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Photosensitive Ionomer. IV. Preparation of Mercurous Copoly(vinyl alcohol-methacrylate) and Properties of the Plate

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Mercurous copoly(vinyl alcohol-acrylate) was studied in order to produce a new type of photosensitive system by applying the disproportionation reaction of mercurous acetate to an ionically crosslinked polymer.[1,2] It was found that the plate prepared thereform was sensitive to ultraviolet light, and that a dark brown relief image was formed by a printing-out process. The latent image could be amplified by reducing development; visible image formation was due to metallic mercury which was isolated as a product of the disproportionation and reduction of mercurous ion. The latent image was also intensified by oxidizing development; relief image formation was ascribed to the ionic crosslinking by mercuric ion formed in the disproportionation and oxidation of mercurous ion. We have studied mercurous copoly(vinyl alcohol-methacrylate), comparing its image-forming characteristics with those of copoly(vinyl alcohol-acrylate).

Experimental

Preparation of Mercurous Copoly(vinyl alcohol-methacrylate) and Photosensitive Plates. Various copolymers of methacrylic acid with vinyl alcohol were prepared from methacrylic acid, vinyl acetate and xylene in the quantities given in Table 1, in the same way as copolymers of acrylic acid.[1] One g of copolymer of methacrylic acid with vinyl alcohol was dissolved in 50 m*l* of water and exactly neutralized with 0.5 N sodium hydroxide. Under vigorous agitation in the dark, the mercurous nitrate solution was added to the sodium copoly(vinyl alcohol-methacrylate) solution. The solution turned into a milky white emulsion. The mercurous salt of the copolymer was separated by centrifugation at 10000 rpm. The mercurous salt precipitated was again uniformly dispersed in a small quantity of water, spread over glass plates, and left to dry.

Results and Discussion

Film Formation and Spectral Sensitivity. In preparing the emulsion, the volume of the mercurous nitrate solution was at first so controlled that an equimolar amount of nitrate and sodium ions was sustained in the copolymer solution. However, the emulsion did not dry up to a smooth, transparent layer and could not be used as a photosensitive layer. The volume of the mercurous nitrate solution was therefore determined in order to obtain a good photosensitive layer, taking into consideration the fact that too much mercurous methacrylate decreased the film-forming ability of the copolymer and too small an amount of it did not bring about the fixing ability. The wedge spec-

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1) K. Sugita and S. Suzuki, *Polym. J.*, **2**, 283 (1971).
2) S. Suzuki and K. Sugita, *Photogr. Sci. Eng.*, **15**, 464 (1971).

Table 1. Preparation and properties of photosensitive layer

Copolymer number	Raw materials[a]			Polymeric acid		Emulsion	Image-forming characteristics			
	Methacrylic acid, g	Vinyl acetate, g	Xylene, g	Yield, wt%	η_{sp}/C[b]	Hg methacrylate in copolymer[c]	Film formation	Photosensitivity	Development	Fixation
501	0.5	9.5	1.0	21.5	8.6	8.3	0	0	0	×
502	0.5	9.5	2.0	12.9	6.3	10.9	0	0	0	×
505	0.5	9.5	5.0	14.1	4.8	16.2	0	0	0	×
510	0.5	9.5	10.0	22.4	3.4	14.8	0	0	0	△
1001	1.0	9.0	1.0	31.0	6.7	17.3	0	0	0	×
1002	1.0	9.0	2.0	32.0	5.6	14.6	0	0	0	△
1005	1.0	9.0	5.0	34.6	4.6	15.0	0	0	0	0
1010	1.0	9.0	10.0	32.5	4.1	13.2	0	0	0	△

a) 0.1 g of benzoyl peroxide was used as an initiator in each case.
b) A reduced viscosity, η_{sp}/C, was measured at 30°C on an aqueous solution of the copolymer (0.25 g/100 m*l*).
c) Calculated value (in wt%) by assuming that the quantity of mercurous ions in the nitrate solution was quantitatively fixed to side chains of each copolymer.

trogram showed that the layer turned dark brown on exposure to light ranging from 250 to 315 nm. Irradiation was performed with a low-pressure mercury lamp.

Photosensitivity and Reducing Development. Each photosensitive plate was divided into three parts, the first part being irradiated for 50 min, the second for 1—2 min, and the third not at all. The first turned dark brown, and a photographic image was formed on the plate by a printing-out process. The second remained transparent and could not be distinguished from the third. The plate was immersed in a hydroquinone solution (1 g in 20 m*l* of water and 80 m*l* of alcohol). In a few minutes, the second part became dark grey, but not the third. Development was completed in 10—15 min. This means that irradiation for 1—2 min formed a latent image which could be developed into a visible image on the plate.

Fixation and Oxidizing Development. The plate made from Copolymer 1005 (see Table 1) was stepwise irradiated for 50, 5, and 0 min, respectively, and placed in a mixed solvent of acetic acid (15 m*l*), water (15 m*l*), and alcohol (70 m*l*). In 10—15 min the photosensitive layer of the second and third parts swelled and became detached from the plate, but that of the first part was unchanged. The polymer remaining on the plate formed a relief image. In the case of the plates from Copolymer 510, 1002, and 1010, the layer of the first part was swollen and partly dissolved away. The exposed layers which were made from Copolymer 501, 502, 505, and 1001 and irradiated for 50 min, were dissolved away and the image could not be fixed.

The plate which was irradiated stepwise by changing exposing duration was immersed in a potassium permanganate solution (0.05 g in 30 m*l* of acetic acid and 70 m*l* of water). The layer in the exposed area for 50 min exposure remained on the plate. Though the surface of the layer for 5 min exposure turned insoluble, the inner part of the layer remained soluble, and the latent image could not be intesnified to a relief image by oxidizing development.

Comparison with Acrylate Plates. When the image-forming characteristics of mercurous copoly(vinyl alcohol-methacrylate) are compared with those of mercurous copoly(vinyl alcohol-acrylate), smaller photosensitivity, imperfect fixation, and failure of oxidizing development are notable. Irradiation for 30—50 min gave the methacrylate plate a print-out image and that for 1—2 min a latent image. On the other hand, irradiations for 20—30 min and for 0.5—1 min were sufficient to form a print-out image and a latent image, respectively, on the acrylate plate under the same exposing conditions. A relief image was fixed on the methacrylate plate made from Copolymer 1005, but the areas of the plate from which the photosensitive layers had become detached were not perfectly transparent, some residual layers being left. The selective swelling of unexposed layer was deduced to be due to the difference in bond strength of ionic crosslinkages.[1] The methyl substituent of methacrylate group may decrease the difference in bond strength.

Failure of oxidizing development can be explained by the intrinsic optical property of copoly(vinyl alcohol-methacrylic acid); this copolymer partly absorbed ultraviolet light ranging from 250 to 350 nm. It might be difficult for disproportionation to occur in the inner part of the photosensitive layer on exposure.

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