaching, to which Hilsch and Pohl attributed the presence of colloids.

Christy and Dimock[9] suggested that no color centers were formed by X-ray irradiation in a pure large crystal of TlCl. This is also the case for AgCl crystal. A large AgCl crystal showed almost no coloration upon irradiation when it was very pure, the addition of copper being necessary to give the UV coloration.

A small amount of chalcogen impurities such as S^{2-} and Se^{2-} produced an absorption peak near 400 mμ when a TlCl crystal is quenched from high temperatures without irradiation. The peak disappeared and another band (colloidal band) appeared near 600 mμ when the crystal was kept at room temperature. The study made by Christy and Dimock[9] and other previous works[5-8] would imply that a large TlCl crystal should contain some kind of impurity if it is colored by UV irradiation and that there is a possibility for the formation of Tl colloids in TlCl crystal.

Experimental

Preparation of TlCl Crystal. TlCl crystals were prepared by melting TlCl powder (Alfa Inorganics, Inc., U.S.A.). The powder was heated in a small pyrex beaker in an electrically heated furnace in air at 500°C. The molten mass of TlCl was slowly cooled down in the furnace. From the clear but slightly greyish solidified mass of TlCl crystal, rectangular pieces, about $20\times10\times1$ mm^3, were cut off with a razor blade, and, to make the surface smooth, were remelted between two thin sheets of glass which were easily peeled off after cooling. The thickness of plate samples was 1.0—1.4 mm. To incorporate a given impurity cation into "pure" TlCl, a given amount of the corresponding metal chloride was mixed with TlCl powder before the first melting.

Preparation of Glass. Composition, preparation, and properties of photochromic glasses containing TlCl crystallites were described in detail in a separate paper.[4]

For the present suty, a batch mixture consisting of KPO_3 25, $Ba(PO_3)_2$ 25, $Al(PO_3)_3$ 50, TlCl 12, NaCl 6, Cu_2O 0.03 parts by weight was melted in a platinum crucible at 1200°C for 20 min. A glass plate 8 mm × 20 mm × 1 mm was heated at 420°C for 10 hr to precipitate TlCl crystallites, and then subjected to measurement.

Light Exposure and Transimission Measurement. A black ray lamp with main emission peak at 3660 Å (General Electric Model F6T5) was used as UV-light source. The sample plate was placed at a distance of 4 cm from the lamp. An infrared heating lamp of 250 watts was used as a visible light source to cause bleaching of darkened samples. The sample was placed at a distance of 36 cm from the lamp, with filters which permitted light of wavelengths 530—680 mμ. To avoid possible temperature rise in the sample during exposure air was blown to the sample by an electric fan. Transmission measurements were made with a recording spectrophotometer Model Spectronic 505 of Bausch and Lomb Company. For the sake of simplicity "absorption"

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[1] W. H. Armistead and S. D. Stookey, *Science*, **144**, 150 (1964).

[2] G. P. Smith, Paper 108, 7th Intern. Congr. Glass, Brussels, Belgium, July 1965.

[3] F. Seitz, *Rev. Modern Phys.*, **23**, 328 (1951).

[4] S. Sakka and J. D. Mackenzie, *J. Amer. Ceram. Soc.*, **55**, 553 (1972).

[5] J. W. Mellor, Treatise on Inorganic and Theoretical Chemistry, Vol. V, p. 438 (1924).

[6] C. Renz, *Helv. Chim. Acta*, **2**, 704 (1919).

[7] H. Fesefeldt, *Z. Phys.*, **64**, 741 (1930).

[8] R. Hilsch and R. W. Pohl, *ibid.*, **64**, 606 (1930).

[9] R. W. Christy and J. D. Dimock, *Phys. Rev.*, **141**, 806 (1966).

or "absorbance" will be used throughout this paper to indicate the increment of absorption or absorbance over that of the samples before UV irradiation. Throughout the experiments, the samples were kept in darkness in a dessicator to avoid possible effects of room lights and diffuse sunlight.

Results

Preliminary Results for the Effect of Impurity on Darkenability. A small amount (0.05 mol%) of various chlorides was incorporated into TlCl by melting powder mixture and the resultant doped TlCl mass was exposed to UV light. The chlorides tried were $CaCl_2$, VCl_3, $MnCl_2$, $FeCl_2$, $NiCl_2$, CuCl, $CuCl_2$, $SrCl_2$, AgCl, $CdCl_2$, $PbCl_2$, $BiCl_3$, InCl, $CeCl_3$, and $SmCl_2$. Some of these chlorides gave grey, yellow, or brown color to the TlCl mass before irradiation. In spite of this original discoloration, it was possible to tell the effect of impurity on UV darkenability qualitatively. It was found that Cu, Ag, and In have a remarkable effect in promoting the coloring of the TlCl crystal induced by UV irradiation. "Pure" TlCl and Cu-doped TlCl crystalline pieces will be used for further experiments.

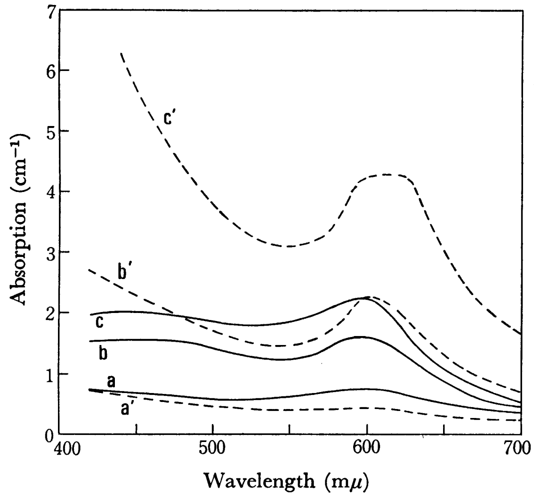

Fig. 1. Absorption spectra of TlCl crystals darkened by UV exposure. Solid lines (a', b', c'): "Pure" TlCl. Broken lines (a', b', c'): Cu-doped TlCl. Time of exposure: a 6 min, a' 1 min, b and b' 30 min, c and c' 60 min.

Darkening by UV Irradiation. TlCl samples were exposed to UV light for different periods of time ranging from one to 60 min. Some examples of the absorption curves are shown in Fig. 1. The increase in absorption coefficient due to irradiation is plotted as a function of wavelength. In TlCl: Cu sample, darkening was quite remarkable on the surface facing the UV light source. In the "pure" TlCl sample, no particularly dark surface layer was detected. In spite of the difference, plots were given with the use of nominal absorption coefficient for a comparison of the darkenabilities.

We see that an absorption band is developed with a peak around 600 mμ and, at the same time, the absorption increases in the range of wavelengths shorter than 500 mμ. The increase in the latter absorption is particularly remarkable in Cu-doped sample.

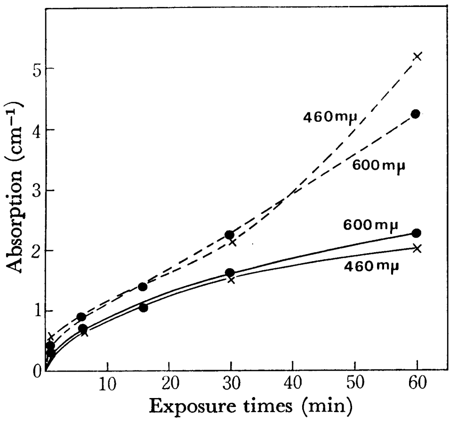

Fig. 2. Absorption change of TlCl crystals with increasing time of exposure to UV. Solid lines: "Pure" TlCl. Broken lines: Cu-doped TlCl.

Figure 2 shows the growth of a peak near 600 mμ and a band less than 500 mμ as a function of exposure time. The absorption coefficient at 600 mμ was chosen as a measure of absorption for the former and that at 460 mμ for the latter. We see that TlCl: Cu darkens at a faster rate than "pure" TlCl. The growth of the absorption at 460 mμ is almost parallel to that at 600 mμ, although the former grows slightly faster in Cu-doped TlCl when exposure time is long (30—60 min).

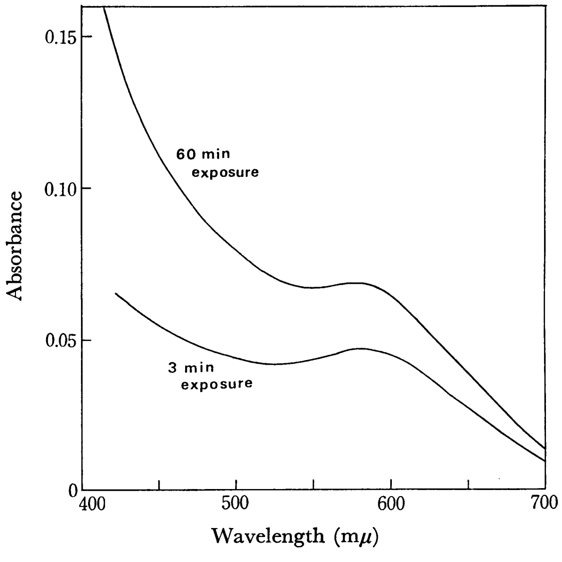

Fig. 3. Absorption spectra of glass darkened by UV exposure. Thickness of the sample: 0.67 mm.

Figure 3 shows the absorption in the TlCl-containing photochromic glass caused by UV irradiation. It can be seen that the general shape of the absorption curve is similar to that of TlCl crystals, especially TlCl: Cu sample. There is an absorption band with a peak at 580 mμ, which is a little shorter than those (600—610 mμ) for TlCl crystals, but pretty close. In the range of the wavelengths smaller than 500 mμ, there is another band.

Exposure of Darkened Samples to a Longer Wavelength Light. Irradiation of UV colored samples by a visible light causes the bleaching in color. Absorption

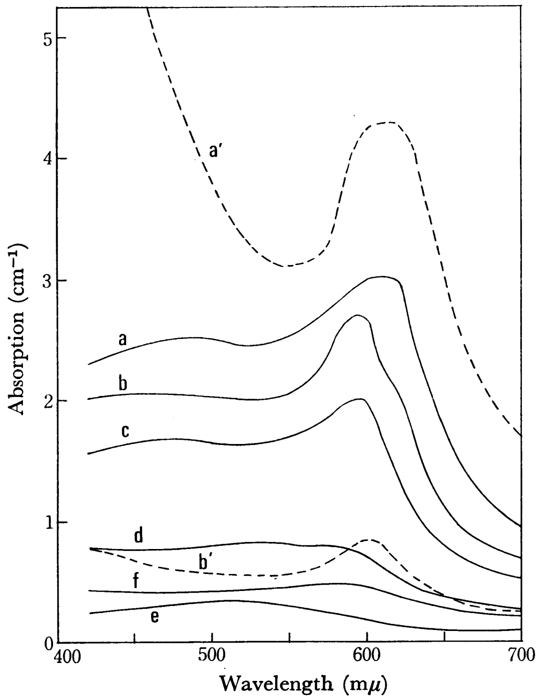

Fig. 4. Fading of color by visible light exposure. a: "Pure" TlCl after UV exposure of 2 hr (before bleaching). b: 1 min bleaching by visible light through filters. c: 2 min bleaching. d: 16 min bleaching. e: 26 min bleaching. f: 1 min bleaching by visible light without filters. a′: Cu-doped TlCl after UV exposure of 1 hr. b′: 20 min bleaching by visible light through filters.

curves obtained in the process of bleaching by a visible light containing rays ranging from 530 to 680 mμ are shown in Fig. 4.

From a series of cruves for "pure" TlCl (solid line), it can be seen that the band with a peak at 600 mμ becomes weak at a greater rate than in the absorption at shorter wavelengths. Thus the curves d and e have no distinct absorption peak around 600 mμ, while there is some absorption left around 500 mμ. It is true, however, that all absorption is decreased by irradiation and disappears eventually. When the sample is exposed to light without filters which permit only 530—580 mμ, the 600 mμ peak is found to remain more or less noticeable (see curve f). On the other hand, no preferential decrease in absorption is found in the case of TlCl: Cu from the curve b′ which has a distinct 600 mμ-band.

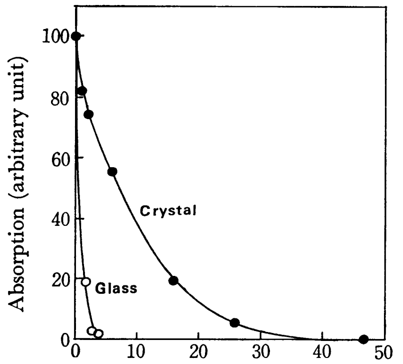

Fig. 5. Fading of UV-colored TlCl crystal and TlCl-containing glass upon visible light exposure.

Figure 5 shows the absorption change at 600 mμ with time of exposure to the bleaching light for "pure" TlCl crystal and the TlCl-containing glass. Both the crystal and glass are bleached, the rate being larger for the glass.

Heating of Darkened Samples. Fading is accelerated by heating the darkened samples. "Pure" TlCl and Cu-doped TlCl samples were heated at 40, 55, and 66°C for 30 to 60 min, but no fading occurred. The absorption spectra remained the same.

On the other hand, it was found that the darkened TlCl glass was bleached slowly at room temperature and rapidly at higher temperatures.

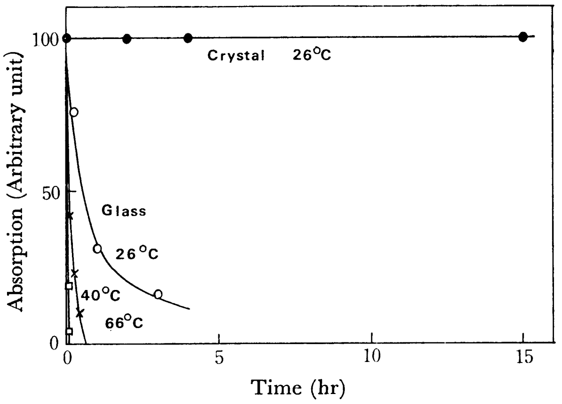

Fig. 6. Fading of UV-colored TlCl crystal and TlCl-containing glass in darkness.

Figure 6 shows the change in absorption at 600 mμ with time for the UV-colored crystalline TlCl plate and TlCl-glass sample kept at room temperature (26°C) in darkness. It is seen that with the TlCl plate sample no change in absorption is observed in 15 hr, while the darkened glass sample loses 50% of its absorption in about half an hour (b). Other curves show that the rate of fading of the glass increases sharply as the temperature rises.

Discussion

Effect of Impurity. Some impurity ions promote the darkenability of a TlCl crystal remarkably. For an explanation of the effect of copper ion the results obtained by Moser *et al.*10) on silver chloride might be useful. They found that the presence of a small amount of cuprous ions promotes the darkenability of a silver chloride crystal noticeably and suggested that the cuprous ion might act as a trap for a positive hole produced by UV irradiation, changing into a cupric ion. If there is no cuprous ion, positive holes may be easily recombined with electrons and, as a result,the darkenability of a silver chloride crystal will be low. They also suggested that it is possible to interpret the photolytic absorption curve of a copper containing AgCl crystal as the sum of the absorptions due to dissolved cupric ions and photolytic silver. The absorption of cupric ions in an AgCl crystal can be described by a

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10) F. Moser, N.R. Nail, and, F. Urbach, *J. Phys. Chem. Solids*, **9**, 217 (1959).

curve which is high in intensity at 400—450 mμ, becoming low rather rapidly with increasing wavelength toward 600—700 mμ.

A similar mechanism seems to be applied to the action of copper ion in a TlCl crystal. The absorption of TlCl: Cu increased remarkably in the wavelength range of 420—500 mμ upon UV irradiation compared with "pure" TlCl (Fig. 1). This can be attributed to the formation of Cu^{2+} ions from Cu^{+} ions in the TlCl: Cu crystal. The non-irradiated TlCl: Cu crystal had a little higher absorption in this wavelength region than the non-irradiated "pure" TlCl crystal, which can be attributed to possible presence of Cu^{2+} ions even before irradiation. It will be reasonable to assume that there are Cu^{+} ions as well as Cu^{2+} ions in the non-irradiated TlCl: Cu crystal, the Cu^{+} ions working as trapping centers for positive holes and promoting darkenability of the TlCl crystal.

Fading of Darkened Crystals by Visible Light. Darkened TlCl crystals are bleached by visible light (530—680 mμ), restoring then to their original state. A process reverse to the darkening by UV irradiation is believed to occur. Thallium atoms or their small aggregates (colloids) will absorb the light quanta and release electrons, which will be recombined with positive holes.

It should be noted, however, that the change in absorption spectra with increasing exposure of the crystal to the bleaching light is not monotonic (Fig. 4). Namely, the absorption near 600 mμ disappears faster than the absorption at shorter wavelength region. This is interpreted in terms of preferential (selective) bleaching.[8]

For bleaching, the visible light of wavelengths 530—680 mμ was used. The centers which absorb this light must have been destroyed preferentially. It was found that bleaching by light covering the whole visible region was less preferential (Fig. 4, curve f).

In contrast to "pure" TlCl, Cu-doped TlCl crystal showed no such preferential bleaching. The cause of the difference has not been clarified. A possible explanation may be that some of the light quanta are absorbed by Cu^{2+} ion sites because these ions have absorption also in the range 530—680 mμ, and the light energy is transferred to the centers responsible for the absorption at shorter wavelength region, destroying the centers. This will give relatively less preferential bleaching.

Comparison of the Behavior of a TlCl Crystal with TlCl-Containing Glass. From Figs. 3, 5, and 6 it is clear that the darkening behavior of a glass can be explained on the basis of that of a TlCl crystal. Like the TlCl crystal the TlCl-containing glass becomes dark upon UV irradiation, giving an absorption curve with a peak near 600 mμ. The increase of absorption in the region 420—500 mμ will be explained by the presence of copper ion since a TlCl crystal shows the same tendency when doped with copper ion.

The quick bleaching of a darkened glass by visible light exposure would also be explained by a similar behavior of a TlCl crystal, although the rate appears different, the glass being bleached much faster. It is interesting to note that there is a great difference in thermal fading behavior. The darkened TlCl crystals show almost no thermal fading under the experimental conditions, 15 hr at room temperature and 2 hr at 66°C, while the darkened TlCl-containing glass is bleached by 50% in 30 min at room temperature and by 100% in 5 min at 66°C (Fig. 6).

If we assume that thermal fading and optical bleaching is initiated by the release and migration of positive holes (Cl°) which have been produced as a result of UV irradiation in darkening process and trapped somewhere in the TlCl crystal and TlCl-containing glass, trapping sites would be crystalline defects or crystal grain boundaries in the case of TlCl crystals and crystal-glass interfaces in the case of the photochromic glass. In the glass the size is too small for the crystallites to have dislocation or grain boundaries. There is no reason for considering that the bonding of the UV-induced reaction products (electrons, holes, Ag and Cl atoms) with crystalline defects is stronger than that with crystal-glass interfaces. Such a situation may be justified, however, if it is considered that glass is generally chemically inert near room temperature and its composition is quite different from that of the TlCl crystal or possible reaction products.

Our results indicate that the above view is reasonable, *viz.*, the effect of the presence of glassy matrix is shown.

We acknowledge the support of the Glass Division of PPG Industries, Inc., U.S.A.