JOURNAL OF IMAGING SCIENCE AND TECHNOLOGY® • Volume 46, Number 2, March/April 2002

Imaging Characteristics of Diazo Resin with a Dialkylamino Group for Screen Printing

Kieko Harada, Masahito Kushida, Kyoichi Saito and Kazuyuki Sugita▲

Faculty of Engineering, Chiba University, Inage-ku, Chiba, Japan

Hirotada Iida

Toyo Gosei Kogyo Co., Ltd., Ichikawa-shi, Chiba, Japan

When photolysis of diazo compounds with dialkylamino groups is compared with photolysis of diazo compounds with other substituents, quantum yields ϕ are larger and thermal decomposition rates are slower than for the other substituents, respectively. These properties are suitable for sensitivity and thermal stability for diazo resins. In this study, the imaging characteristics of a diazo resin with dialkylamino groups (MDR) are reported and compared with the conventional diazo resin with the phenylamino group (DPR) for screen printing. The photosensitive diazo compounds with the dialkylamino group, p-N,N bis(3-aryloxy-2-hydroxy-propyl) amino benzene diazo compound (MD), has λ_{max} at 382 nm, and shows little absorption in the visible region. The transmittance of the diazo resin MDR based on MD in PVA film at 400 nm after exposure with a high pressure mercury lamp was 10 % higher than that of DPR which is a condensation product between p-diazodiphenylamine (DPD) and formaldehyde. Molar extinction coefficient (ε) and quantum yield (ϕ) of MD at 365 nm were similar to those of p-dimethylaminobenzene diazo compounds (DED). The values of ε and ϕ were 1.3 times and 1.2 times as large as those of DPD, respectively. The degradation temperature (TD) by thermogravimetric analysis of MDR was 5°C lower than that of DPR, but the storage stability of MDR was superior. We propose that the high photosensitivity, the bleaching characteristics, and the superior storage stability should make MDR a useful thick resist layer for screen printing.

Journal of Imaging Science and Technology 46: 159–164 (2002)

Introduction

Diazo compounds are the photosensitive components for the vesicular processes and UV fixable thermal recording,[1,2] binders for phosphors powders on multicolor screens,[3–5] contrast enhancement lithography (CEL) materials,[6,7] photoacid generators, (PAG)s, for microlithography resists[8] and for thermally crosslinking type PS plates,[9] and photosensitive emulsions for the screen printing in printed circuit board (PCB) fabrication. The photosensitive emulsions for screen printing comprise polymer colloids and photosensitive materials, e.g., potassium ferrioxalate, ammonium dichromate and diazo compounds. The conventional diazo resin (DPR) which is a condensation product between p-diazodiphenylamine (DPD) and formaldehyde has been used for photosensitive screen printing plates. DPR, although having many advantageous properties as the practical photosensitive compounds, also has several characteristics which need to be improved. The first problem is that, because it contains DPD as the basic structural unit, it has an absorption in the visible region at 420–500 nm, and it is difficult to handle it without it decomposing under visible light. The second problem is inadequate photosensitivity of the currently used DPR. The third problem is the marginal photobleaching characteristics of this diazo resin.

Recently, multifunctional diazo compounds with dialkylamino groups are reported as improved alterenatives for DPD. When the properties of diazo compounds with the dialkylaminogroup are compared with those of diazo compounds with other substituents, quantum yields[10,11] Φ are larger and thermal decomposition[12,13] rates are slower than with other substituenns, respectively. These properties are suitable in terms of sensitivity and thermal stability for practical diazo resins.

Many types of multifunctional diazo groups have been introduced, e.g., styrene and maleic anhydride copolymer with diazo groups (SMD),[14] p-diazoaniline dibromopropene condensate (DBC),[15] and polyaddition products of p-diazoanilines to glycidyl ether styrene (MDR).[16,17] Copolymer and diazo groups in SMD are bonded by means of an ester linkage which is easy to hydrolyze and thereby damages the storage stability. DBC is difficult to prepare. However, various multifunctional diazo compounds can be prepared by use of glycidyl ether. The resin MDR based on the photosensitive diazo compounds with the dialkylamino group, p-N,N-bis(3-aryloxy-2-hydroxy-propyl) amino benzene

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Original manuscript received March 23, 2001

▲ IS&T Member

diazo compounds (MD) is prepared by the reaction of poly(acethylaniline) and glycidyl ether .

In this study, the imaging characteristics of the diazo resin with dialkylamino groups (MDR) are reported and compared with those of the conventional diazo resin with phenylamino groups (DPR) for screen printing.

Experimental

Materials

Chemical formulas of materials employed are shown in Fig. 1. The diazo compound, MD, was synthesized in the following way[16,17] as shown in Scheme: p-aminoacetanilide, 15.0 g (0.1 mole), was dissolved in 180 g of acetic acid and 30.0 (0.2 mole) g of glycidylphenylether was added little by little at 25°–30°C under agitation; agitation was continued for 3 hrs at approximately 30°C and then for 6 hrs at approximately 40°C. Then 50 g of 35% hydrochloric acid was added, and the mixture was agitated at 75°C for 8 hrs to achieve deacetylation. After cooling to approximately 50°C, 40 g of water were added, cooled to 3° to 5°C, 7.6 g (0.11 mole) of sodium nitrate dissolved in 20 g of water were slowly dropped in at this temperature. After the completion of the addition, agitation was continued for 1 hr to achieve diazotization. Ammonium hexafluorophosphate, 18.0g (0.11 mole), was dissolved in 150 g of water and added to the diazotized solution at 5°–10°C under agitation. After 30 min, 150 g of water were added dropwise, agitated for 1 hr; the precipitated product was isolated by filtration. The precipitate was washed twice with iso-propylether, and dried under vacuum. The yield was 45 g.

MDR was synthesized in the following way: p-cyanoehtylaminoacetanilide, 20.3 g (0.1 mole), was dissolved in 60 g of acetic acid and 18.5 g of polyglycidylether of a phenol-formaldehyde resin with an epoxy equivalent of 175 were added, and reacted at 30°–35°C for 4 hrs, and then warmed to 40°–45°C. Sulfuric acid, 70 g (40%), was the added, and the mixture was agitated at 75°–80°C for 12 hr for deacetylation of the acetylamino group and hydrolysis of the cyanoethyl group into a carboxyethyl group. Water, 100 g, was added, the mixture was cooled to 3°–5°C and a solution of 7.3 g (0.105 mole) of sodium sulfite and 15 g of water was dropped in over about 1 hr at the same temperature; the mixture agitated for 30 min to complete diazotization. The diazotized solution was poured into 400 g of 15% salt solution at 5°C under agitation to liberate a paste-like diazo compound. This paste-like substance was removed, and triturated with iso-propyl alcohol, and dried under vacuum. The yield was 32 g.

The conventional diazo resin, p-diazodiphenylamine-4-diazonium sulfate salt-formaldehyde condensate (DPR) was synthesized as follows: diphenylamine-4-diazonium sulfate, 14.5 g (0.05 mole), was dissolved in 50 g of ice-cooled concentrated sulfuric acid, and 1.2 g (0.04 mole) of paraformaldehyde were slowly added at 5°–8°C, and agitated at 8°C for 2 hr. This mixture was dropped into 200 g of ice-cooled iso-propyl alcohol, and vacuum dried. The yield was 11 g.

Diphenylamine-4-diazonium hexafluorophosphate (DPD) and p-N, N-diethylaminobenzenediazonium hexafluorophosphate (DED) were synthesized as follows: p-diazo diphenylamine-4-diazonium sulfate (DPS), 14.5 g (0.05 mole), or p-N,N-diethylaminobenzenediazonium chloride zinc chloride (DEZ), 18.0 g (0.05 mole), was dissolved in water. Ammonium hexafluorophosphate, 18.0 g (0.11 mole), was dissolved in 150 g of water and added dropwise into the diazo solution at 5°–10°C under agitation. The precipitates were filtered and washed with iso-propyl alcohol. The yield of DPD and DED were 20.0 and 16.0 g, respectively.

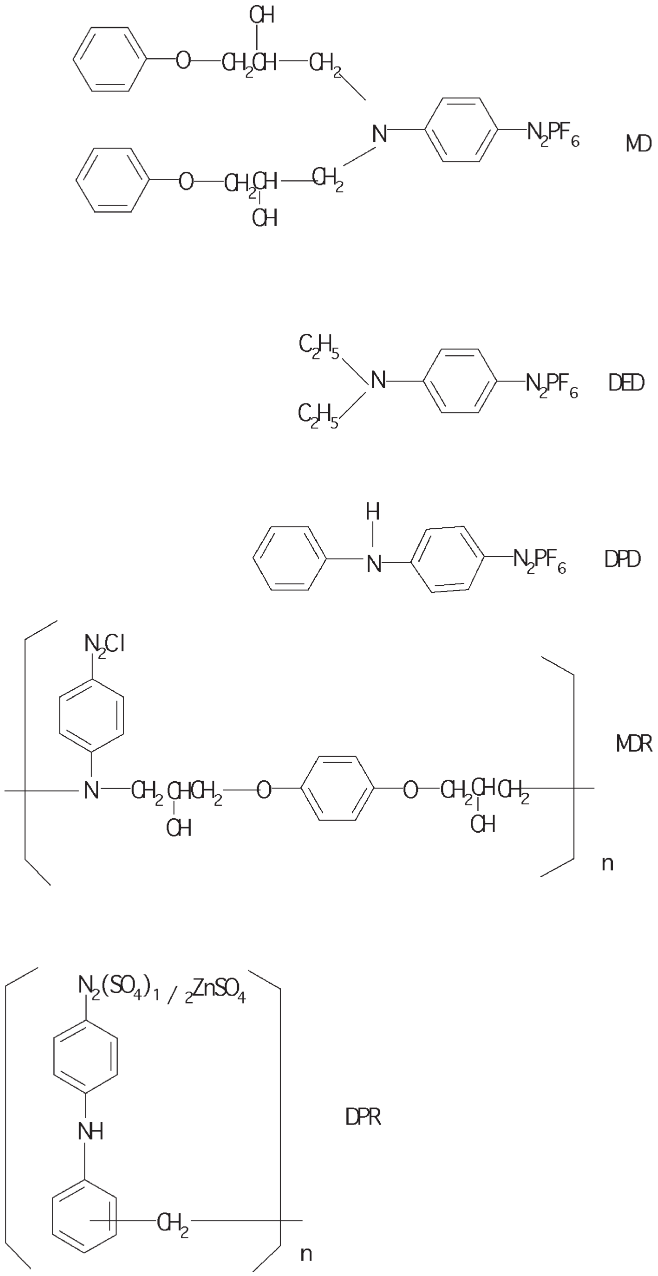
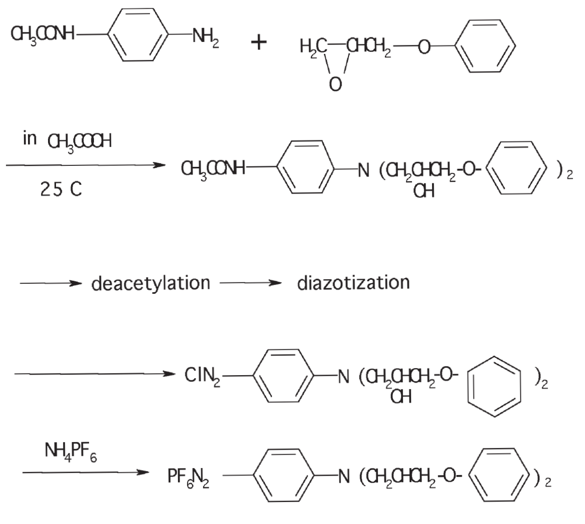


Figure 1. Chemical formulae of monomeric diazo compounds and diazo resins.

DPS and DEZ were obtained from Tokyo Kasei Kogyo Co. LTD. DPR was obtained from Murakami Screen Co. LTD.

Film Specimen Preparation

The diazo resin films were formed on a glass plate by spincoating a polymer solution containing a matrix polymer, polyvinylalcohol, 3.0 g (PVA), diazo resin, 0.2 g (MDR or DPR), and water; 30 ml and 20 ml water yield coating were 2.4 µm thick and 3.6 µm thick, respectively. Then, the diazo resin films were cured by a soft bake at 70°C for 20 min.



Scheme

Measurements

The solutions were irradiated with a super-high pressure mercury lamp, USH 250, through a Mastuda UV-D2 filter (Transmitting: 300-400 nm UV light) . The light intensity was measured to be 3.14 mW/cm^2 with a thermopile, Eppley Thermopile (Air Type). Absorption spectra were measured with a Shimazu UV 180 spectrophotometer. Thermal analyses were performed with a Mac Science 001 Thermal Analyzer System at a heating rate of 5°C/min for TGA and DTA under N_2 atmosphere.

Results and Discussion

Absorption Spectrum

Absorption spectra of model diazo compounds, p-diethylaminobenzenediazonium (DED), p-N,N-bis (3-aryloxy-2-hydroxypropyl)aminobenzene diazo compound (MD), and p-diazodiphenylamine (DPD) in 2-methoxyethanol solution are shown in Fig. 2. The spectrum of MD is similar to that of DED, and both exhibit λ_{max} of sharp absorption bands at 380 nm, whereas the conventional diazo compound, DPD, has a broad band with λ_{max} at 378 nm and an absorption tail in the visible region of 400–500 nm. Molar extinction coefficients (ε) of diazo compounds are shown in Table I. The value of ε of MD was nearly equal to that of DED, and 1.3 times as large as that of DPD.

Absorption spectra of multifunctional diazo resin, MDR and conventional diazo resin, DPR in aqueous solutions at pH 3 are shown in Fig. 3. The spectra of MDR and DPR are similar to those of MD and DPD, respectively.

Photodecomposition of Diazo Compounds in Methanol

Diazo compounds, DED, MD and DPD were irradiated with a high pressure mercury lamp. The amount remaining of the diazo compound after irradiation was calculated from the change of absorbance at 380 nm and is shown, plotted against irradiation time, in Fig. 4. The slope of the plot for MD was similar to that for DED. The initial slope for DPD was as steep as that of MD, but is gradually decreased to a value less than that for MD.

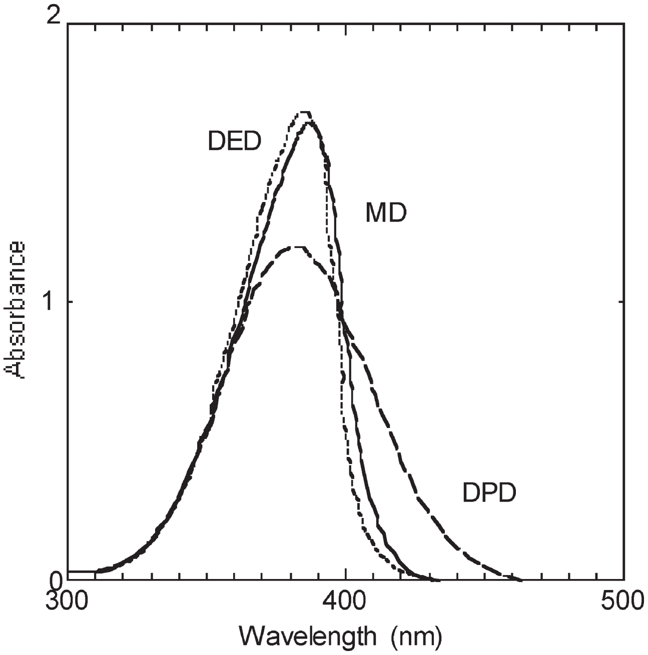


Figure 2. Absorption spectra of model diazo compounds, DED, MD and DPD in 2-methoxyethanol.

TABLE I. UV Characteristics of Model Diazo Compounds and Diazo Resins

	λ_{max} (nm)	ε	Φ
DED	380[a)]	41,500[a)]	0.63[c)], 0.64[c,11)]
MD	382[a)]	40,750[a)]	0.66[c)]
DPD	379[a)]	30,250[a)]	0.56[c)]
MDR	382[b)]		
DPR	378[b)]		

a) in 2-methoxyethanol
b) in aqueous solution at pH 3
c) in methanol[11]

The number of quanta absorbed by the solution in the photolysis were calculated from the light intensity, divided by the energy of the UV line and the absorbance at 366 nm due to the diazo compound. Quantum yields (Φ) for photodecomposition of diazo compounds are also shown in Table I. The value of Φ for MD was close to that for DED and 1.2 times as large as that of DPD.

Photodecomposition of Diazo Resins in PVA Film

The residual diazo resins, MDR and DPR in PVA films after UV irradiation were measured by uv spectrophotometry, and remaining weight % of diazo resin is plotted against the irradiation time in Fig. 5. Photodecomposition of MDR was faster than that of DPR. When the film thickness increased 1.5 times, the decomposition speed of MDR changed little, but that of DPR became significantly slower.

Photobleaching of the resin film shown in Fig. 6 indicates that MDR has a slightly weaker absorption in the UV region after exposure than does DPR. The transmittance of MDR film at 365 nm was 10 % higher than that

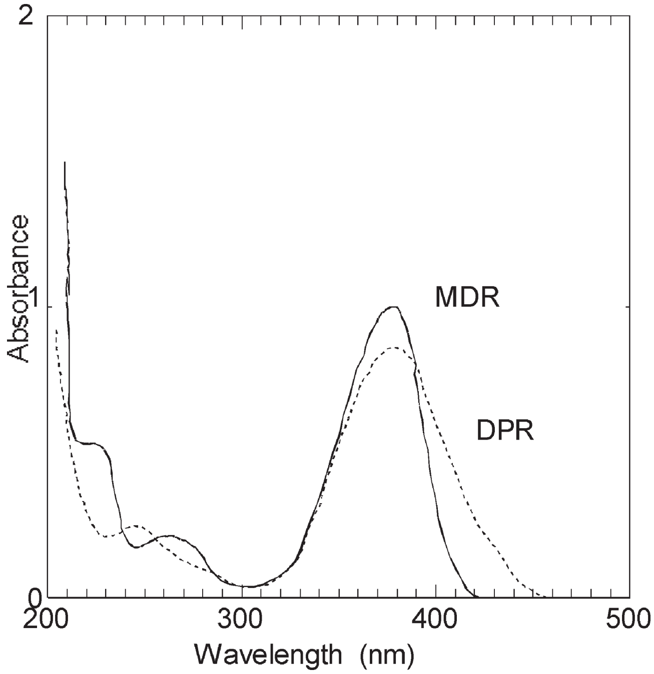


Figure 3. Absorption spectra of diazo resins, MDR and DPR. Aqueous solution at pH 3

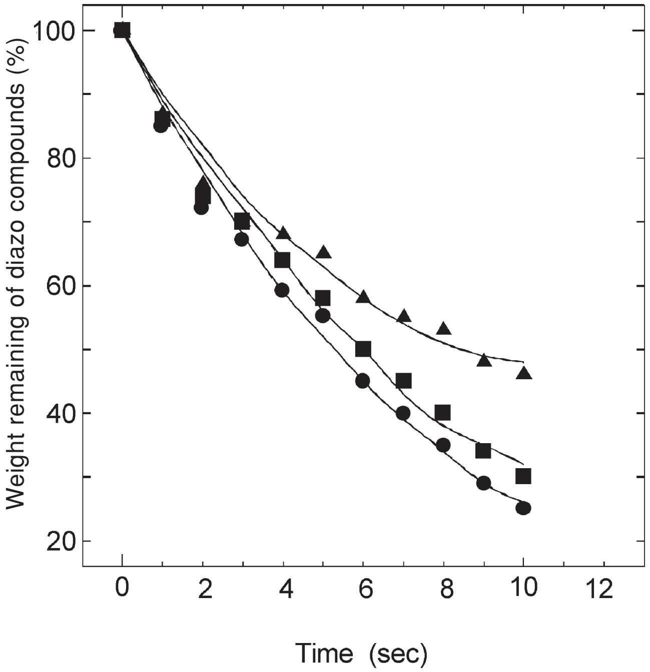


Figure 4. Photolysis of model diazo compounds, MD, DED and DPD in methanol at a concentration of 1×10^{-3} mol/l: ● MD; ■ DED; ▲ DPD

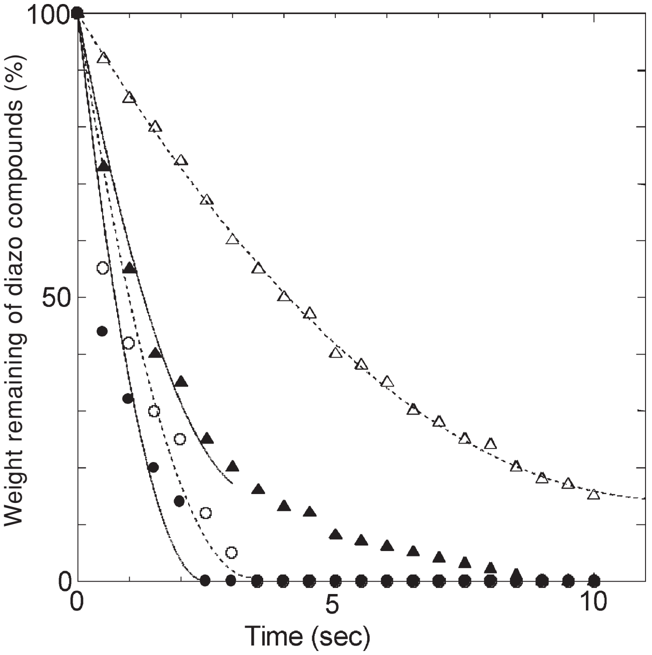


Figure 5. Photolysis of diazo resins, MDR and DPR in PVA films. ●,○ MDR; ▲, ○ DPR. Film thickness: — ●, ▲ 2.4 μm; ..., ○, Δ 3.6 μm.

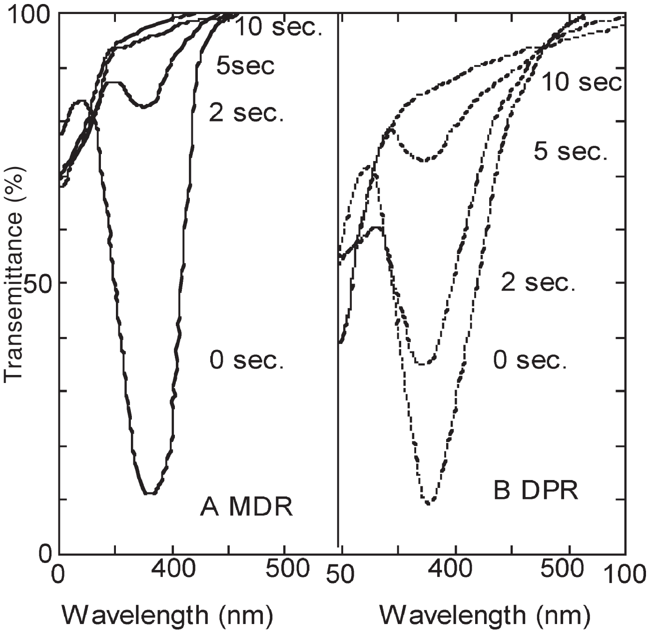


Figure 6. Photobleaching of diazo resin, MDR and DPR in PVA films. Film thickness: 2.4 μm, Incident light power: 3.14 mW/cm^2

of DPR, which suggests more UV light penetrating into the inner part of the MDR resist film. The MDR film compared with DPR has much less visible light absorption after exposure, showing less colored photoproducts.

The diazo resist solutions were coated on substrates, exposed to the mercury lamp and developed with water at 25°C for 1 min. The sensitivity of the resists was obtained as the exposure dose ($E_{1/2}$) which was required for 50% retention of thickness of the resist layer. $E_{1/2}$ of MDR and DPR were 2.5 mJ/cm^2 and 12 mJ/cm^2, respectively.[18]

Thermal Decomposition

The degradation temperatures, T_d, were obtained from TGA curves, and are shown in Table II. T_d of MD was

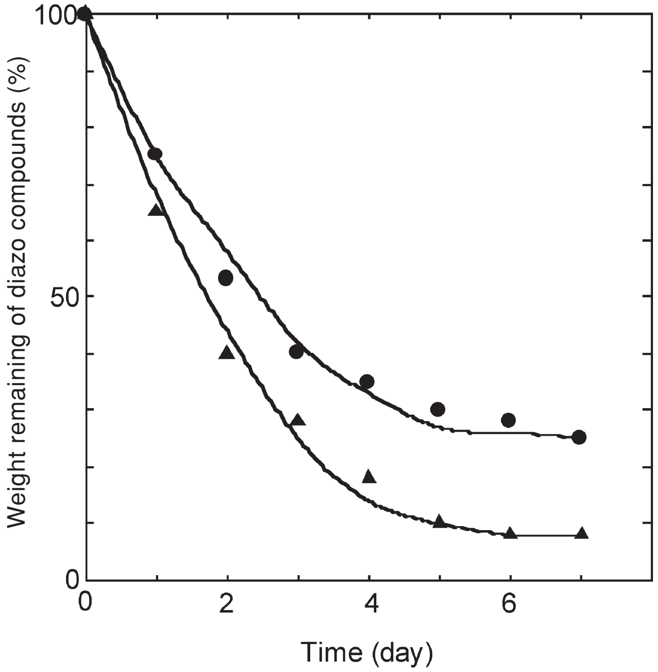


Figure 7. Thermal decomposition of neat diazo resins at 55°C in aqueous solutions at pH 3: ● MDR, ▲ DPR.

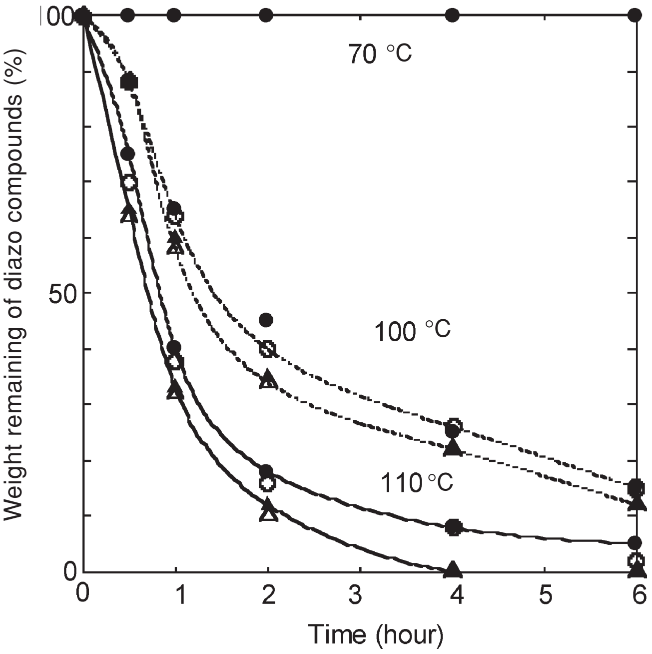


Figure 8. Thermal decomposition of diazo resins, MDR and DPR in PVA films. ● MDR A; ❍ MDR B; ▲ DPR C; and Δ DPR D.

TABLE II. Thermal Characteristics of Model Diazo Compounds and Diazo Resins

		T_d a) (°C)	log k b) (50°C)	E_a c)
DED		153.6		
MD		129.1		
DPD		149.1		
MDR		120.8		
	2.4 μm thick		−6.6	33
	3.6 μm thick		−7.1	34
DPR		125.4		
	2.4 μm thick		−6.7	30
	3.6 μm thick		−7.7	31

a) Thermal decomposition temperature determined by DSC Analysis,
b) Thermal decomposition rate of film,
c) Activation energy of film,

20°C lower than that of DPD, and T_d of MDR was 5°C lower than that of DPR .

In order to the estimate storage stability, decomposition rate of the compounds in aqueous solutions was measured under light shielded conditions. Aqueous solutions at pH 3 of neat diazo resins, MDR and DPR were stored at 55°C in the dark, and the absorbance at λ_{max} of the UV absorption spectrum was measured every 24 hrs. It can be seen from the results in Fig. 7 that the thermal decomposition of MDR was slower than that of DPR.

The thermal decomposition of diazo resins MDR and DPR in PVA films were measured at various temperature in the dark. The plots of the weight remaining of the diazo compounds (%) against storage times are shown in Fig. 8. The storage stability of MDR was better than that of DPR, at both temperatures studied. The thermal decomposition rate of diazo resins conforms first order kinetics. Activation energies, E_a, as obtained from the plots of log k against 1/T are shown in Table II. The E_a of MDR and DPR films were not dependent on the film thickness; the E_a of MDR was larger than that of DPR.

The MDR had a lower T_d, but superior storage stability, which may be explained by a slower decomposition rate at 55°C and below, and by a greater temperature dependence, i.e., higher activation energy for thermal decomposition.

Conclusions

The diazo resin with a dialkylamino group, MDR, has a λ_{max} at 382 nm, and shows little absorption in the visible region. The transmittance of MDR film at 365 nm after exposure was 10% higher than that of the conventional diazo resin, DPR. When the film thickness of DPR increased 1.5 times, the photodecomposition rate of DPR film slowed down while that of MDR did not. The values of ε and Φ of MD were 1.3 times and 1.2 times larger than those of DPD, respectively. The storage stability of the MDR resist was also superior. We propose that the high photosensitivity, improved bleaching characteristics, and superior stability should make MDR a useful thick resist layer for screen printing. ▲

Acknowledgment. The authors thank Dr. H. Kikuchi, Mr. N. Tochizawa and Ms. M. Kimura for their helpful suggestions.

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