

Investigations on Photochemical Reactions of Sensitized Novolac Resin Composition as Positive Working Lithographic and Microlithographic Applications

Key Words:

photoresist, formulation, positive - working, novolac, diazonaphthoquinone sulfonic acid,

*H. Mivehchi**

Chemistry Group of Jahad Daneshgahi, Sharif University of Technology, Tehran - Iran.

ABSTRACT

Photosensitive formulations comprising diazonaphthoquinone novolac resins have been widely used as positive working lithographic and microlithographic materials [1,2,3].

To enhance the light sensitivity of the formulations, ester adducts of photosensitive agents based on diazonaphthoquinone sulfonic acids are currently being employed. It has been found that the composition based on the esters of the sensitive agents with cyclic alcohols, and phenols, including novolac resins, responds well to the requirements of the positive printing plates, namely high image resolution upon ultraviolet radiation, adhesion and coatability to the aluminium plates.

INTRODUCTION

In general photosensitive materials are imageable organic polymers that are coated on or laminated to a substrate. The exposure of a resist produces a latent image that is later developed to produce the image pattern. Development is the selective dissolution of the polymer coating removed from the substrate. Depending on the mechanism involved, the outcome of exposure and development can produce either positive or negative images [1].

After exposure and development the image produced protects the underlying substrate so that the patterns of the uncovered areas can be transferred into a substrate either by chemical or by physical processes. The polymer image thus "resists" the attack of the etching process therefore these polymers have become known as resists.

Differential solubility in development is due to low molecular weight molecules, low molecular weight polymers and polymer fragments dissolving faster than high molecular weight polymers. And in addition there is a wider range of solvents to dissolve them. One of the strategies in the development of photoimage materials has been focused around the solubility change that would lead to a high resolution image. This has been achieved by initiating a photofunctional group change from hydrophilic to hydrophobic or vice versa [1].

Most positive photosensitive materials involve the photofunctional change of naphthalenequinone diazides or more commonly called diazonaphthoquinones in novolac resins. Although negative resists utilize the bisazides in polyisoprene matrix, and are also vastly used, there has been a continuing trend toward positive resist systems. They can produce high resolution, high quality patterns, good adhesion to printing plates and homogeneous coatability. The diazonaphthoquinone - novolac system becomes base soluble upon ultraviolet light exposure, and exhibits less swelling and image distortion during the development. Current formulations are capable of submicrometer resolution with excellent control of critical dimensions and edge profiles [2].

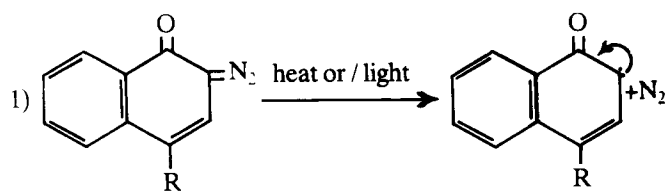
The chemistry of these photofunctional change groups schematically is presented below.

This system in its general form was developed in the 1950's [4 - 7], but the photolysis of this class of substances was elucidated in 1940 [8].

Upon photolysis the hydrophobic naphthalene diazoquinone sulfonate ester is converted to a carboxylic acid with the evolution of nitrogen, and hence the polarity of the novolac film is greatly increased.

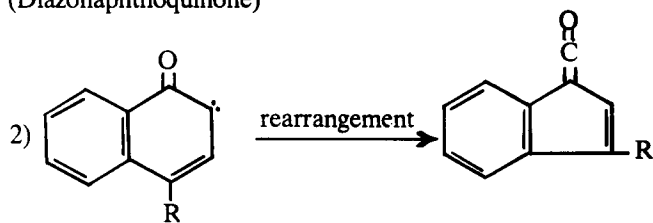
For practical reasons, the 4 - or 5 - sulfonic or carboxylic

- * Present address: Polymer Research Center of Iran, P.O.Box 14185/458, Tehran, Iran.



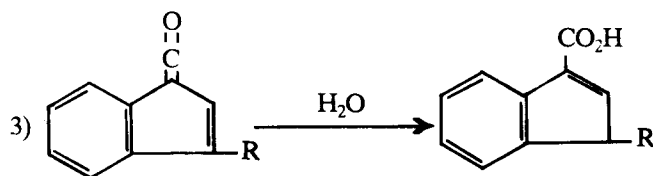
1, 2 - Naphthoquinone Diazide
(Diazonaphthoquinone)

A keto - carbene



A keto - carbene

A ketene



A ketene

An indene carboxylic acid

acid esters of naphthoquinone diazides with phenol derivatives are usually employed instead of the parent substances. These esters are synthesized by reaction of the sulfonyl chlorides or carboxylic acid chlorides of naphthoquinone diazide with the corresponding mono - or polyfunctional phenols [3].

Thus functional R group can be varied with a wide range of conditions without eliminating the solubility of the diazonaphthoquinone being exposed to light. Thus the functional group R, which might frequently be a polymer, can be optimized for desirable characteristics such as coatability and adhesion as well as non - polymeric groups which can be optimized for high resolution imaging.

EXPERIMENTAL

The experimental procedures consisted of the following steps:

(A) The synthesis of the chemical agents such as novolacs, photosensitive substances, and the ester adducts of the diazonaphthoquinone sulfonic acid salts.

Novolac production:

Materials: meta and para cresols, formalin solution (35%), oxalic acid, phosphoric acid, butyl acetate, ethylene glycol monoethyl ether and paraformaldehyde.

Synthesis: The equal mixtures of cresol isomers were heated to 90-95°C, followed by the addition of 2.6% by weight of formalin solution (35%), which was filtered just prior to use. While the temperature of the reaction mixture was maintained

between 90 - 95°C throughout the addition of the formalin solution, it was raised to 100°C after the addition, and was kept at this temperature for 1 hour. After that 0.66% by weight of phosphoric acid was added to the whole mixture, and then the water content of the reaction vessel was removed under vacuum distillation, while the reaction temperature was kept between 65-70°C. This was followed by the addition of solvents to dilute the reaction medium. The solvents recommended so far have included butyl acetate and ethylene glycol monomethyl ether acetate (methyl glycol acetate), but the latter was replaced with ethylene glycol monoethyl ether with close properties such as boiling point, density and vapour pressure as methyl glycol acetate.

The solvents' temperature however, was as much as 90°C during the addition, but at the end the temperature of the mixture was raised to 100-105°C, and was kept so for 1 hour until paraformaldehyde of 1.5 to 7% by weight was gradually, and along with complete stirring, added to the reaction mixture. The reaction was carried out in several batches to obtain polymers with different solution viscosities, viscosity average molecular weights and the OH number [9].

Viscosity average molecular weights were between 1600-1800, OH No: 1200-700, solution viscosity: 80cp at 20°C.

Sensitizers production:

Materials: 1 - amino - 2 - hydroxy naphthalene - 4 - sulfonic acid, copper sulfate, concentrated hydrochloric acid, sodium nitrite, thionyl chloride, N, N dimethyl formamide, cyclohexanol, terpene hydrate, ethanol (absolute and 60%), alizarene and the novolac resins from part one production.

Synthesis: Diazonaphthoquinone:

To prepare the diazonaphthoquinone sulfonic acid salt, the 1 - amino - 2 - hydroxy naphthalene - 4 - sulfonic acid (4 - amino - 3 - hydroxynaphthalene - 1 - sulfonic acid) was diazotized by dissolving 15g of the naphthalene sulfonic acid in 100 cc water, and warmed to 80-90°C while being stirred. The temperature was reduced to 5°C and 1.25g dehydrated copper sulfate was dissolved in the mixture, and 4.5g sodium nitrite was gradually added along with thorough stirring.

The whole reaction mixture was kept still, and reddish orange crystals of the diazo were obtained by the addition of concentrated hydrochloric acid. The crystals were then filtered on a büchner flask, and air dried while protected from exposure to light [10]. The yield obtained was above 90% with a decomposition temperature of 124°C.

Diazonaphthoquinone sulfochloride:

The diazonaphthoquinone sulfonic acid (0.04 mole) was dissolved in 60 cc N, N dimethyl formamide, and while the temperature was kept between 30 - 40°C, thionyl chloride (2.5cc) was added slowly. The stirring was carried out for 20 minutes. Finally the temperature was reduced to -3°C and ice water (1400 ml) was added. The product was collected by

filtration and dried at 60°C [11].

Diazonaphthoquinone sulfoesters:

To prepare the esters of diazonaphthoquinone sulfochlorides, the reported synthesis of cyclohexanol ester [12] was adopted, and the preparations of the esters were carried out in suitable conditions which have not previously been reported.

The ester of cyclohexanol:

For the first ester mentioned above, cyclohexanol (2 parts by weight) was mixed in pyridine (20 parts by volume). Then diazonaphthoquinone sulfochloride (5.4 parts by weight) was added at room temperature, since an increase in temperature hardly takes place, the temperature of the reaction mixture was raised to 35°C and mixed well, and the mixture was kept standstill for 24 hours. Finally the mixture was poured into cold, diluted (x 6) hydrochloric acid (150 parts by volume). The yellow precipitate was filtered and washed with water and recrystallized in absolute ethanol, and was readily soluble in benzene. The substance had a decomposition temp of 124°C.

The ester of terpene hydrate:

At first the terpene hydrate (1.5 parts by weight) and diazonaphthoquinone sulfochloride (6 parts by weight) were mixed in pyridine (10 parts by volume) at room temperature, mixed well and kept still for 24 hours. The mixture was finally mixed with 25 parts by volume of alcohol (60%). The precipitate was filtered, washed with water and recrystallized with absolute ethanol. The yellow crystals had a decomposition temperature of 160°C.

The ester of alizarine:

On the basis of the reported material, naphthoquinone diazosulfo - 4 benzoyl pyrogallol (alizarine yellow A), the ester formation was carried out with 1, 2 dihydroxy anthraquinone (alizarine) with pyridine as a catalyst.

The ester of novolac resin:

The mixture of novolac resin solution (10g) and diazonaphthoquinone sulfochloride (1g) was stirred in 10cc N, N dimethyl formamide, mixed well, and finally kept for 24 hours.

(B): The second part of the project involved the film formation test of photosensitive mixture containing the polymer with photosensitive moieties.

The polymer and photosensitive adducts were coated on the aluminium plates by Spinner EC101 of Headway Research Incorporated. The surface thickness was examined by Surfometer SF 200 made by Planer. The surface homogeneity and thickness were examined, and the layers thickness ranged between 1.0 - 1.12µ for the roughest part of the surface. The adhesion to the plates was strong enough that it could not be scraped and did not show any sign of

delamination throughout the exposure test, development and further heating tests.

(C): The third part of the project involved the ultraviolet light radiation testing on the samples.

The radiation exposure was optimized for best thickness, revolution / minute of film coating, and ultraviolet radiation source. The development solvent testing, including the pH of the medium and duration of development were the most important sets of tests carried out at the final stage of experimental work.

The optimal values obtained were as follows:

- The speed of plate rotation for film formation = 1000 rpm for 30 seconds.
- The thickness of the film formed on the aluminium plates = 1µ.
- UV source: UV lamp of 800 Watts.
- The development solvent: alkaline solution of sodium meta silicate with the pH range of 12-12.5.
- The duration of positive image formation, in the range of 3-10 sec.

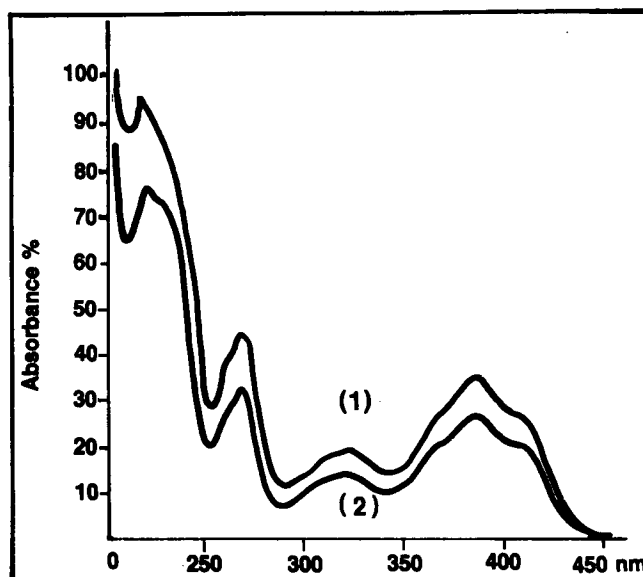


Figure 1: Absorption Spectra of the Photosensitive Esters: (1) Cyclohexanol ester (47 ppm); (2) Terpenehydrate ester (66 ppm)

CONCLUSION

In the investigations carried out to examine the behaviour of some photosensitive compositions which had been very widely reported, we were able to formulate a positive photosensitive composition with new photosensitive ester adducts.

The formation of cyclohexanol and terpenehydrate adducts are confirmed by spectrophotometric examinations, by using Perkin & Elmer 550 S UV VIS spectrophotometer. The compounds, after 30 months of shelf life show several distinct absorbance characteristics in the deep - near UV regions, between 310 nm and 420 nm (with two shoulders at

380 nm and 415 nm) and at 245 nm (figure 1). The shape of the absorption curves coincide with other diazonaphthoquinone absorption curves reported before [13].

All the peaks practically disappear after 10 minutes of UV irradiation of 366 nm by using the Camag UV Cabinet II Instrument of 8 Watt, low pressure mercury tube (Figures 2, 3).

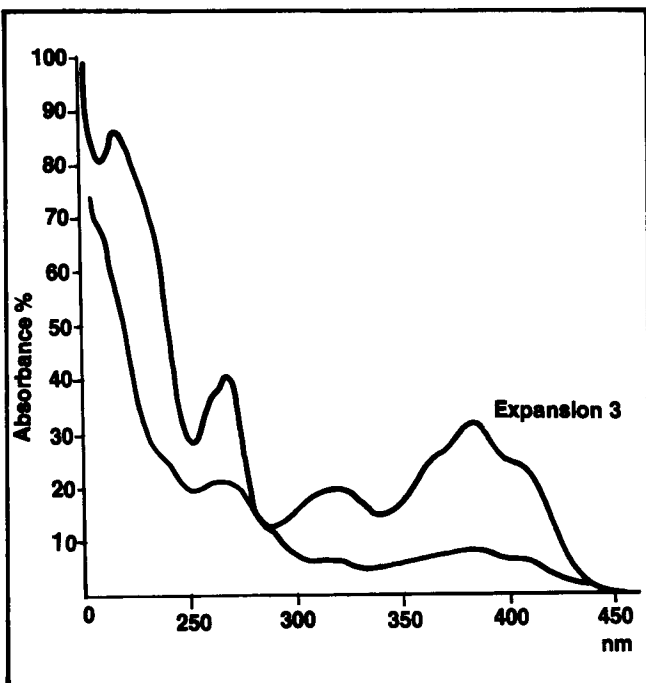


Figure 2: Absorption Spectra of Cyclohexanol Ester Before and After UV Irradiation

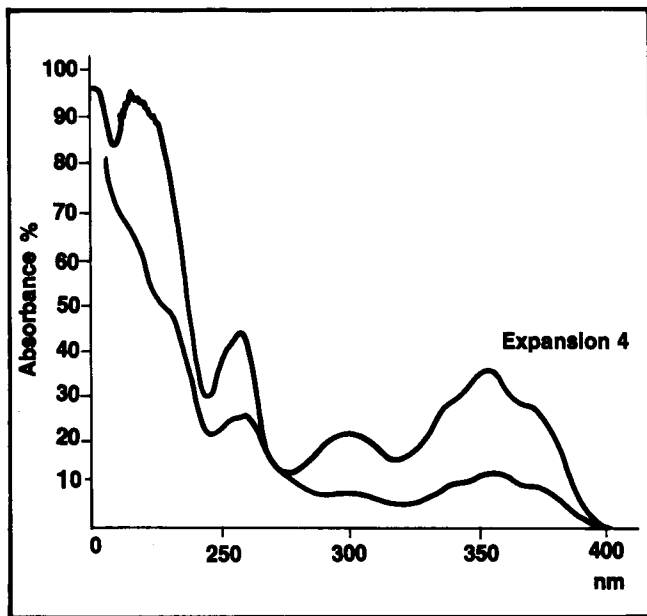


Figure 3: Absorption Spectra of Terpenhydrate Ester Before and After UV Irradiation

REFERENCES

- [1] Turner, R: Daly. R. C, *Comprehensive Polymer Science*, Vol 6, P 183 Pergamon Press, 1989.
- [2] Frass Werner, *Imaging Technology, Encyclopedia of Industrial Chemistry*, Vol A 13, P 613, Ullmann's VCH, 1989.
- [3] Moss. S.J., Ledwith. A, *the Chemistry of Semi - Conductor Industry Chap 9*, Chapman & Hall, 1987.
- [4] Süss, O. et al. *Liebigs, Ann. Chem.*, 593, 91-126, 1955.
- [5] Süss, O., *Z. Wiss. Phot.*, 50, 476 - 517, 1955.
- [6] Brit Pat 708, 834.
- [7] Belg Pats 497, 206; 500, 222.
- [8] Süss. O. *Justies Liebigs Ann. Chem.* 556 (65 - 84), 1944.
- [9] Offen 26 16 992.
- [10] *Methoden Der Organischen Chemie*, bd. 7 Teil 36, Houben Weyl, 1979.
- [11] *Chemical Abstract* 65: 3808a, 1966.
- [12] U.S Pat 2,767, 092.
- [13] Babich. E., Shaw.J, Hatzakis. M., Paraszczak J. IBM T.I.Watson Research Centre. *Polymer Preprints*, Vol 29, No1. September 1988.

