Study of Binder Resins Used in Presensitized Lithographic Printing Plate

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In this paper, through esterifying reaction of poly(styrene-co-maleic anhydride) resin with hydroxyethyl acrylate, acryl group and free carboxylic acid are introduced into the side chain of resins. So the developing speed in alkaline solution and photosensitive properties are improved. Through comparing five kinds of resins, a good result was obtained. The photosensitivity, resolution and halftone dot repetition of printing plate used A-3 resin have 6.05 mJ/cm^2 , $4 \mu\text{m}$ and 2% respectively.

Keywords: binder resin, ring-opening reaction, photopolymerization

1. Introduction

The presensitized plates of photopolymerization have many virtues, such as high sensitivity, long printing runs. In recent years a great interest has been focused on these materials, especially their application of computer to plate in printing industry[1-3]. The binder resin is an important component, it influences mechanical properties and developability of printing plate. There are two types of binder resins, one liner resin without unsaturated group, the other with unsaturated group at the end of main chain and side chain[4]. In this paper we adopted modified poly(styrene-co-maleic anhydride) resin by hydroxyethyl acrylate. Through esterifying reaction, acryl groups were introduced into the side chain of resins and then primary binder resins were turned into functional resins. We also studied the influence of different esterification number to developability, sensitivity, resolution and halftone dot repetition.

2. Experimental

2.1 Synthesis of reactive resins (A series resins)

Five grams poly(styrene-co-maleic anhydride) (PSMA), 0.1g imidazole, and 0.05g hydroquinone were dissolved in 120ml methylethylketone(MEA). Then hydroxyethyl-acrylate(HEA) was dropped into the flask. The solution was reacted for 5 hour at $60\text{--}65^\circ\text{C}$, and then poured into a large amount of 5% aqueous solution of acetic acid to precipitate the reactive resin[the half-ester of poly(styrene-co-maleic acid) by HEA]. The resin was obtained by filtration and purified by dissolving in MEK and precipitating from aqueous solution of acetic acid. The purification was repeated twice, followed by vacuum drying to constant weight.

2.2 Measurement of acid value and alkali solubility

(1) Using Cresol red as the indicator, titrating

with 0.1M KOH-EtOH solution.

(2) The solution prepared according to Table 1 was coated on 2.5cm×15cm aluminum plates that have been electrolyzed and oxidated, followed by drying at 100 °C for 2 minutes, and then 1% polyvinyl alcohol (PVA) solution was coated and dried at 100 °C for 2 minutes. Using 21-step stouffer wedge as the mask, the plate was exposed to a light of 1KW high-pressure Hg lamp positioned at a distance of 10 centimeters for 10 seconds. After imagewise exposure, the plate was developed with a solution of 5% Na₂CO₃ at 25 °C for 30 seconds. After washing with water, the image was observed.

2.3 IR spectrum analysis of A series resins

Carry IR spectrum analysis on A series resins with PERKIN-ELMER 983G IR spectrum analysis instrument.

2.4 Photosensitivity measurement of A series resins

2.4.1 Measurement of step

The same procedure as described in section of 2.2(2) was repeated. Then the photosensitivity was calculated. The photosensitivity (E , mJ/cm²) was defined as the minimum exposure energy insolubilizing the layer, and is calculated

$$E = I_0 \times T \times t$$

where I_0 is the incident light intensity(mJ/cm²s), T is the transmittance of the step at which the

photosensitive layer begins to be insolubilized and t is exposure time(s).

2.4.2 Exposure experiment of resolution signal strip

The same procedure as described in section of 2.2(2) was repeated, except for using the resolution and halftone dot signal strip in place of 21-step stouffer wedge.

3. Results and discussion

3.1 Analysis of acid value and alkali solubility

A series resins were synthesized according to different molar ratio. The results about titration of 0.1M KOH-EtOH solution and solubility in 5% Na₂CO₃ solution were observed, as shown in Table 2.

From the results, it can be obtained that through using HEA, the resins were improved. Because of the ring-opening reaction of some anhydrides, they gained free carboxylic acids and then advanced the developing speed in alkaline solution. The ring-opening reaction of some anhydrides was shown.

Table 1 Makeup of alkali solubility test

Makeup Weight%	Resin	Polyfunctional acrylate	Biimidazole co-photoinitiator
	20	75	20

Table 2 The results of acid value and alkali solubility

No.	Molar ratio		Acid value	Alkali solubility
	PSMA	HEA		
A-1	1.00	0	316	Difficult
A-2	1.00	0.15	300	Common
A-3	1.00	0.30	288	Easy
A-4	1.00	0.45	264	Easy
A-5	1.00	0.60	246	Easy

3.2 Analysis of IR spectrum of A series resins

IR spectras of A-1 and A-5 were shown in Figure 1.

Figure1. IR absorption variation of A series resins

From these spectras, it can be observed that the ring-opening reaction was taken place indeed. The 1770cm^{-1} frequency of anhydro carbonyl stretching vibration ($\nu_{\text{C=O}}$) in spectra (a) had become the 1730cm^{-1} frequency of carboxyl and ester carbonyl stretching vibration and the 1770cm^{-1} frequency of anhydro carbonyl stretching

vibration in spectra (b). It can also be found that there were the 1220cm^{-1} frequency of ester symmetrical C-O bond stretching vibration [$\nu_{\text{s(C-O-C)}}$] and the 1080cm^{-1} frequency of ester anisomeric C-O bond stretching vibration ($\nu_{\text{as(C-O-C)}}$) in spectra (b). These all proved that some anhydrides in primary resins had been reacted and built some carboxyls and esters.

3.3 Analysis of A series resins photosensitivity

(1) The step measurements of A-1, A-2, A-3 and A-5 were made, and then all E value were calculated. The results were shown in Table 3.

The results indicated that the photosensitivity was improved about one time at ratio 1:0.15 than that at ratio 1:0, but the photosensitivity without much variety at ratio more than 1:0.3. There were two reasons:

- (i) Through opening the ring of anhydride and linking HEA, the resins increase unsaturated bonds and then advance photocrosslinking.
- (ii) Through opening the ring of anhydride and linking HEA, the side chains of resins formed free carboxylic acids and then accelerate development in alkaline solution.

(2) Analysis of exposure experiment results of resolution signal strip

Exposure experiments of A series resins were made. The results were shown in Table 4.

The results indicated that the resolution was improved obviously along with the increase of HEA amount. It was the highest at A-4 and had a little decline at A-5. The results were almost consistent with the results of step measurements.

Table 3 The results of A series resins photosensitivity

No.	Molar ratio		E (mJ/cm^2)
	PSMA	HEA	
A-1	1.00	0	11.35
A-2	1.00	0.15	6.66
A-3	1.00	0.30	6.05
A-5	1.00	0.60	6.05

Table 4 The resolution and halftone dot repetition of A series resins

No.	Molar ratio		High-exposure	Light-exposure	Halftone dot repetition
	PSMA	HEA			
A-1	1.00	0	20 μ m	20 μ m	>5%
A-2	1.00	0.15	10 μ m	10 μ m	2%
A-3	1.00	0.30	4 μ m	4 μ m	2%
A-4	1.00	0.45	7 μ m	7 μ m	2%
A-5	1.00	0.60	7 μ m	7 μ m	2%

4. Conclusion

It can be concluded that through using HEA, some anhydrides of PSMA resins are carried through the ring-opening reaction. So they obtain some free carboxylic acids and unsaturated esters. These not only advance the developing speed in alkaline solution, but also enhance photosensitivity, resolution and halftone dot repetition.

Acknowledgments

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