Effects of Diazonaphthoquinone Groups on Photosensitive Coating

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ABSTRACT: Diazonaphthoquinone (DNQ)-novolak photosensitive materials are important in lithography. DNQ groups play an important role in the photosensitive coating. However, there are no reports on the relationship between content of DNQ groups and properties of the coating. The properties include alkali resistance, isopropanol resistance, and abrasion resistance, the key factors in lithography. The experimental results show proper content of DNQ groups can ensure higher sensitivity, finer resolution, and better abrasion resistance in lithography.

Key words: lithography; photosensitive coating; diazonaphthoquinone group; novolak resin; esterification degree

INTRODUCTION

Lithography especially positive presensitized plate (PS plate) is widely used in the print industry. It is popularized with low cost and simple equipment. Diazonaphthoquinone (DNQ)-novolak photosensitive materials have been used in positive PS plate since they were invented by Oskar Süss.[1] The materials show many advantages such as high sensitivity from *I* line (wave length 365 nm) to *G* line (wave length 436 nm)[2,3] and friendly environment.[4] Debmalya Roy has suggested a novel photoreaction mechanism of the materials deduced from ^{1}H NMR and ^{13}C NMR spectra.[5] Now an intramolecular rearrangement reaction known as the Wolff rearrangement is suggested for the photoreaction mechanism of DNQ in the materials.[6,7] After the loss of diazo group a ketene is finally formed.[8] As shown in Figure 1.

The photoreaction of DNQ groups makes the coating change from insoluble to soluble in dilute alkali aqueous solution. This contributes to forming image on the PS plate. With increasing concerns to higher sensitivity and finer resolution the components of photosensitive coating should be investigated systematically. Up to date, there are no reports on how the content of DNQ groups affects the properties in photosensitive coating. Via systematical experiments, we found the proper content of DNQ groups can bring about good properties in photosensitive coating.

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MATERIALS AND METHODS

Novolak resins were obtained from Weihai Economy & Technology Zone Tiancheng Chemical Engineering (Weihai, China), and used as received. 1,2-Naphthoquinone-2-diazo-5-sulfonyl chloride (DNQ-5-Cl) and photo active compounds (PACs, as seen in Fig. 2) were obtained from Taixing city East Industrial Corporation (Taixing, China), and also used as received. All other chemicals were obtained from Beijing Chemical Reagents Company (Beijing, China) and used as received.

Molecular weight and polydispersity of novolak was determined by gel permeation chromatography (LC-10AVP, Japan). Exposure machine is SBK-III from China. Esterification degree was evaluated by element analysis (Vario El, German).

Solubility of PAC

W_1 g of PAC was dissolved in 10 mL 0.5% sodium hydroxide or 35% isopropanol aqueous solution at room temperature by stirring. After PAC was immersed in the solution for several hours the solution was filtered. The deposited PAC was washed with distilled water for 2–3 times and dried and weighed as W_2. The saturated solution weighed W_3. Through the formula $(W_1 - W_2)/W_3 = S/(S + 100)$ (S = solubility in alkali aqueous), the solubility in

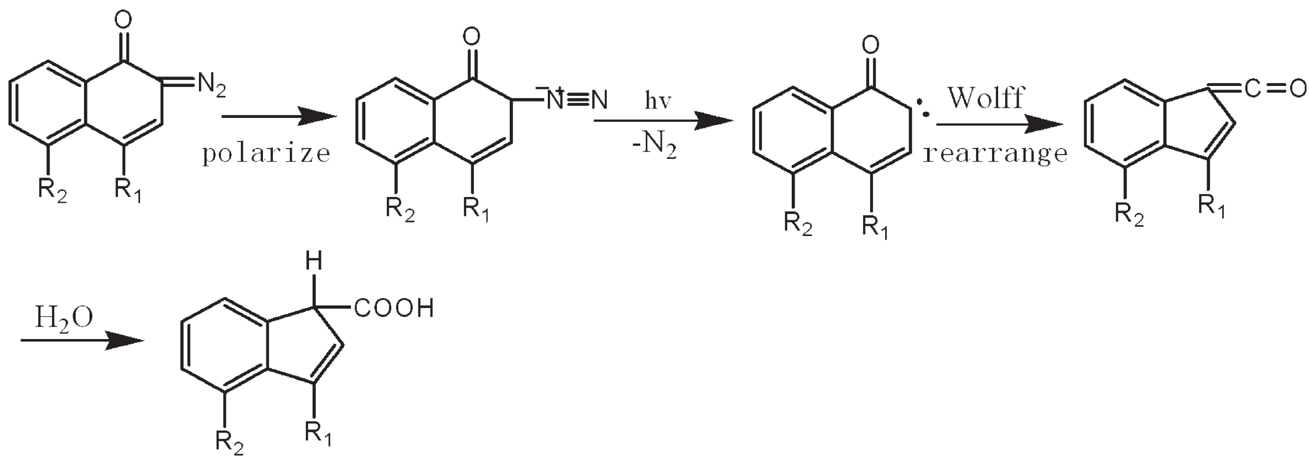

Figure 1 Scheme of photoreaction of diazonaphthoquinone group R_1 = —H or —SO_3R, R_2 = —SO_3R or —H, R = a ballast resin.

alkali or isopropanol aqueous solution can be calculated.

Preparation of photosensitive coating

The content of novolak and PAC was calculated by changing B/P ratio (B, novolak resin; P, PAC) from 1 : 7 to 7 : 1 and photo acid generator (1%) and background dye (0.5%) was mixed together in a flask. The mixture was dissolved in 7 mL of glycol monoethyl ether and 7 mL of butanone. The resulting solution was spin coated on the electrolytic grained and anodized aluminum plate. Aluminum plate's thickness was 0.3 mm and the anodic film was 3 g/m^2, the arithmetic mean of the absolute departures of the roughness profile from the mean line (Ra) was about 0.6 μm. The coating thickness was controlled at ca. 2 g/m^2. Then the plate was dried for 3 min at 120°C in an oven.

Evaluation methods for characterization of photosensitive coating

Alkali resistance or isopropanol resistance

A coated aluminum plate was cut into 10×10 cm^2 and weighed W_1. The plate was immersed in aqueous solution that contained 0.4% NaOH, 3% $Na_2SiO_3{\cdot}9H_2O$, or 35% isopropanol for 2 or 30 min at room temperature, then washed by pure water. The plate was dried and weighed W_2. Then the remained coating was removed by acetone. The plate was dried and weighed W_3. The value of residual film ratio of alkali or isopropanol resistance was calculated by the formula $(W_2 - W_3)/(W_1 - W_3) \times 100\%$.

Abrasion resistance

W_1 g of coated plate with 10×10 cm^2 was put into ultrasonic vibrator and immersed in certain amount of water. Then the plate was vibrated for 30 min with water at 50°C and dried, and weighed W_3. The value of residual film ratio of abrasion resistance was calculated by the formula $(W_2 - W_3)/(W_1 - W_3) \times 100\%$.

RESULTS AND DISCUSSION

Proper binder resin

Binder resin was responsible for the intensity of the coating and the formation of film.[9] The resin can interact with DNQ groups by hydrogen bonds in PAC. At the same time the property of alkali or isopropanol resistance was improved. Figure 3 shows the scheme of interaction between DNQ groups and binder resin.[10]

Different novolak resins were used as binder resin in photosensitive coating, and the results were summarized in Table I. N-215 was synthesized by novolak resin with low molecular weight and DNQ-5-Cl.

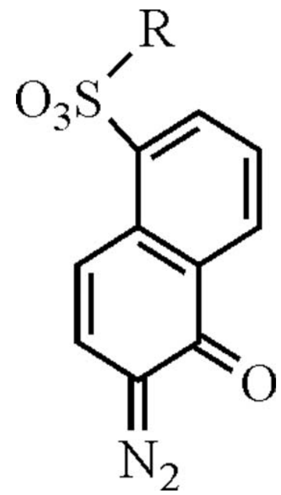

Figure 2 Scheme of PAC, R = a novolak resin with low molecular weight.

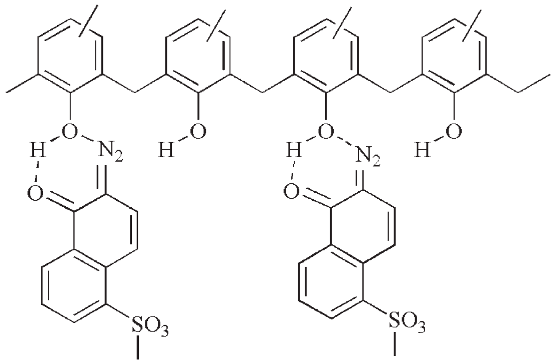

Figure 3 Scheme of binder resin form hydrogen bonds with DNQ groups of PAC.

The esterification degree was about 30%. Binder resins 1–8 were novolak resins in different molecular weight and polydispersity.

From Table I, it can be seen that different binder resin changed the properties of the coating. Binder resin with proper molecular weight and good alkali resistance, excellent isopropanol resistance should be considered.

In the following a novolak resin with M_w about 8000, $M_w/M_n = 3.2$ was applied in photosensitive coating as binder resin to measure the properties of the coating.

Relationship between solubility and esterification degree of PAC

The esterification degree should be modified according to different ballast resins.[11] Ballast resin was a series of polymer with hydroxyl to introduce photosensitive groups. PAC was synthesized by novolak resin with low molecular weight and DNQ-5-Cl. To find the best esterification degree of PAC, the solubility in dilute alkali and isopropanol aqueous solution of synthesized PACs were examined. The different esterification degrees contribute to different properties of the coating. Figure 4(a,b) used pyrogallol acetone (PA) resin ($M_w = 4493$, $M_w/M_n = 2.7$) and novolak resin ($M_w = 2390$, $M_w/M_n = 2.4$) as ballast resin, respectively.

The solubility in 0.5% alkali solution embodied the inhibiting or accelerating dissolving ability in development solution of PACs, and 35% isopropanol aqueous solution was usually used as plate wetting agent. The preferable result was lower esterification degree and lower solubility in alkali solution or isopropanol leading to the inhibiting ability of PACs better and print life longer.

As seen in Figure 4(a,b) the solubility of a PAC in isopropanol or alkali solution fell to the minimum at above 60% for the PA ballast resin. While for a novolak resin with esterification degree above 30%, the solubility got to the minimum.

According to present results, it suggested when the esterification degree of a ballast resin was above 60%, the inhibiting ability was strong, and the sensitivity was poor. If the degree was below 20% the alkali resistance ability of photosensitive coating will descend. Moreover, if the esterification degree increases, the solubility of a PAC in alkali developing solution will decrease. This would lead to residue on the non-imaging area.

Effect of alkali resistance

As can be seen from Figure 5(a,b), the esterification degrees for PA resin ($M_w = 4493$, $M_w/M_n = 2.7$) were arranged for 65.7%, 33.6%, 28.9%, and 20.2%, and for Novolak resin ($M_w = 2390$, $M_w/M_n = 2.4$) were 37.2%, 30.7%, 19.7%, 15.0%, correspondingly. The esterification degree and the content of DNQ groups derived from the elemental analysis. With the increase of the content of DNQ groups (increase of esterification degree) the plots were flatten. According to the imaging experiment, the steeper of the plot slope, the easier to adjust alkali resistance and development latitude. The plots in Figure 5(b) had similar shapes as Figure 5(a). But as shown in Figure 5(b) esterification degree of novolak resin had little effect on the graphs.

A PAC with lower esterification degree has poor inhibiting ability, but has better dispersing in the coating due to the formation of hydrogen bonds with binder resin. On the contrary, PAC with very high esterification degree was difficult to form hydrogen bond with all DNQ groups, which in turn leads to the formation of DNQ cluster.

Effect of isopropanol resistance

Relationship between content of DNQ groups and isopropanol resistance were also studied. After

TABLE I
N-215 as PAC with Different Binder Resins

Number	1	2	3	4	5	6	7	8
Molecular weight (M_w)	2390	2417	4156	4200	4502	5438	6414	8000
M_w/M_n	2.4	2.5	3.5	3.8	4.5	3.2	4.8	3.2
Alkali resistance residual film ratio (%)	90.3	32.2	5.6	2.9	3.3	10.5	7.1	94.5
Isopropanol resistance residual film ratio (%)	81.7	82.0	82.3	67.7	78.9	74.0	70.0	93.0

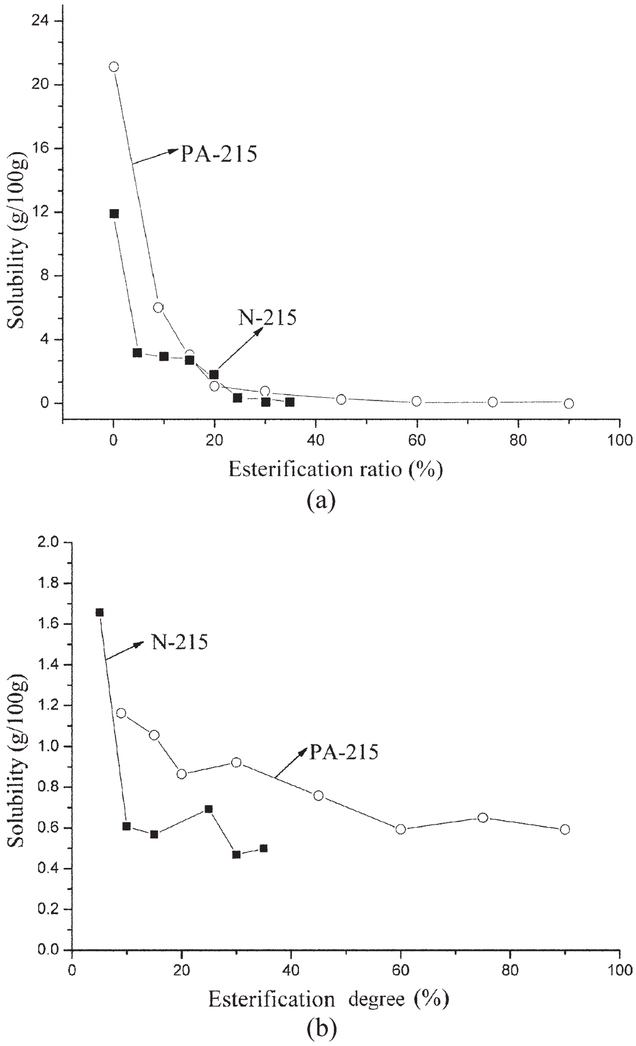

Figure 4 (a) Solubility in 35% isopropanol aqueous solution. (b) Solubility in 0.5% sodium hydroxide aqueous solution.

photosensitive emulsion was spin coated on aluminum plate and dried, the alkali and isopropanol resistance residual film ratio were calculated.

From Figure 6(a,b) it can be seen that the graphs were similar to that of Figure 5(a,b). However when PA and novolak resins were in different esterification degree the trends of graph were different dramatically.

The mechanisms of alkali and isopropanol resistance may be similar, where DNQ groups in photosensitive coating form hydrogen bonds with binder resins and the bonds inhibit dissolving in alkali as well as in isopropanol solution. If a PAC in low esterification degree it contributes to form hydrogen bonds. The more symmetrical and compact hydrogen bonds disperse the better alkali and isopropanol resistance. If the hydrogen bonds are not compact enough, the alkali or isopropanol solution will erode the part lack of the bonds. After the plate dipped in the alkali or isopropanol solution, the loosening of the coating layer brings badly effect on the abrasion resistance.

The scheme of phenomenological description was shown in Figure 7.[12,13]

When the photosensitive coating was dipped in alkali solution, it will form penetration zone on the surface of the coating first. If the alkali or isopropanol solution dissolved the photosensitive coating it must pass through penetration zone (a penetration process). The process was fulfilled by anion from novolak resin. It was the anion that forms hydrophilic point. In this process the decision step was the diffusion speed of the cations. Hinsberg[14,15] considered the dissolution speed formula of the unexposed sensitive coating in alkali solution was as following:

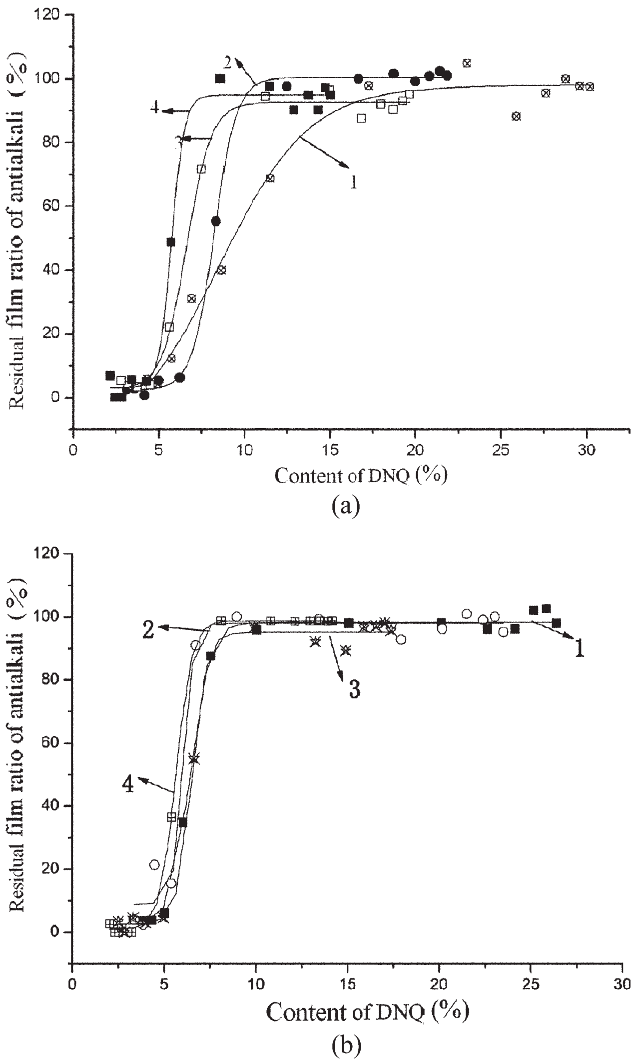

Figure 5 (a) Content of DNQ and alkali resistance residual film ratio, PA resin esterification degree: Graph 1 (65.7%), Graph 2 (33.6%), Graph 3 (28.9%), and Graph 4 (20.2%). (b) Content of DNQ and alkali resistance residual film ratio, Novolak esterification degree: Graph 1 (37.2%), Graph 2 (30.7%), Graph 3 (19.7%), and Graph 4 (15.0%).

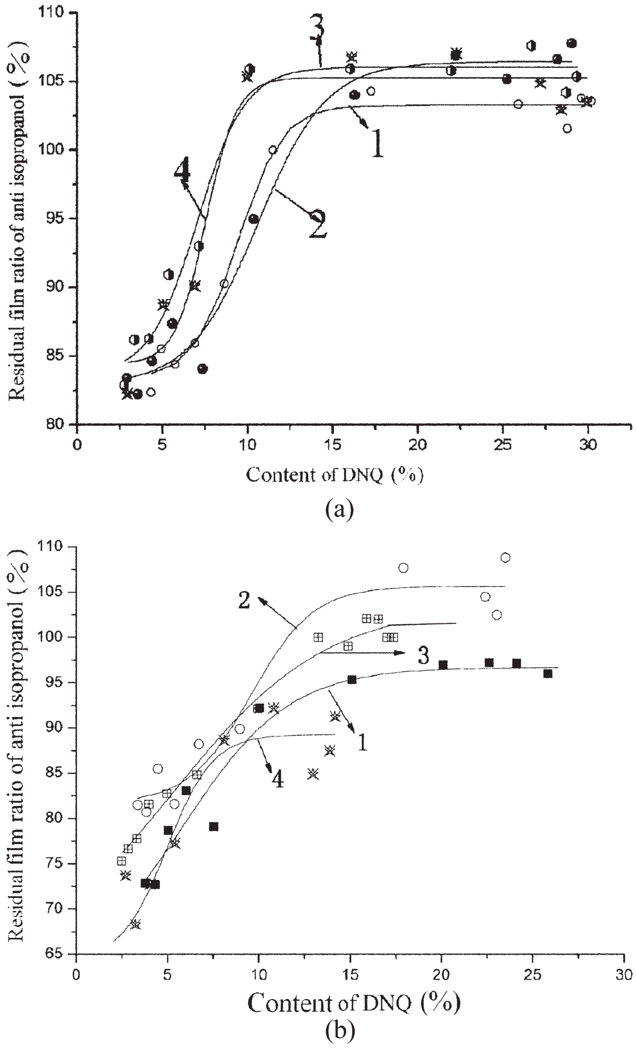

Figure 6 (a) Content of DNQ and isopropanol resistance residual film ratio, PA resin esterification degree: Graph 1 (65.7%), Graph 2 (33.6%), Graph 3 (28.9%), and Graph 4 (20.2%). (b) Content of DNQ and isopropanol resistance residual film ratio, Novolak esterification degree: Graph 1 (37.2%), Graph 2 (30.7%), Graph 3 (19.7%), and Graph 4 (15.0%).

$$R_0 = 2.3 \times 10^5[Na^+][OH^-]^{3.7}$$

In the molecular process binder resin in the photosensitive coating contains phenolic hydroxyl which will solve in alkali solution.

The process decision step for isopropanol is similarity rule. In the photosensitive coating, PAC in high esterification degree prefers to aggregate. So the binder resins which are not formed hydrogen bond will be solved by alkali or isopropanol solution. Once the binder resins are eroded off, the layer will be loosened. For PAC in low esterification degree the equably dispersing hydrogen bond will form. This increases the anti alkali and anti isopropanol ability, effectively.

Effect of abrasion resistance and imaging performance

There were many methods to evaluate abrasion resistance, such as dry grinding, damp grinding, and nick, etc.,[16] but these methods can not reflect the abrasion resistance exactly.

A new efficient method depicted as evaluation methods B was used to get the residual film ratio of abrasion resistance. The same plate was applied in practical printing and the abrasion resistance was checked. It was found that the experimental results were very similar to the practical abrasion resistance results. Through the experiment, it can be seen that the abrasion resistance was affected not only by molecular weight and structure of binder resin but also by the content of DNQ groups. Hydrogen bonds have the same effect on abrasion resistance as alkali and isopropanol resistance do. If the coating have compact and enough hydrogen bonds abrasion resistance will be strong. When the residual film ratios of alkali resistance and isopropanol resistance got to 99% abrasion resistance was excellent.

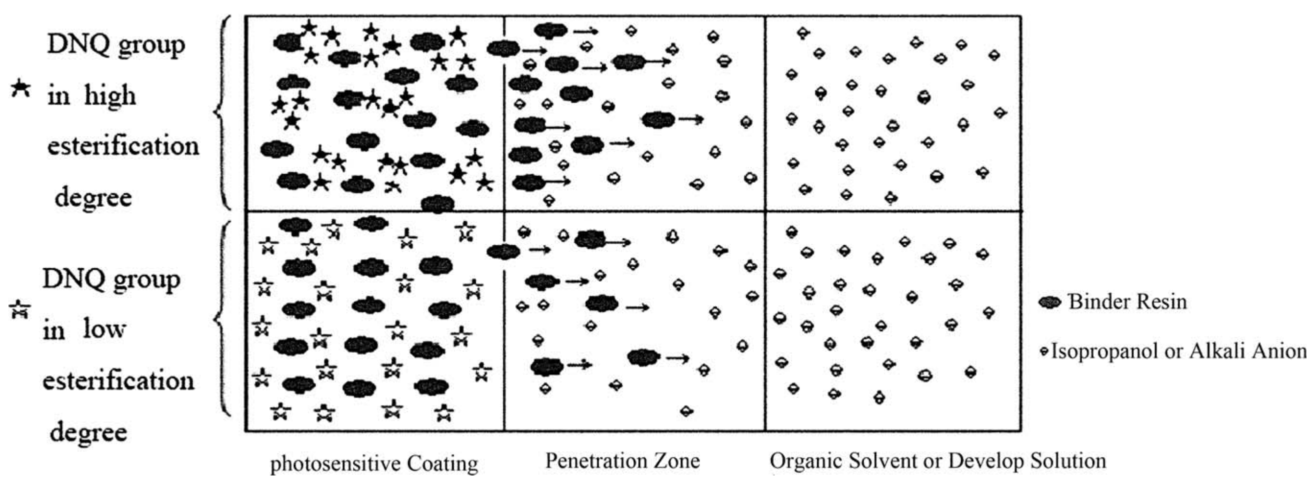

Figure 7 Dissolve process of photosensitive coating layer in alkali or isopropanol solution.

Imaging experiments indicate that with the increase of content of DNQ groups the sensitivity will decrease. On the contrary, with the decrease of the content of DNQ groups, the sensitivity will increase. So we had to better adjust the content of DNQ groups to 20–30% by changing the esterification degree of PACs. The excellent coating with high sensitivity (about 80 mJ/cm^2), high resolution (2–99% dots, 4 μm line), and better abrasion resistance (20–30 ten thousand print) can be reached.

CONCLUSIONS

Through the systematical experiments the relationship between the content of DNQ groups and the properties of photosensitive coating has been explored. The properties are affected not only by the content of DNQ groups but also the intensity of hydrogen bonds among DNQ groups and binder resins. The proper content of DNQ groups (about 20–30%) makes photosensitive coating have high sensitivity (about 80 mJ/cm^2), high resolution (2–99% dots, 4 μm line), better abrasion resistance (20–30 ten thousand print). The results are important and useful in lithography technology.

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