Photographic Process in the Silver-containing Glass Exposed to U.V.- and Gamma-Radiation

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To investigate the mechanism of the photographic process in the silver-containing glasses, their spectral absorption curves from room temperature to 550°C were measured successively after exposure of the glasses to U. V. or γ-radiation. Developments of the absorption bands associated with the latent image and also with the permanent image were confirmed.

INTRODUCTION

Since the development of the photosensitive glasses by Dalton, Stookey, and Armisted[1], the mechanism of the photographic process in the glass has excited not only a practical but an academic interest to the glass researchers because of its close relation with the structure of glass.

The photographic reactions in the glass have been considered to proceed in different ways depending upon the kind of radiation[2]. According to the conception of Stookey[1,2], who has made valuable contributions to this subject, the mechanism of photographic process in the glass exposed to U. V. may be explained as follows : Exposure of the glass to U. V. causes emission of photoelectrons from lightsensitive ions such as silver, gold, cuprous, and cerous ions which are contained originally in minute amounts in the glass. The photoelectrons emitted are temporarily held in a metastable activated state at trapping centers, forming the so-called latent image. When the glass is subsequently heated to elevated temperatures the trapped electrons are released and captured by metal ions such as silver, gold, and cuprous ions to form atoms. The atoms grow to submicroscopic colloidal particles forming the so-called permanent image in the glass.

The true character of the latent image is still obscure : As to the nature of the trapping centres described above, Stookey assumed that they would be metal ions such as silver ions or some "lattice imperfections" in the glass network. In the silver-containing glass exposed to the high-energy radiation such as X-rays, Weyl, Schulman, Ginther, and Evans[3] also assumed the presence of trapped electrons in a metastable state in its photographic process. They considered these electrons to be in a similar state to that of electrons in F-centres or electron capturing metal ions in the interstitial lattice in alkali halide crystals. However, it is doubtful that this state of the trapped electrons is the same as that indicated by Stookey

The present study has been undertaken to throw a light upon the nature

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of the latent image produced in the photosensitive glass in the photographic process. For this purpose the changes of the light absorption spectrum of the irradiated glass with temperature were measured successively during heating from room temperature to 550°C with a spectrophotometer equipped with a specially designed small furnace for heating the glass specimen. In order to investigate the influence of the wavelength of radiation upon the formation of latent image U. V. and γ-rays were used for irradiation.

EXPERIMENTAL PROCEDURE

The glass used in the experiments had the following composition : 15 mol% $K_2O \cdot 10BaO \cdot 75SiO_2 \cdot 0.05AgCl$ and $0.03CeO_2$. Potter' s flint (>99.9% in weight) and chemicals of analytical reagent grade were used for the preparation of the glass batch. Melting was done in a sintered alumina crucible at about 1400°C for 2 hours in an electric furnace using silicon carbide heating elements. After melting the glass was poured into moulds, annealed, then ground to the required size 6 × 20 × 0.5 mm and polished to an optical finish.

The glass specimens were irradiated with U.V. or γ-rays. The irradiation sources employed were :

(1) A high-pressure Hg lamp, type SHLD-500, Nihondenchi Co. The U.V. of the wavelength shorter than about 300 mμ is considered to be able to transfer electrons, as γ-rays and X-rays do, from non-bridging oxygens to the conduction band[4]. In order to draw a clear distinction between U.V. and γ-rays in their effects on the photographic process, a glass filter was placed before the lamp to cut the U.V. shorter than 300 mμ. The useful band of U.V. for photography is reported to lie between 300 and 350 mμ[1].

(2) 10 curie cobalt-60 in a specially designed small irradiator installed at the Ceramic Laboratory, Institute for Chemical Research, Kyoto University, Takatsuki, Osaka.

U.V.- and γ-radiation were performed by placing the glass pieces at a distance of, respectively, 50 mm from the Hg lamp for 60 min., and 15 mm from the cobalt source of 10 curies for 20 hours. In the latter case a dose rate at a surface of the glass piece was 35×10^3 roentgens/hour. Twenty hours' irradiation represents a total surface dose of 7×10^5 roentgens. For both U.V.- and γ-radiation, the exposures described above caused the absorption intensity approach almost a saturation value and was also found to be the most suitable in producing an absorption spectrum which was neither too small nor too large for the best analysis.

The spectrophotometric measurements with the irradiated glasses were carried out in the following manner. Two pieces of glass, one irradiated and the other unirradiated, were put in a specially designed small furnace attached to a spectrophotometer (Hitachi EPU-2A type), heated at a rate of 3°C per minute from room temperature to 550°C, and the optical density $\log(I_0/I)$ of these specimens (in which I_0 is the fraction of light transmitted for the unirradiated specimen and I is the fraction of light transmitted for the irradiated

specimen, both for the same temperature) was measured successively during heating as a function of the wavelength in the 220 to 800 mμ-range. The furnace described above was a modification of the Sundheim and Greenberg furnace[5]. Its detailed construction will be described in a separate publication.

EXPERIMENTAL RESULTS

a. Experiment with γ-Radiation

The results of measurement with the γ-ray irradiated glass are shown in Fig. 1. A curve denoted by 20°C (room temperature) shows the change in absorption spectrum with γ-radiation. There are two strong absorptions ; one at about 250 mμ, the other at about 355 mμ. On heating from room temperature to 250°C, the latter peak diminished in intensity almost to zero, whereas the former remained almost unchanged (an apparent decrease in intensity with the former band should be explained as the result of the diminishment of the 355 mμ peak which extends its tail to 250 mμ). Over 250°C, a new absorption began to appear at about 260 mμ whereas the

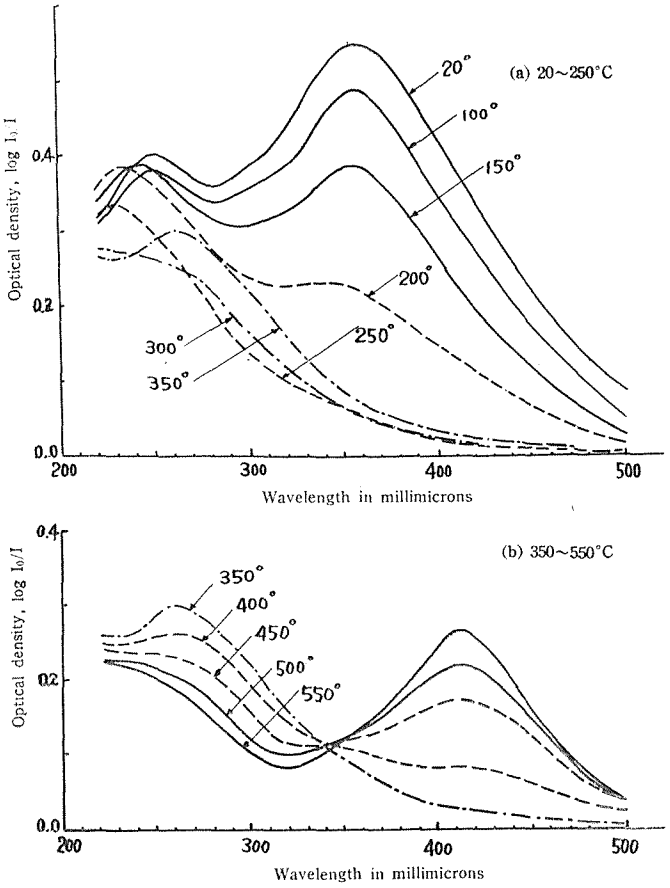

Fig. 1. Absorption curves of the γ-ray irradiated glass showing changes occvring during heating.

absorption first formed at about 250 mμ decreased in intensity. The new 260 mμ absorption reached a maximum in intensity at 350°C. From 350°C to 550°C a newer absorption peak began to appear at about 410 mμ while the secondly appeared 260 mμ peak diminished.

b. Experiment with U.V.-Radiation

The results with the U.V. irradiated glass are shown in Fig. 2. A curve denoted by 20°C (room temperature) shows the change in absorption with the U.V.-radiation. An absorption at 250 mμ which appeared in the case of γ-radiation is also observed in this spectrum, but another strong absorption at 355 mμ, which appeared in the case of γ-radiation, is not observed in this case. This should be specially mentioned as a great difference between U.V.- and γ-rays in their irradiation effects. Except for the 355 mμ absorption the change of absorption spectrum with temperature showed almost the same tendency as that for the γ-ray irradiated glass, *i. e.*, on heating two new peaks, about 260 and 410 mμ, appeard successively in the temperature range from about 250 to 350°C and from 350 to 550°C.

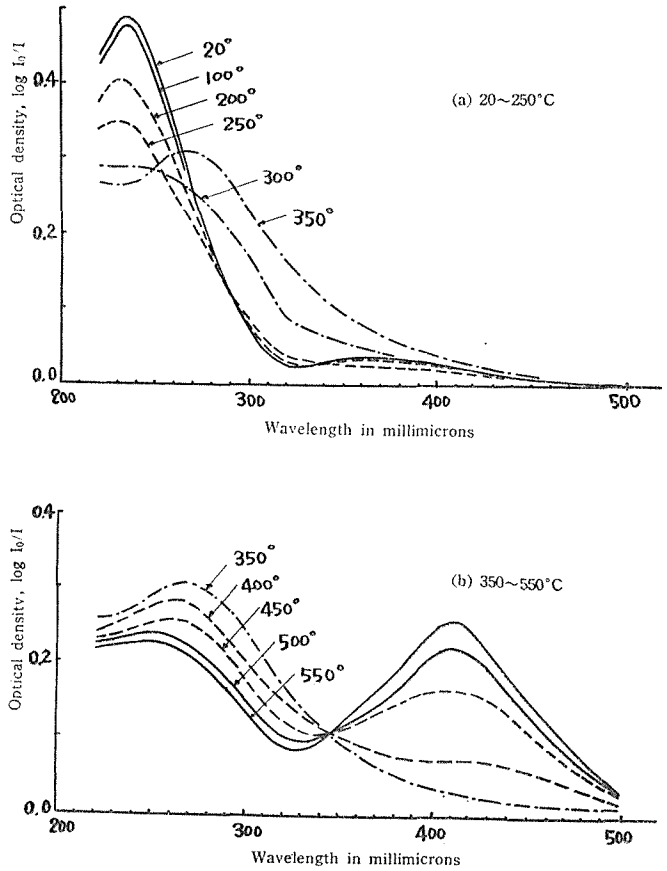

Fig. 2. Absorption curves of the U.V. irradiated glass showing changes occuring during heating.

DISCUSSION

(a) Analysis of Absorption Spectra

When an absorption spectrum consists of a number of different absorption bands, the absorption maxima in the spectrum appear in the positions somewhat different from the true ones because of the effects of their superposition, *i. e.*, the absorption maxima actually observed in the spectrum do not indicate their true positions.

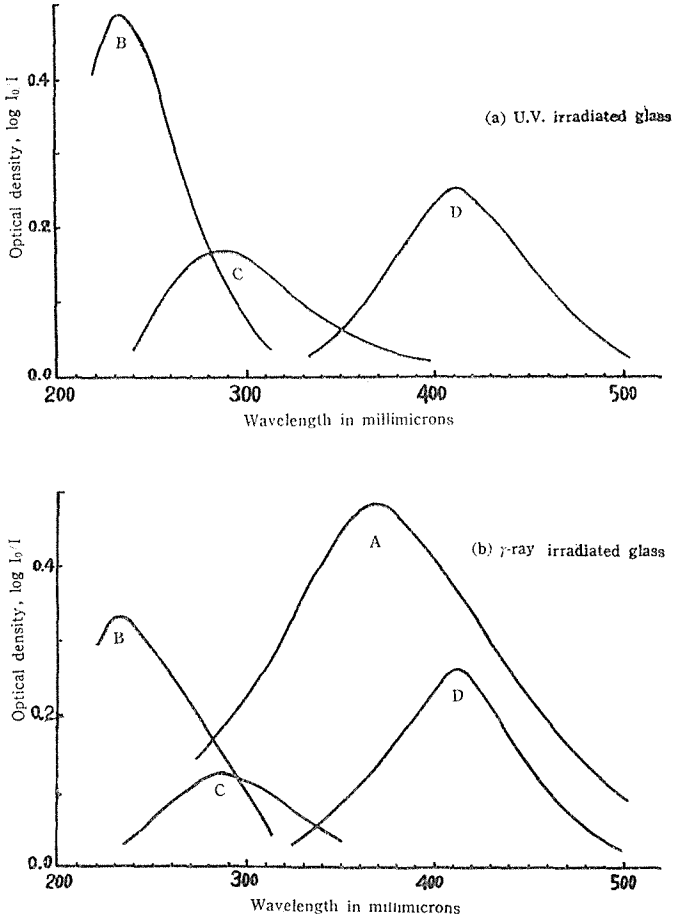

Fig. 3. Absorption bands developed in the photographic process. (after aralysis)

Analysis into independent bands was made for each of the all spectra shown in Figs. 1 and 2 on the assumption of each band having symmetry about its maxima, together with the consideration of the changes of the spectra with temperature. As has been already pointed out by Levy[6], the changes of broadening of an absorption band may be either a temperature broadening or due to the atomic configuration of the surrounding lattice having high degree of disorder. Therefore it is reasonable to assume that either of these effects would bring about a symmetrical broadening of an absorption band. Fig. 3 (a) and (b) show the

results of analysis ; each curve shows the shape of the independent absorption bands at the temperatures where the intensity of each band reaches a maximum. It should be mentioned specially that, except for the 360 mμ band, the positions of the analyzed bands developed at the same range of temperatures are in good accord with each other for both the glasses irradiated with γ-rays and U.V. Details of the bands thus analyzed are given in Table 1. Denotation of the bands by the symbols, A, B, C, D was made for the convenience of the future discussions. These associated centers will be referred to as the A, B, C, and D centers respectively.

Table 1. Absorption bands developed in the silver-containing glass in the photographic process.

Bands	Radiation	Max. positions (after analysis)	Appeared	Diminished
A	γ-rays only	360 mμ	During irradiation at room temp.	50~250°C
B (Latent image)	U.V. or γ-rays	235 mμ	During irradiation at room temp.	220~300°C
C (Latent image)	U.V. or γ-rays	285 mμ (approx.)	250~350°C	350~550°C
D (Permanent image)	U.V. or γ-rays	412 mμ	Over 350°C	(Still remained at 550°C)

(b) Interpretation of A, B, C, and D Bands

The A and D bands. The A and D bands in Table 1 were already found by Weyl and Schulman,[3] and Yokota and Shimizu[7] respectively. Weyl and Schulman found an absorption band at about 340 mμ in the X-ray irradiated silver-containing glass. They attributed this band to centers similar to F-centers produced in the silver-containing alkali halide crystal. Since the A band has been produced under the same condition it is suggested that it arises from the same cause as discussed by Weyl and Schulman. A deviation in position of the A band (360 mμ) from that observed by Weyl and Schulman (340 mμ) would be due to the difference of their base glass compositions.

Referring to the mechanisms proposed by Kats and Stevels[1], Stookey[2] gave a more detailed picture of the structure of this type of center, suggesting that it is probably the one such as a P- or Q-center in the following reactions:

$$\text{Glass} \xrightarrow{\text{X-rays}} \text{trappeed electron}$$

D-center (Ag^+ and Na^+ in neighborhood of two non-bridging oxygen)

$$\text{X-rays} \nearrow \text{P-center } (Ag^+ \text{ in interstice, with trapped electron})$$
$$\text{X-rays} \searrow \text{Q-center (Excess Oxygen with two trapped electron holes)}$$

For the formations of P and Q centers the emissions of electrons from non-bridging oxygen ions must occur, and this is possible only when the glass

accepts the high-energy radiation such as γ-, X-rays, and the U.V. shorter than about 300 mμ. This would be an explanation for the absence of the A band in the glass irradiated with the U.V. longer than 300 mμ.

Yokota[7] found a sharp absorption band at about 410 mμ in the silver containing glass (SiO_2 82.5, LiO_2 12.5, K_2O 2.5 ; Ag 6.4×10^{16} cm^{-3}, Ce 1.6×10^{18} cm^{-3}) which was subjected to the U.V.-radiation and subsequent heat treatment up to 590°C. Yokota attributed this band to the submicroscopic silver colloids in the glass. Since the D band was formed under almost the same condition, it is suggested that it arises from the same cause as indicated by Yokota.

The B and C bands. To the authers' knowledge nothing has been reported about the B and C bands. As the B band is produced by irradiation at room temperature as in case of the A band it seems also to be due to combinations of a great affinity for electrons. In marked contrast to the A band, the B band appeared even with the U.V. (longer than 300 mμ) irradiated glass. Therefore, it is considered that the release of electrons from oxygen, which was assumed for the formations of the A band (the associated centers are P and Q centers after Stevel *etc.*), does not need to occur for the formation of the B band. This leads to the conclusion that the resulting structure of the B centers would not consist of oxygen ions with electron holes.

A more detailed explanation of the structure of the B centers is at present still a matter of speculation. Stookey has proposed an idea that by U.V.-radiation electrons are knocked from photosensitive ions (Ag^+, Ce^{+3} *etc.*) into quasi conduction band and captured temporarily by ions of a great affinity for electrons such as silver ions. The authors' experiment with the glass of the same base composition but containing no cerium oxide indicated that both U.V.- and γ-radiation caused neither the formation of the B band nor that of the C band. This fact indicates that the lattice imperfections forming the B centers are associated not only with the electronic configuration of silver ion but also that of cerium ion.

On heating the glass over 220°C the B band begins to diminish, and the C band begins to appear almost at the same time. This could be explained by the rearrangement of structure of the B centers to a more stable form, *i.e.*, the structure of the C centers. The new centers (the C centers) might be atomic silvers or just the ones having almost the same structure as that of the B centers. Further discussions of the structure of the C centers would need more detailed informations of the character of the C band.

(c) **Mechanism of the photographic process.** At room temperature radiation-freed electrons are not able to combine with silver ions to form atoms because of the rigidity of the environment of silver ions. For the formation of atoms, therefore, the electrons must be held temporarily by some lattice imperfections at least until the glass network gains its freedom of deformation. The B and C centers are the ones formed at the time when the electrons are in such a metastable state, and therefore are considered to be called as the latent images. They serve alternatively during heating as the trapping centers for electrons until the deformation of the glass network starts.

The A centers which are produced only by the high-energy irradiation (γ- and X-rays) are not so stable as the B centers and have decomposed themselves in the course of heating, allowing electrons to return their original positions. Therefore, the centers should not be called as the latent images.

Except for the formation of the A centers the mechanism of the photographic process is considered to be basically the same for the both glasses irradiated with the long wave U.V. rays (longer than about 300 mμ) and the rays of higher energy (γ-, X-rays and the U.V. shorter than about 300 mμ).

SUMMARY

The spectral absorption curves of the silver-containing photosensitive glasses from room temperature to 550°C were measured successively after exposure of the glasses to U.V.- or γ-radiation. In both specimens exposed to U.V. and γ-radiation, developments of the following three absorption bands were confirmed; the 235 mμ band developed on exposure, the 285 mμ developed on heating from 250 to 350°C, and the 412 mμ band developed over 300°C. The former two were considered to be due to the centers associated with the latent image, and the latter the centers associated with the permanent image.

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