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MEASUREMENT OF PHOTOCHEMICAL CHANGES OF PRESENSITIZED OFFSET PRINTING PLATES BY FOURIER TRANSFORM INFRARED PHOTOACOUSTIC SPECTROSCOPY

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Fourier transform infrared photoacoustic spectroscopy(FTIR-PAS) was applied to the measurement of photochemical changes of presensitized offset printing plates. FTIR-PAS was found to be a useful method for obtaining direct information on structural changes of photosensitive resins on roughened metal surface.

Recent investigations[1-5] have shown the usefulness of the FTIR-PAS for the structural elucidation of opaque solid samples. However, few studies on the analysis of practical industrial materials have been reported. In this letter, we firstly demonstrate the application of FTIR-PAS to the measurement of photochemical changes of photosensitive resins on rough-surface aluminum plates. Samples investigated in this study are two kinds of presensitized offset printing(PS) plates, that is, positive working and negative working PS plates which have begun to be used widely as lithographic printing plates in printing industries, and the characterization of these materials has been desired.

The measurement system for FTIR-PAS was composed of a home-made PAS attachment and a Digilab model FTS-15 FTIR spectrometer, and its details were described in the previous paper.[5] FTIR-PAS spectra were measured at 4 cm^{-1} resolution using 2500 scans. The positive working PS plate was prepared by using substituted o-naphthoquinonediazide as a photosensitive resin. The photosensitive resin was coexisted with other resins such as novolac type phenolic resins which were used as a binder. These resins were dissolved in ethylene-glycol-monoethylether, and the solution was deposited on an electrochemically roughened and anodized aluminum plate, and dried. As for the negative working PS plate, substituted p-diazodiphenylamine was used as a photosensitive resin, and it was coexisted in the sample with copolymers of p-hydroxyethylmethacrylate and methylmethacrylate etc. which were used as a binder. The sample was processed according to the same procedures as the one used in preparing the positive working PS plate. The irradiation was carried out under ambient conditions by use of a metal halide lamp. The wave length of the excitation light was 400 nm and its energy was about 720 mJ/cm^2. The thickness of the organic layer on the aluminum plate was approximately 3 μm, which was estimated from the amount of organics on the substrate(3 mg/cm^2).

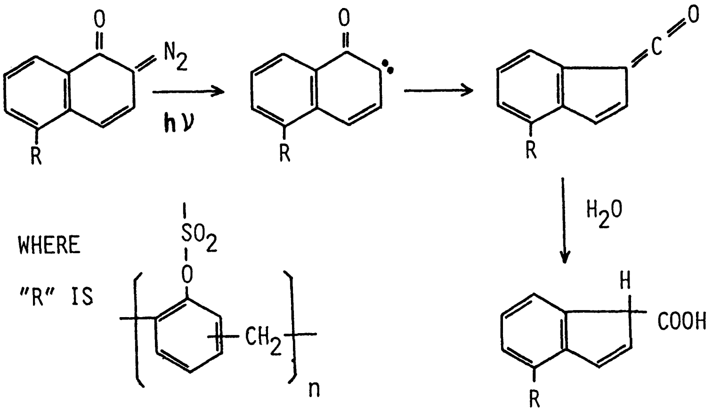

Fig. 1 Photolysis of substituted o-naphthoquinonediazide.

It has been reported[6,7] that the photolysis of substituted o-naphthoquinonediazide follows the reaction scheme shown in Fig. 1. The excitation of diazoketone produces a ketocarbene which undergoes a rearrangement to a ketene. The ketene is then attacked by water to form the 3-indenecarboxylic acid. If the reaction proceeds along the above-mentioned scheme, it can be expected that the infrared absorption band due to diazo group disappears, and the one due to carboxylic acid group appears as the sample is struck by the visible light.

Figure 2 shows the spectral change of the positive working PS plate with exposure to the excitation light. The spectrum at the middle part(B) was obtained without exposure to the light, and the top one(A) was measured after the irradiation. The bottom spectrum (C) was obatined by dividing the top spectrum by the middle one. In Fig. 2, the peak at about 2350 cm^{-1} is due to the atmospheric absorption of carbon dioxide in the optical path. In Fig. 2 (C), the positive and the negative going features represent the increased and the decreased infrared bands with exposure to the light, respectively. It can be immediately seen that the absorption bands at about 2160 and 2120 cm^{-1} which are assigned to diazo stretching vibrational mode disappear and the new band at about 1720 cm^{-1} which is assigned to carbonyl stretching vibrational

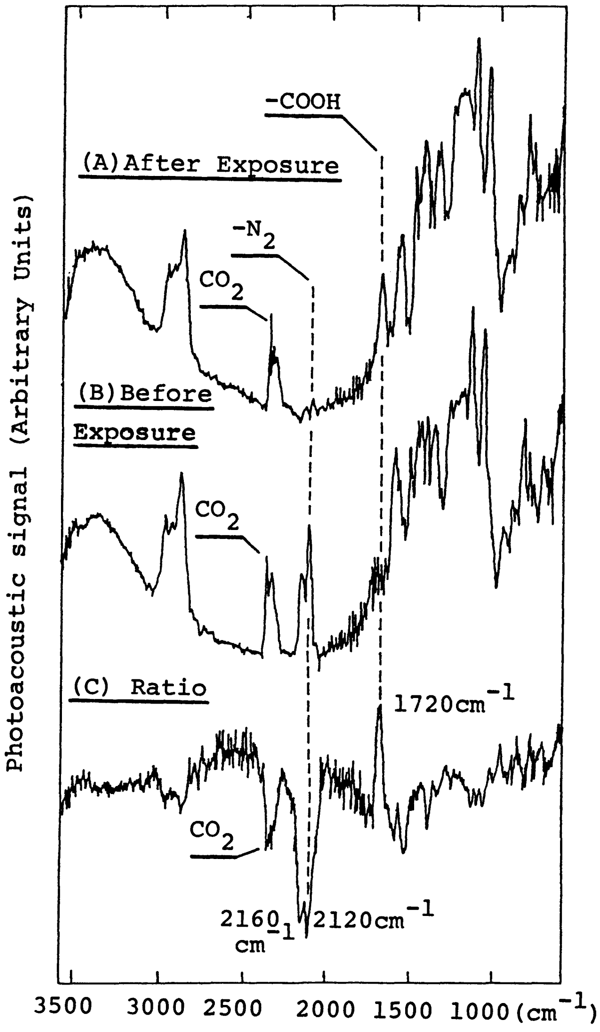

Fig. 2 Spectral change of positive working PS plate with exposure to the light.

mode appears after the exposure to the light. The disappearance of the diazo group stretching bands reflects the photoelimination of a nitrogen molecule, and the appearance of the carbonyl group stretching band is consistent with the formation of 3-indenecarboxylic acid.

Substituted p-diazodiphenylamines are postulated[8)] to photodecompose by the reaction scheme shown in Fig. 3. That is, diazonium salts are decomposed by light and react with OH groups of a binder by free radical reactions. If the reaction proceeds along the above-mentioned scheme, it can be expected that the infrared absorption band due to diazo group disappears after the exposure to the light.

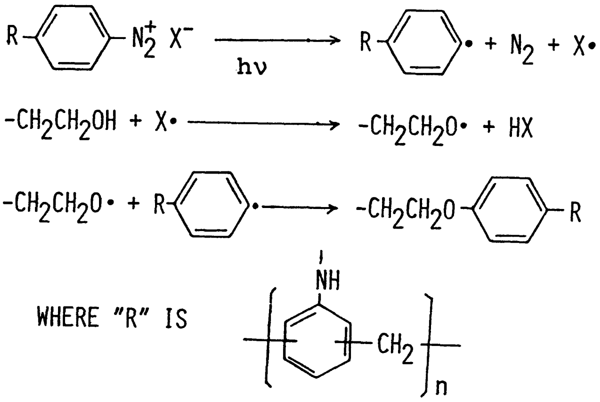

Fig. 3 Phtolysis of substituted p-diazodiphenylamine.

Figure 4 shows the spectral change of the negative working PS plate with exposure to the excitation light. It can be immediately seen that the intensity of the absorption band at about 2160 cm^{-1} due to diazo group decreases remarkably after the exposure to the light. This observation reflects the photoelimination of a nitrogen molecule in the photolysis of substituted p-diazodiphenylamines.

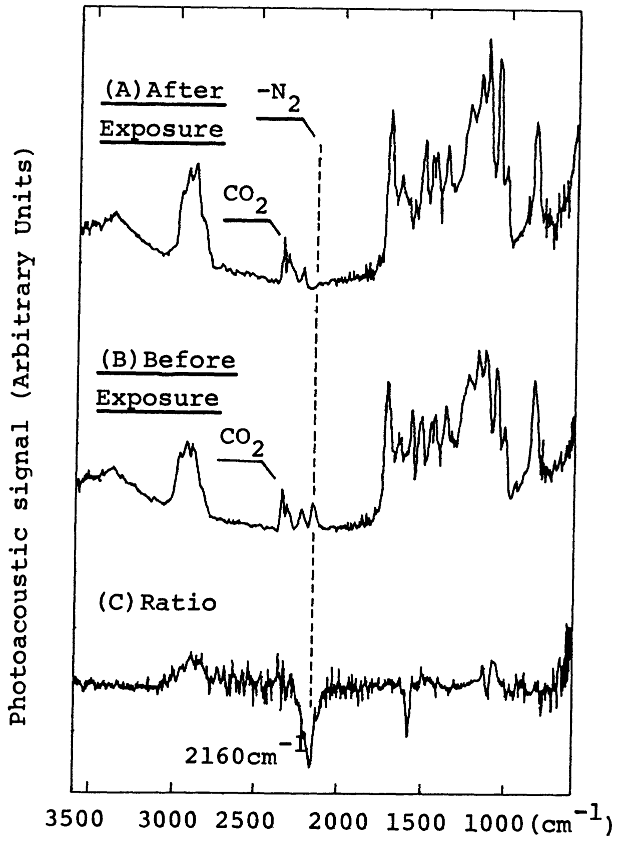

Fig. 4 Spectral change of negative working PS plate with exposure to the light.

The authors already examined the photolysis of PS plates by means of FTIR reflection absorption spectrometry(FTIR-RAS)[9,10)] in which spectra could be measured in the limited wave number region of 2000-600 cm^{-1} because of the low reflectivity of aluminum substrates in the higher wave number region. Moreover, measurements of spectra around 960 cm^{-1} and 1200 cm^{-1} were difficult in FTIR-RAS because of absorptions of aluminum oxide on the aluminum substrate. On the other hand, infrared spectra of PS plates could be obtained in the whole wave number region by means of FTIR-PAS. The spectral changes of PS plates obtained by FTIR-PAS were found to be fairly coincident with the ones obtained by FTIR-RAS.[9,10] As shown in Figs. 2 and 4, however, there are several absorption bands which can not be measured by FTIR-RAS, and which can not be explained by the photoreaction schemes shown in Figs. 1 and 3. For example, in Fig. 4, the increase of the intensity of infrared bands at 2800-3000 cm^{-1} which are assigned to aliphatic C-H stretching vibrational mode can be observed after the irradiation. This result can not be explained simply by the photolysis shown in Fig. 3. These observations suggest that complex photoreactions of photosensitive resins may occur in the presence of non-photosensitive resins which are used as a binder, although it is not doubtful that the main photolysis of PS plates investigated in this study is photoelimination of a nitrogen molecule. In order to obtain more detail information on the photolysis, more experimental investigations are required, and work is now continuing to clarify it.

For the structural elucidation of organic coatings on metal surface, infrared reflection absorption or infrared emission spectrometry has been used as a non-destructive analytical method.[9-13] However, there are several disadvantages in these spectrometry. It is known in the infrared emission spectrometry that if the thickness of the coatings become larger than a few hundred nanometer, spectral distortion can occur because of self-absorption. It is also known that high quality spectra can be hardly obtained by the infrared reflection absorption spectrometry, if the surface of metal substrates is roughened, or if the coatings on metal surface are thick. On the other hand, direct information on the structural changes of photosensitive resins on roughened aluminum plates can be obtained easily by means of FTIR-PAS. FTIR-PAS, therefore, can be useful for analysing the photochemical changes of photosensitive resins on metal surface.

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