Tung Oil-Pyrogalllic Acid Resin (TPA) and Its Application to a Positive Photoresist

Yu Shangxian, Gu Jiangnan, Wang Fang and Fu Xiaoyuan
Institute of Application Chemistry, Beijing Normal University
12 College South Road, Beijing, China

Luo Ting
Beijinig Univeristy of Posts and Telecommucations

A tung oil-pyrogalllic acid resin(TPA) was synthesized successfully. After that, an ester condensation reaction between TPA and 1,2-naphthoquinone 2-diazide 5-sulfochloride(NAC-5) was carried out resulting in the naphthoquinone diazide sulfonated tung oil-pyrogalllic acid resin(NAC-5-TPA) as shown in formula[1]:

It can be used for a positive resist developed by alkaline solutions. The minimum quantity of exposure energy required for the colour change of this resist and the quantity of exposure energy required for preparing the plate were 23.9mJ/cm² and 320mJ/cm² respectively. It has considerably high resolution power and acid and organic solvent resistances.

Quantum chemical studies on the mechanism of the reaction of introducing pyrogalllic acid into tung oil have been performed, the results obtained are as follows: When oxalic acid was used as a catalyst, the reaction is mainly orbital controlled. The research on the reaction kinetic of UV-photolysis process for NAC-5-TPA resin indicated that the photolysis reaction follows the rule of a first-order reaction and is a pure photolysis process.

1. Introduction

The synthesis of tung oil-resorcin resin has been reported⁽¹⁾. Some photosensitive characteristics of the resin used as a negative photoresist has been determined as well⁽²⁾. In order to find the probability and relative activity of introducing phenols into tung oil, we made some relevant calculations using quantum chemistry method on the basis of the foregoing studies. The results showed that pyrogalllic acid not only has more net charges at the 4th and 6th positions of its benzene ring, but also possesses a highest HOMO energy which is tens of times higher than that of other phenols. Therefore we concentrated all our attention and successfully synthesized tung oil-pyrogalllic acid resin, from which, and together with 2,1,5-naphthoquinone diazide sulfochloride(NAC-5), an ester condensation reaction was carried out resulting in a product(NAC-5-TPA) as shown in formula [1]. Thus, a pretty good positive resist was obtained.

2. Experiments and results

(1) Synthesis of tung oil-pyrogalllic acid resin(TPA)

87.0g(0.1mol) of refined tung oil, 63g(0.5mol) of pyrogalllic acid and 2.7g(0.03mol) of oxalic acid were added into 40-50g of dioxane solvent contained in a four-necked round bottom flask. The flask was then heated to 100°C with stirring and N₂ protection for 1 hour and after that, the reaction was carried out at 100-120°C under reflux for 3 hours. Then about 100ml of No.200 solvent gasoline was added into the flask with thorough stirring for 30 min. Then the content in the flask was slowly poured into about 1000ml of distilled water held in a beaker. The light yellow resin precipitated. After the oil layer and water being removed the resin was washed by hot distilled water three times to remove the unreacted oil-soluble substances and pyrogalllic acid. The resin was dissolved in acetone or dioxane and then the solution was poured into a three-necked flask in which the water and solvent were distilled off under stirring and N₂ protection. Thus the product, 140g of refined tung oil-pyrogalllic acid resin(TPA), was obtained. The yield was 93.03% while the introducing rate was around 84%, i.e. on average approximately 4.2 molecules of pyrogalllic acid were introduced into each tung oil molecule. The IR spectrum of the product was determined. The absorption of phenol hydroxyl group at 3360cm⁻¹ and that of benzene ring at 1605cm⁻¹ were obvious, while that of the conjugate double bonds in tung oil at 3010cm⁻¹ almost disappeared thoroughly.

The TPA resin was soluble in alcohol, acetone, dioxane, THF, DMF, cyclohexanone, ethyl cellosolve, n-butyl acetate, and alkali solution. It was insoluble in gasoline and benzene. It was a transparent yellow solid with stickability and a soft point lower than 30°C. Its viscosities at different concentrations are shown in Fig.1.

(2) Synthesis of naphthoquinone diazide sulfonated pyrogalllic acid(NAC-5-TPA)

14.3g(0.01mol, hydroxyl 0.135mol) of TPA resin, 20g(about 0.07mol) of 2,1,5-naphthoquinone diazide sulfochloride(NAC-5) were added into 120ml of acetone or dioxane contained in a four-necked round bottom flask. After both were dissolved with stirring at 30-40°C, 37g of 10% solution of Na_2CO_3 were added at 40°C, 1-2 drop per second. The reactants were continually stirred for 1-2 hours. Then the content in the flask was poured into ten times its weight of distilled water with stirring and a solid was precipitated which was separated by vacuum filtration and washed 3-5 times, then dried in vacuum until its weight became constant. Thus 26.6g of dry, yellow, powdery product was obtained with a 84% yield. Its IR spectrum is shown in Fig.2. The absorption of hydroxyl at 3380cm^{-1} disappears obviously. The absorption of quinone diazide at 2150cm^{-1} and that of aromatic ring at about 1600cm^{-1} appear or increase considerably. These indicate the product is NAC-5-TPA, the very thing we expected.

NAC-5-TPA resin was soluble in acetone, cyclohexanone, dioxane, ethyl cellosolve, ethyl cellosolve acetate, n-butyl acetate, THF and DMF. It was insoluble in hexane, gasoline, water and dilute alkali solution. The viscosities of 20% and 25% solution of NAC-5-TPA resin in ethyl cellosolve at 25°C were 9.8 cp and 14.5 cp respectively.

Fig.1. Change of viscosity of TPA with concentration (25°C)

Fig.2. IR spectrum of NAC-5-TPA (coating method)

(3) Preparation of the photoresist

- (A) Photopolymer(P): NAC-5-TPA resin mentioned above (solid content 25-35%)
- (B) Binder resin for film formation(B): m-cresol novolac or t-butyl novolac (solid content 75-65%)
- (C) Dye: crystallized violet or alkaline blue 80 (solid content <1%)
- (D) Solvent: ethyl cellosolve etc. (the total solid content of the photoresist solution prepared being 10-20%)

The photoresist solution was filtered by a press filter with polytetrafluoroethylene filter film having pores $0.2\text{-}1\mu\text{m}$ in diameter in a clean-room.

(4) Some properties of the photoresist

The viscosity of a 15% solid content solution of the photoresist in ethyl cellosolve at 25°C was 8.0 cp.

A 2 μ m thick layer of coated photoresist (B/P=2.5) on aluminium film was immersed in corresponding developer, then the rate of the residual film(R) was determined (Table 1).

Table 1. Rate of the residual film (immersed for 5 min)

Developer	0.6%NaOH and 1.2%KCl	2%Na ₂ SiO ₃	2%(CH ₃) ₄ NOH	2%Na ₃ PO ₄
R non-exposure (%)	93.5	94.8	96.8	99.0
R exposure (%)	0	0	0	8.4

Its acid and organic solvent resistances using the same method are given in table 2.

Table 2. Organic solvent and acid resistances

Organic solvent or acid	Xylene	Petroleum ether	Solvent gasoline	40%FeCl ₃ (40°C)	85%H ₃ PO ₄ (50°C)
R (%)	99.5	99.5	99.5	100	100

The photosensitivity of the photoresist (B/P=2.5) was determined. The minimum quantity of exposure energy required for the colour change and the quantity of exposure energy required for preparing the plate were calculated to be 23.9 mJ/cm² and 320mJ/cm² respectively.

The effect of B/P on the resolving power before and after etching aluminium is given in table 3. The photoresist was coated on aluminium and formed a layer 2 μ m thick during the determination.

Table 3. Resolving power (line width) before and after etching Al film

B/P	1.0	1.5	2.0	2.5	3.0
Before etching (μ m)	2.0	1.5	1.0	1.0	2.0
After etching (μ m)	5.0	5.0	3.0	3.0	5.0

Light source: metal-halide lamp (1.78mJ/cm²sec)

Developer: 4% Na₂SiO₃

Etching agent: 85% H₃PO₄ (50°C)

3. Discussion

(1) The mechanism of the reaction between pyrogalllic acid and tung oil

The reaction between pyrogalllic acid and some conjugate double bonds of tung oil, macroscopically, is almost the same as the reaction of introducing catechol⁽³⁾, resorcin and m-cresol⁽⁴⁾. The mechanism is shown in Fig. 3. That is, tung oil forms a structure containing a positive carbon ion which is an electron receptor (shown as B) while pyrogalllic acid acts as an electron donor. Thus, reaction (C) and (D) take place and (E) is produced.

Fig.3. Scheme of the reaction mechanism of introducing phenols

Microscopically, it is necessary to make clear whether the reaction is net charge or orbital controlled.

The net charges and energies of the highest occupied orbitals (HOMO energy level) for several phenols are given in table 4. We can see for pyrogallol the net charge values are bigger at the 4th and 6th positions on benzene ring. Yet these net charges are on the lower side in active sites data of other phenols given in table 4, while its HOMO energy level is about tens of times higher than that of other phenols. It is realized experimentally that when oxalic acid being used as the catalyst, the introducing rates of pyrogallol and resorcin are much higher than that of other phenols. The initial rates of introducing them are ten times or even greater than that of phenol. Therefore it is apparent that the reaction of introducing pyrogallol is mainly orbital controlled.

Table 4. Net charges and energies of HOMO energy level for several phenols

PHENOLS					
HOMO (eV)	-8.8923	-8.8838	-8.5837	-8.7479	-0.1354
NET CHARGE (e)	2	-0.1425	-0.1268		-0.2297
	3	-0.0185		-0.1142	
	4	-0.0961	-0.0760	-0.0548	-0.1232
	5	-0.0280	-0.0322	-0.0528	-0.0029
	6	-0.0847	-0.0803	-0.1143	-0.1218

(2) Kinetics in UV-photolysis process for NAC 5-TPA resin

A series of IR spectra of NAC-5-TPA resin were determined under UV irradiation. The changes of the absorption of naphthoquinone diazide group at 2150cm^{-1} were measured. A plot of $\text{Log } D_t$ against t is shown Fig.4. which is a straight line (because D_t depends directly on the concentration C_t of the absorption group). It is clear that the reaction follows the rule of a first-order reaction and is classed with pure photolysis reaction.

Fig.4. A plot of $\text{Log } D_t$ - t for UV-photolysis process

4. References

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