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Synthesis of an Environmentally Friendly Phenol-Free Resin for Printing Ink

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Phenol-free resin was synthesized and its printing ink properties were investigated. The phenol-free resin was produced by esterification of poly phthalate and Diels-Alder adduct of rosin anhydride. Compared to rosin modified phenolic resin, eco-friendly phenol-free resin showed better vehicle properties in terms of gloss, yellowing, runability, and storage stability. The results suggest the utility of phenol-free resin instead of conventional rosin modified phenolic resin.

Key Words : Diels-Alder reaction, Condensation, Phenol-free resin, Printing ink, Poly phthalate

Introduction

Lithographic offset printing ink is composed of pigment, vehicle, and additives. Organic and inorganic pigments are used for ink color. These pigments are transported and fixed to paper by the vehicle, which is composed of resin, oil, and hydrocarbon solvents. Rosin modified phenolic resin **1** is generally used as the resin of vehicle components (Fig. 1).[1] Rosin modified phenolic resin **1** is synthesized by the reaction of resol and rosin esters. Resol is prepared by polymerization of alkyl phenols and formaldehyde, and has a methylene linked linear structure. Rosin esters are prepared by the esterification of natural rosin and polyhydric alcohols (Fig. 1). Rosin modified phenolic resin has a high molecular weight and good solubility in organic solvents.[2] Printing ink made of rosin modified phenolic resin shows good printability in terms of transfer, drying, and resistance in high-speed (10,000-20,000 sheet/min) printing presses.

Although rosin modified phenolic resin is a necessary component for assuring good printability,[3] alkyl phenols and formaldehyde cause various problems for human health and the environment. Alkyl phenols, including bisphenol A, are a suspected endocrine disruptor.[2a] For example, use of nonyl phenol has been prohibited for printing ink vehicles since 2010. Formaldehyde is classified as a potent carcinogen, and use of formaldehyde in industry is regulated. Because of these concerns, environmentally friendly resins that replace phenolic resin need to be developed. Some research has been reported on this topic. Japanese researchers have presented methods for the synthesis of formaldehyde free resin.[4] However, the reported printing ink properties are not satisfactory.

One important synthetic reaction of rosin is the formation of adducts with dienophiles, such as maleic anhydride or acrylic acid, *via* the Diels-Alder reaction at temperatures of 180-210 °C. These adducts have been used to prepare vinyl ester resins for coating applications[5a] or water soluble non-ionic sulfactants.[5b] However, this process has not been reported with the polyester resin of rosin adduct used as a vehicle for printing inks. The aim of this work is to use rosin adducts to produce phenol and formaldehyde-free resin for printing inks. We report the synthesis and characterization of polyester resin obtained by reacting rosin maleic anhydride adduct, polyester of phthalic anhydride, and glycerol. Another goal of the present work is to evaluate the prepared polyester resin derived from rosin as a vehicle for lithographic offset inks.

Experimental

Materials. Phthalic anhydride (PA), glycerol, maleic anhydride (MA), magnesium oxide (MgO), and xylene were purchased from Aldrich Chem. Co. Rosin acids (RA) were separated and purified as described previously[6] to give an acid number (a.n.) of 183 mg KOH g^{-1}. All chemicals were used as received. Infrared spectra were recorded on a Bruker Vertex 70. ^1H NMR spectra were recorded on a Varian at 300 MHz in $CDCl_3$ (δ 7.20 ppm).

Synthesis of Polyester Adduct (5). A 0.5 L reaction flask equipped with a thermometer, Dean stark separator, condenser, mechanical stirrer and N_2 inlet was charged with

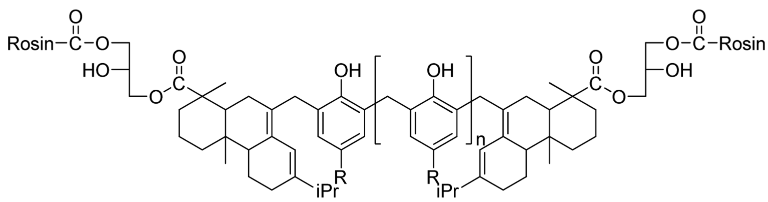

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Figure 1. Structure of a typical rosin modified phenolic resin.

phthalic anhydride (**2**) (17.8 g, 0.12 mol), glycerol **3** (22.2 g, 0.24 mol), and MgO (0.1 wt % on the basis of the total weight of reactants). The reaction mixture was heated to 200 °C for 12 hrs, and the reaction was stopped when the acid number was 20 mg KOH g^{-1}. This crude mixture of poly phthalate **5** was used for the next step without purification.

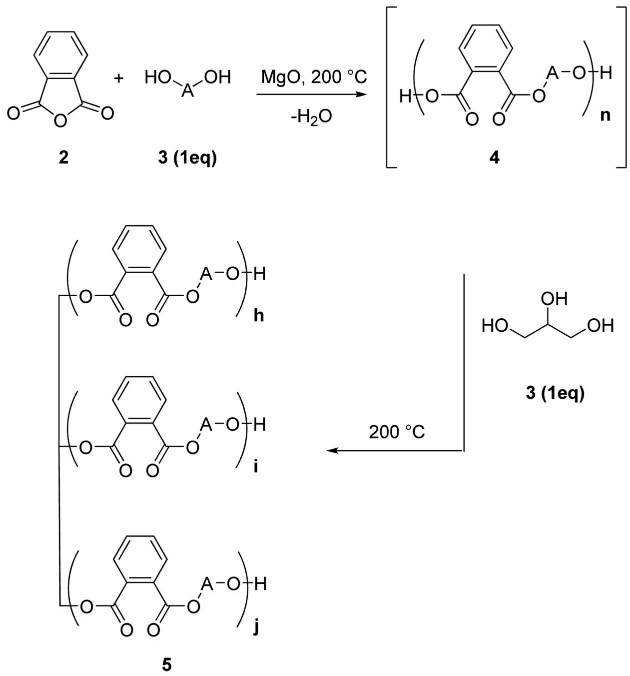
Synthesis of Phenol-Free Resin (8). A 1 L reaction flask equipped with a thermometer, Dean stark separator, condenser, mechanical stirrer, and N_2 inlet was charged with Rosin **6** (a mixture of abietic and levopimaric acid[5b]) (52.4 g, 0.17 mol) and maleic anhydride (7.6 g, 0.08 mol). The reaction mixture was stirred at 180 °C for 2 hrs. Poly phthalate **5** was then slowly added and the reaction mixture was stirred at 260 °C for 2 hrs. The reaction was stopped when the acid number was 20 mg KOH g^{-1}. Xylene 5% was added as solvent and removed from the final product by heating under reduced pressure.

Measurement of Resin Properties. An acid value is determined by directly titrating a known weight of the sample dissolved in alcohol. Acid value is normally expressed in terms of the milligrams of KOH required to neutralize 1 g of the sample. Resin viscosity was measured by a Laray viscometer. The molecular weight (Mw) was evaluated by gel permeation chromatography (Agilent) with a differential refractometer.

Evaluation of Vehicle Properties. Vehicle properties, including gloss, yellowness, runability, and storage stability, were evaluated for two samples. The gloss of vehicles was measured as the ratio of reflected to incident light for the sample. Reflected light is measured by a photocell set at the corresponding angle to receive reflected light. Using the RI printability tester, 0.1 mL of vehicles was printed on the same paper. After drying the vehicle, gloss was measured. Higher gloss values are considered better results. The yellowness of samples was evaluated by the same method as gloss measurements. After a UV curing machine passed on the samples at a speed of 30 m/min 10 times, b values were measured by spectrophotometer. The Ink-O-meter is a machine that simulates the rollers on a press and measures the force required to split an ink film at press speed. A counterweight on a bar connected to the rider roller measures the force required to keep the rider roller in place. This force is referred to as a tack. Runability was evaluated by the tack value obtained with the Ink-O-meter at 800 rpm. The measured time was 10 minutes. Small changes in tack value are desirable for ink properties. Storage stability was evaluated from the viscosity detected by a Laray viscometer during a period of 15 days. Small changes in viscosity indicate a more stable sample.

Results and Discussion

In the present investigation, new eco-friendly resin was synthesized as a vehicle for ink. To imitate the structure of phenolic resin **1**, a phenyl group linked backbone is essential. For this purpose, we considered poly phthalate **5**, which is the condensation product of phthalic anhydride **2** and



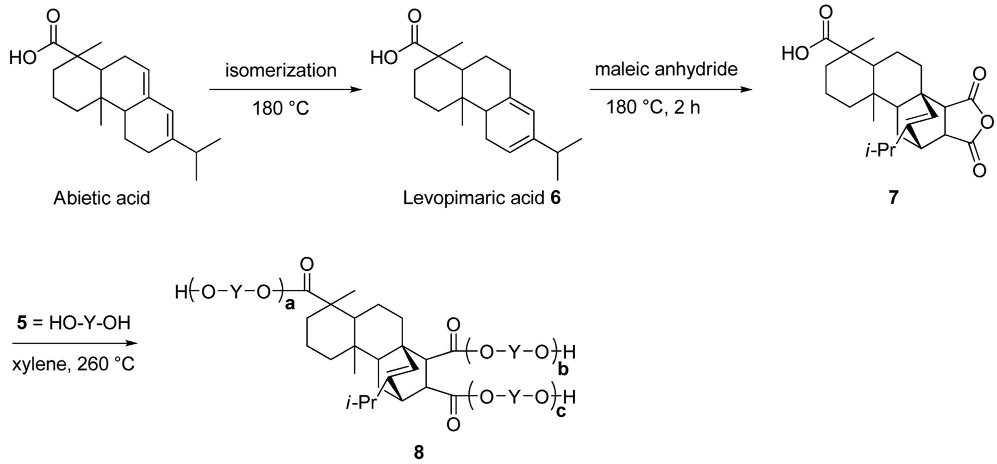
Scheme 1

glycerol **3**. In the presence of catalytic magnesium oxide, phthalic anhydride was reacted with glycerol to provide poly phthalate **5** (Scheme 1). Poly phthalate **5** was used as a polyhydric alcohol for the condensation reaction with the acid part of rosin.

The Diels-Alder adducts of rosin acids and maleic anhydride or acrylic acid proved to be suitable for polycondensation reactions. Rosin acid exists in various isomers, including as abietic and pimaric acid. Although levopimaric acid **6** is the only isomer that can undergo Diels-Alder reactions, abietic acid is present as a major component of the total rosin acids. However, other isomeric rosin acids can assume the structure of levopimaric acid **6** through isomerization at high temperatures without using solvents.[7] On heating at 180 °C, abietic acid isomerizes to levopimaric acid **6**, which reacts with maleic anhydride to form Diels-Alder adduct **7** (Scheme 2) as an *endo*-form. Although several types of Lewis acid catalysts, such as *p*-toluene sulfonic acids, H_3PO_4, and heterogeneous acid, have been known to accelerate the Diels-Alder reaction,[5b,8] at elevated temperature the reaction proceeded enough to complete the preparation of rosin anhydride adduct **7**.

Finally, esterification of poly phthalate **5** and modified rosin anhydride **7** at 260 °C provided phenol free resin **8**. The acid value of a resin has significant effects on its stability, printability, flow, gloss, and surface wetting characteristics. Therefore, polymerization was performed until the acid number was 20 mg KOH g^{-1}.

The chemical structure of prepared polyester **8** was confirmed by IR and ^{1}H NMR analysis. The characteristic bands in the IR spectra of **8** are observed at 3509 cm^{-1} as a sharp strong band (γ_{OH} end group), at 1730 cm^{-1} as a sharp strong band ($\gamma_{C=O}$ in COO ester group), at 1476 cm^{-1} as a sharp



Scheme 2

Table 1. Results of Resin Properties

Sample properties	Rosin modified phenolic resin	Phenol-free resin
Acid value (mg)	18	20
Viscosity (sec)	25-26	23-24
MW (g)	~70,000	~70,000

Table 2. Results of Vehicle Properties

Sample properties		Rosin modified phenolic resin	Phenol-free resin
Gloss (%)		50	60
Yellowness (b value)		3.53	1.19
Runability		1.0	0.3
Storage stability (poise, 25 °C)	just made	400	400
	1 day	485	430
	7 days	520	480
	15 days	530	530

medium band (double bond in the hydrophenanthrene moiety), and at 1105 cm^{-1} as a broad strong band (γ_{C-O} of ester group). The ^{1}H NMR spectra of **8** show signals at 6.60-7.23 ppm (aromatic protons from the aromatic unit), 5.07 ppm (H of double bond), 3.50-4.60 ppm (-CH_2OCO, -CHOCO), 2.82 ppm (-CHCOO), 2.23 ppm (-OH of alcohol), and 0.69-2.22 ppm (aliphatic protons of cyclic group).

The synthesized phenol-free resin was a glossy and light yellow solid. Weight average molecular weight was quantified to be 70,000. The viscosity of phenol-free resin was similar to that of phenolic resin (Table 1).

In the present investigation, newly synthesized phenolic-free resin was evaluated as a vehicle for lithographic offset inks. Vehicles for analysis of the new resin and phenolic resin were prepared by mixing 40 g rosin modified phenolic resin, 40 g phenolic-free resin, 20 g linseed oil, and 40 g aromatic-free type petroleum hydrocarbon solvents. For each sample, gloss, yellowing, runability, and storage stability were evaluated (Table 2). Phenol-free resin showed 60% gloss while rosin modified phenolic resin showed 50% gloss. In terms of yellowness (b value), phenol-free resin showed 1.19 and rosin modified phenolic resin showed 3.53. Discoloration of phenol-free resin was much better than that of phenolic resin. Runability results measured by the tack values at 800 rpm for 10 minutes also showed that phenol-free resin was a better vehicle. Storage stability was measured as viscosity by a Laray viscometer. At the time of preparation, viscosity values of 400 poise were observed for both samples. After one day, a value of 430 poise was observed for phenol-free resins while a value of 485 poise was observed for rosin modified phenolic resin. After one week, 480 poise was detected for phenol-free resin while 520 poise were detected for rosin modified phenolic resin. From these results, phenol-free resin is more stable for longer storage durations. These results prove that synthesized phenol-free resin performs better in all aspects than conventional rosin modified phenolic resin as a vehicle of lithographic offset inks.

Conclusion

Phenol-free resin was synthesized by reacting rosin maleic anhydride adduct and the polyester of phthalic anhydride and glycerol. Compared to conventional rosin modified phenolic resin, eco-friendly phenol-free resin showed better vehicle properties, such as gloss, yellowing, runability, and storage stability. The present study encourages the application of new phenol-free resin as a vehicle for lithographic offset inks.

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