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Photosensitive Ionomer. I. Preparation of Mercurous Acrylate and Photosensitive Plates

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Photographic plates were prepared by coating an emulsion consisting of mercurous acrylate, polyvinyl alcohol and water on glass plates. They were found to be sensitive to light ranging from 250 nm to 340 nm. A dark brown image with density *ca.* 0.6 above the fog was formed by a printing-out process. The latent image could be amplified with the reducing developers such as hydroquinone or metol. Image formation was ascribed to metallic mercury which was isolated by photoreduction and/or reduction of mercurous ion.

On exposure to light, mercurous acetate disproportionates to mercuric acetate and metallic mercury[1)] to give dark brown materials as illustrated in Eq. (1). Photoreduction of mercurous ion into metallic mercury is similar to that of silver ion, and mercury is available for photographic image formation.

$$2CH_3COOHg \longrightarrow (CH_3COO)_2Hg + Hg \qquad (1)$$

The ionomer, ionically crosslinked polymer, is well known since 1964. The ionic crosslinkages are $-COO^-\cdots M^+\cdots O^-CO-$ or $-COO^-\cdots M^{2+}\cdots O^-CO-$ formed by adding mono- or divalent metallic ion, respectively, to linear polymer with side chains of carboxyl groups. Though the ionomer has been studied chiefly for the purpose of improving mechanical properties of plastics, no attempt was made for application to photosensitive plastics. As the strength of the ionic crosslinking depends on the valence of metallic ion, the ionomer crosslinked by a metallic ion of variable valence on exposure may become a new type of photosensitive polymer.

Thus, mercuric ion which is produced by photooxidation of mercurous ion, will form crosslinkages, if some linear polymer has side chains of mercurous carboxylate groups. Polymeric mercurous compound is then expected to be a new photosensitive polymer which undergoes hardening by ionic crosslinking, and can be used for lithographic image formation.

We have prepared an emulsion consisting of mercurous acrylate and polyvinyl alcohol which can be regarded as a model emulsion of linear polymer with side chains of mercurous carboxylate and hydroxyl groups, and have studied some photographic properties of the acrylate plate.

Experimental

Materials. Acrylic acid was purified by distillation of a commercial reagent. Polyvinyl alcohol was supplied by Yotsuwa Sangyo K.K. (PVA GL-05, 95% saponified, $\bar{M}n$=22000). The other reagents used were chemicals of extra pure grade.

Apparatus. Titration was performed by using a Yokokawa pH Meter KPH-51B. Wedge spectrogram was obtained with a Ushio Xenon Arc Lamp UXL-500D and a Narumi Monochrometer RM-23. Ultraviolet and visible spectra were taken by measuring the reflection of mercurous acrylate plates with a Shimadzu Spectrophotometer QV-50. Photographic plates, which were irradiated by a Ushio Low-pressure Mercury Lamp ULI-309 (chemical lamp) from a distance of 15 cm, were measured for the photographic reflection density by a Macbeth Densitometer RD-100.

1) G. Brauer, "Handbook of Preparative Inorganic Chemistry," Academic Press Inc., London (1965), p. 1120.

Preparation of Mercurous Acrylate. A 10% aqueous solution of sodium hydroxide was exactly neutralized by acrylic acid, and the concentration of sodium acrylate was determined by titration with 0.5N hydrochloric acid. 14 g of mercurous nitrate was dissolved in 80 m*l* of about 6% nitric acid, and concentrations of mercurous ion and nitrate ion were titrated with 0.1N potassium hydroxide. When the mercurous nitrate solution was added to 8 m*l* of the sodium acrylate solution under vigorous stirring in the dark, mercurous acrylate was precipitated as white flakes. In order to prepare white, stable mercurous acrylate, nitrate ion should be equivalent to sodium ion in the sodium acrylate solution. The white flakes were filtered and washed with water. After drying *in vacuo*, mercurous acrylate weighed 1.64 g (yield 87.2%). This compound gradually decomposes above 150°C without fusing.

Preparation of the Photosensitive Plate. White flakes of mercurous acrylate without drying, were uniformly dispersed in 30 m*l* of 20% aqueous solution of polyvinyl alcohol. The emulsion was spread over glass plates and left to dry.

Results and Discussion

Spectral Sensitivity of the Acrylate Plate. The wedge spectrogram (Fig. 1) shows that the mercurous acrylate was sensitive to light 250—340 nm, when the grayish white plate turned dark brown.

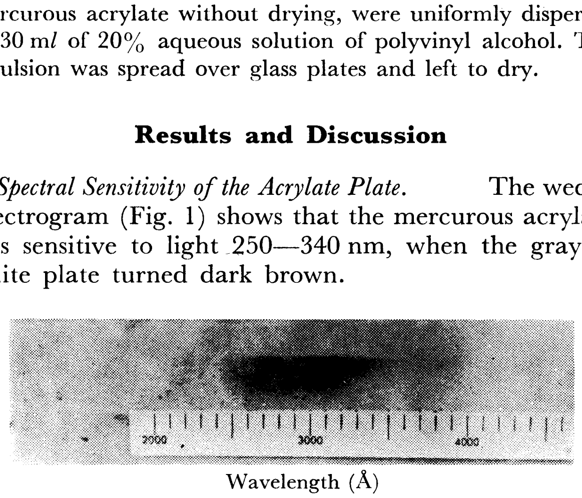

Fig. 1. Wedge spectrogram of a mercurous acrylate plate.

Ultraviolet and Visible Spectra. Reflection spectra were measured for mercurous acrylate plates before and after exposure to ultraviolet light. The results are given in Fig. 2. An absorption below 350 nm, which was found in the ultraviolet spectrum of an unexposed plate, seemed to be closely related with the photosensitivity of the acrylate plate.

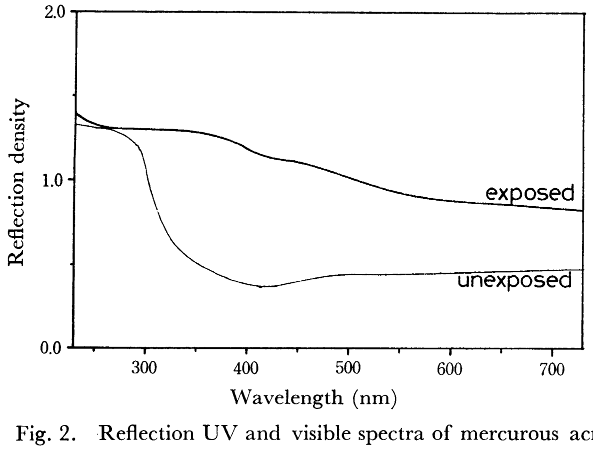

Fig. 2. Reflection UV and visible spectra of mercurous acrylate plates.

Characteristic Curve of the Plate. The plates were placed in a dark box and irradiated by a low-pressure mercury lamp for a certain time and their reflection density was measured. Density was plotted against exposing time. The curve is S-shaped. The maximum density was *ca.* 0.6 above the fog (Fig. 3).

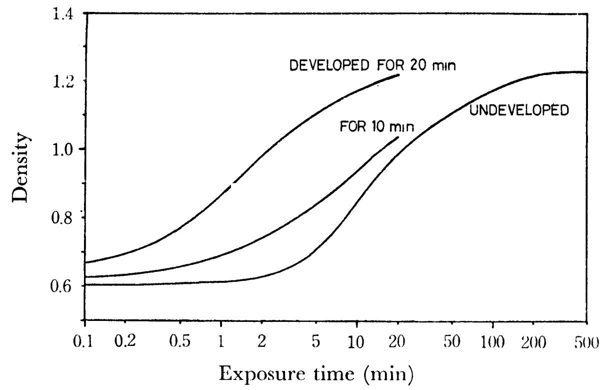

Fig. 3. Characteristic curves of mercurous acrylate plates.

Development of Latent Image. One half of the acrylate plate was irradiated by a low-pressure mercury lamp for two minutes. However, the exposed part was still grayish white and could not be distinguished from the unexposed one. The exposed plate was immersed in an aqueous alcohol solution (water : alcohol=1 : 4, by volume) of hydroquinone. In a few minutes, the exposed part blackened and a distinct difference in color appeared between the exposed and unexposed parts. Fogging was observed on the unexposed part after development for longer than 20 min. Characteristic curves of the acrylate plates, developed in 10 and 20 min respectively, are demonstrated in Fig. 3.

When an aqueous solution of metol or hydroquinone was used for developing, development was completed in 5 min and further development resulted in fogging of the unexposed part. However, the polyvinyl alcohol binder for the mercurous acrylate swelled and the image became detached from the plate when taken out of the developing solution.

Studies on the Preparative Method of the Photosensitive Plate. In the preparation of mercurous acrylate, exact neutralization of sodium hydroxide with acrylic acid was indispensable for excellent photosensitivity of the plate. Otherwise, the plate turned gray while the emulsion was left to dry. Though the density increase smaller because of high fog density, latent images on the gray plate could be developed in the same way as those on a white plate, while no blackening took place in the unexposed part. This may indicate that the gray color was not due to any compounds formed by the disproportionation of mercurous acrylate during the course of drying.

When alkaline solutions such as sodium hydroxide, potassium hydroxide, ammonium hydroxide or hexamethylenetetramine, were used instead of the developing solution, immediate blackening took place on both the unexposed and the exposed parts of the acrylate plate. Blackening caused by alkali may be ascribed to the formation of mercurous hydroxide or mercurous oxide. If the developing solution contains sulfur compounds such as thiourea, sodium thiosulfate, or sodium sulfite, fogging was observed on the unexposed part of the plate. Utilization of gelatin as a binder of the mercurous acrylate gave rise to the fogging of the plate.

The fogging may be due to some dark colored materials formed by the reaction between mercurous ion and the sulfur compounds or basic compounds in gelatin.

Fading and Bleaching of the Image. The black image formed by the developing method as well as the dark brown image formed by the printing-out method were stable and never faded during storage for three months or more.

Treatment of the exposed plate with hydrogen peroxide or nitric acid caused bleaching of the blackened image until no difference in color between the exposed and unexposed parts was observed. Developing by the reducing agent and bleaching by the oxidizing agent suggest that photoreduction of mercurous ion to form metallic mercury, $Hg^{+} \rightarrow Hg$, contributes to the photosensitivity of mercurous acrylate and the formation of image.

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