Reactions of Phenols with Tung Oil

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Synopsis

As regards the aromatic ring substitution reactions of various kinds of phenols with tung oil under acidic conditions, an investigation was made on the influences of the kinds and substitution positions of alkyl groups of the phenols on the reaction. Alkyl phenols increased in reactivity in the order of ortho, meta, and para in the position of alkyl substitution. This can be attributed to the preferential para addition of tung oil to the phenol nucleus as reported in the previous paper. The larger alkyl group gave increased reactivities in the reactions of alkyl phenols with tung oil. This has something to do with compatibilities between phenols and tung oil (differences in solubility parameter between phenols and tung oil).

INTRODUCTION

Phenolic resins[1] used in industry are frequently modified with tung oil so as to have flexibility. Phenols are addition-reacted with tung oil via the conjugated triene structure of α-eleostearic acid, the triglyceride of which is the main component of tung oil, and then reacted with formaldehyde on the phenolic nucleus to yield flexible phenolic resins.

A number of papers have reported on the reaction products between tung oil and phenols, but they have reported little on the reactions between tung oil and phenols.[2–17] The previous report[18] discussed about on the reaction of 3-methyl phenol with tung oil as to the reacted amount and bond position of 3-methyl phenol on the basis of the results of IR, NMR, and HLC analyses. In this report, discussion is made about the influences of the kinds and substitution positions of alkyl groups of phenols on the reactions between tung oil and various kinds of phenols.

EXPERIMENTAL

Reagents. Tung oil of an industrial grade from China was used. Other reagents used are all of the first reagent grade.

Analytical Method

Infrared Analysis (IR). For infrared analysis of samples, Hitachi Co., IR Model 285 was used. An appropriate amount of each sample applied to a thalium plate was subjected to the measurement.

High-Speed Liquid Chromatographic Analysis (HLC). Toyo Soda Co., HLC Model HLC-802, in which one column of TSK G-3000H_6, three columns of TSK G-2000H_6, and RI detector were employed, was used. THF was used as the elution solvent at flow rate of 1.5 mL/min. 100 mg of each sample of tung

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oil and phenols and 200 mg of each sample of the reaction products between tung oil and phenols were respectively accurately weighed in an Erlenmeyer flask with a ground-glass stopper, and dissolved in 10 mL THF.

Reaction of Phenols with Tung Oil. The predetermined amounts of tung oil and a phenol were charged in a 500-mL four-necked flask equipped with a stirrer, a thermometer, a dropping funnel, and a reflux condenser. Then 20% aqueous solution of *p*-toluenesulfonic acid was added dropwise to the mixture being stirred through the dropping funnel at about 25°C. After completion of the dropwise addition of *p*-toluenesulfonic acid, the flask was heated at 80°C for 1 h, and then it was cooled.

RESULTS AND DISCUSSION

Influence of Alkyl Substitution Position in Alkyl Phenols on Reaction

The influence of the alkyl substitution position in alkyl phenols on the reactivity with tung oil was examined by using 2-, 3-, and 4-methyl phenols. In Figure 1 are shown the results of HLC analysis of the reaction products obtained by reacting the methyl phenols with tung oil at a fixed methyl phenol-tung oil charging weight ratio of 7:3 under fixed conditions. In Figure 1 are summarized the reacted amounts of the methyl phenols per mol of tung oil which are calculated from the results of HLC analysis of the reaction products.

In Table I, it was confirmed that in all the reactions the unreacted tung oil did not remain, thus indicating 100% reaction of tung oil with methyl phenols. As demonstrated in Table I, the reactivity varied depending on the methyl substitution position of the methyl phenol. More specifically the reactivities of methyl phenols increased in the order of ortho, meta, and para in the methyl substitution position.

The previous report has revealed, on the basis of the analysis results of the

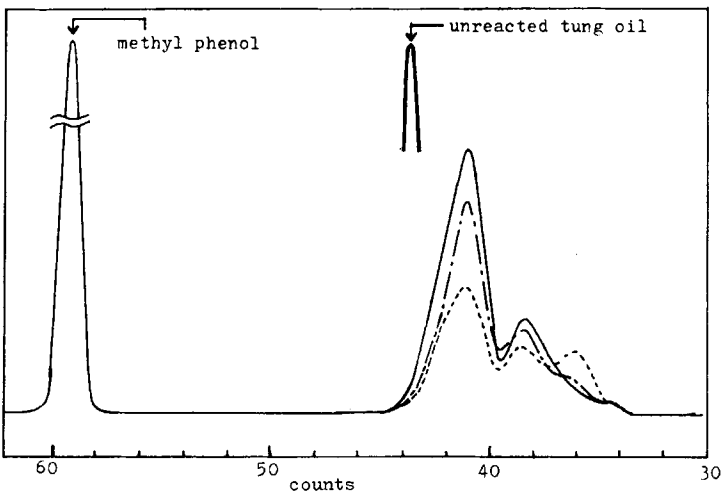

Fig. 1. HLC chromatograms of reaction products of methyl phenol with tung oil; (——) 2-methyl phenol; (·—·) 3-methyl phenol; (- - -) 4-methyl phenol.

TABLE I
Relationship between the Type of Methyl Phenol and the Reaction Molar Ratio of Methyl Phenols and Tung Oil

Type of methyl phenol	Charging molar ratio of methyl phenols to tung oil			Reaction molar ratio of methyl phenols to tung oil		
	Charging methyl phenols (mol)	Charging methyl tung oil (mol)	Methyl phenols/ tung oil molar ratio (mol/mol)	Reacted methyl phenols (mol)	Reacted tung oil (mol)	Methyl phenols tung oil molar ratio (mol/mol)
2-Methyl phenol	0.0129	0.00069	18.7	0.00308	0.00069	4.5
3-Methyl phenol	0.0129	0.00069	18.7	0.00242	0.00069	3.5
4-Methyl phenol	0.0129	0.00069	18.7	0.00175	0.00069	2.5

3-methyl phenol-tung oil reaction products, that tung oil reacts with 3-methyl phenol preferentially at the para position. This coincides with the results reported in this paper. More specifically, 2- and 3-methyl phenols with an active proton at the para position have higher reactivities than 4-methyl phenol with the para position occupied by the methyl group. Despite substantially the same activity of proton at the para position, a difference in reactivity between 2- and 3-methyl phenols may appear because of the effect of steric hindrance of the methyl group adjacent to the para position of 3-methyl phenol, when it is attacked by the attacking reagent, long chain macromolecular tung oil. Thus 3-methyl phenol has lower reactivity than 2-methyl phenol. Consideration must also be given to any possible influence, on reactivity, of compatibilities of tung oil with 2-, 3-, and 4-methyl phenols. However, the fact that the solubility parameters of 2-, 3-, and 4-methyl phenols are 12.5, 11.6, and 12.1, respectively, as against 8.5 in the solubility parameter of tung oil indicates that differences in solubility parameter between the methyl phenols may have little to do with the differences in reactivity.

Figure 1 demonstrates that of the reaction products the 2-methyl phenol-tung oil reaction product was lowest in average molecular weight, largest in amount of methyl phenol-tung oil adduct contained and smallest in amount of tung oil polymer contained. By contrast, the 4-methyl phenol-tung oil reaction product was smallest in amount of methyl phenol-tung oil adduct contained and largest in amount of tung oil polymer contained. As the amount of the reacted methyl phenol is larger, the average molecular weight of the product tends to be lower. This coincides well with the results reported in the previous report that, in the experiment carried out at varied charging molar ratios of 3-methyl phenol to tung oil, an increase in molar ratio of 3-methyl phenol reacted and to a lowering in molecular weight of 3-methyl phenol-tung oil reaction product.

Influence of Alkyl Group in Phenols on Reaction

The influence of the kind of alkyl group in alkyl phenol on their reactivities with tung oil was examined using phenol, 4-methyl phenol, 4-*t*-butyl phenol, and 4-nonyl phenol. In Figure 2 are shown the results of HCL analysis of the reaction products each obtained by reacting a phenol with tung oil at a fixed phenol–tung oil charging weight ratio of 7:3 under fixed conditions. Table II lists the amounts of phenols reacted with 1 mol of tung oil which calculated from the HLC analysis

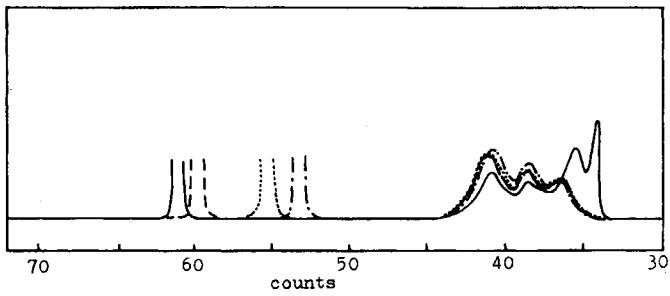

Fig. 2. HLC chromatograms of reaction products of alkyl phenol with tung oil; (—) phenol; (- - -) 4-methyl phenol; (·····) 4-*tert*-butyl phenol; (-·-) 4-nonyl phenol.

of the reaction products. In Figure 2, it was confirmed that in every case no unreacted tung oil remained, thus indicating substantial 100% reaction of tung oil. The amounts of phenols reacted with tung oil decreased in the order of 4-*t*-butyl phenol, 4-nonyl phenol, 4-methyl phenol, and phenol. Especially, phenol reacted in an extremely small amount, compared with the alkyl phenols.

In general, the easiness of chemical reaction depends on the mutual compatibility of reactants, the effect of steric hindrance of any bulky substituents of the reactants, and the influence of electron donability or acceptability of any substituents on the electron density on the carbon atom to be attacked. In the reactions discussed here in this paper, the compatibilities of phenols with tung oil seem to be significant in the easiness of reaction. Comparison between the reactants will be made in solubility parameter useful in evaluating compatibility.

4-Nonyl phenol, 4-*t*-butyl phenol, 4-methyl phenol, and phenol are 9.0, 9.6, 12.1, and 13.8, respectively, in solubility parameter as against 8.5 for tung oil. Thus compatibility with tung oil lowers in this order. Therefore, in this respect the easiness in attack of tung oil cation on the ortho position of phenol ring may decrease also in the same order. The order of actual reactivities of 4-nonyl phenol and 4-*t*-butyl phenol with tung oil was reversed perhaps because of the effect of steric hindrance of longer chain nonyl group of 4-nonyl phenol.

As discussed above, the mutual compatibility of reactants may explain that in principle a smaller group on the para position of a phenol led to a tendency

TABLE II
Relationship between the Type of 4-Alkyl Phenol and the Reaction Molar Ratio of 4-Alkyl Phenols and Tung Oil

	Charging molar ratio of methyl phenols to tung oil			Reaction molar ratio of 4-alkyl phenols to tung oil		
Type of 4-alkyl phenol	Charging 4-alkyl phenols (mol)	Charging tung oil (mol)	4-Alkyl phenols/ tung oil molar ratio (mol/mol)	Reacted 4-alkyl phenols (mol)	Reacted tung oil (mol)	4-Alkyl phenol/ tung oil molar ratio (mol/mol)
Phenol	0.0129	0.00069	18.7	0.00076	0.00069	1.1
4-Methyl phenol	0.0129	0.00069	18.7	0.00175	0.00069	2.5
4-*tert*-Butyl phenol	0.0129	0.00069	18.7	0.00266	0.00069	3.9
4-Nonyl phenol	0.0129	0.00069	18.7	0.00186	0.00069	2.7

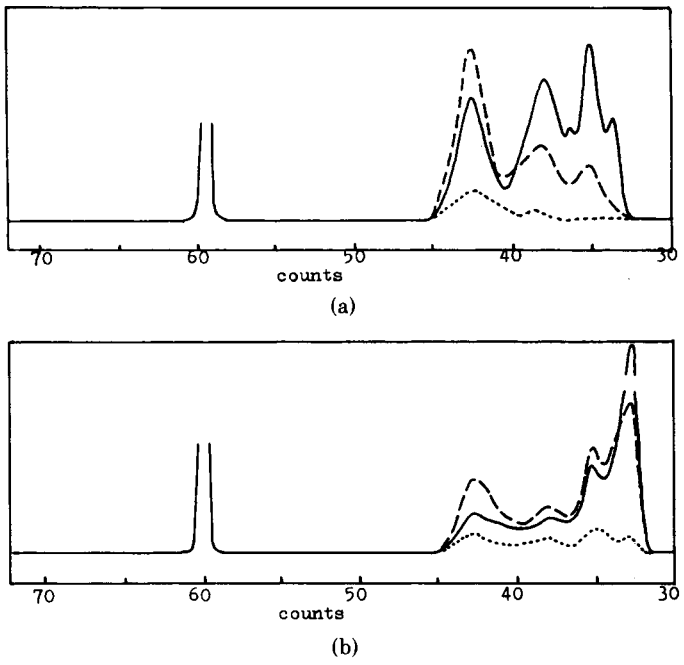

Fig. 3. (a) HLC chromatograms of tung oil 3-methyl phenol reaction products prepared at varied 3-methyl phenol/tung oil weight ratios: (—) 3/7; (- - -) 7/3; (·····) 9/1. (b) HLC chromatograms of tung oil phenol reaction products prepared at varied phenol/tung oil weight ratios: (—) 3/7; (- - -) 7/3; (·····) 9/1.

to give a smaller amount of the phenol reacted with tung oil. For substantiating this, a comparison experiment was made using phenol and 3-methyl phenol both having trifunctionality.

In Figure 3 are shown the results of HLC analysis of the reaction products obtained by reacting phenol or 3-methyl phenol with tung oil at varied charging molar ratio. In Figure 4 are shown the amounts of phenol or 3-methyl phenol reacted with 1 mol of tung oil in the above reactions.

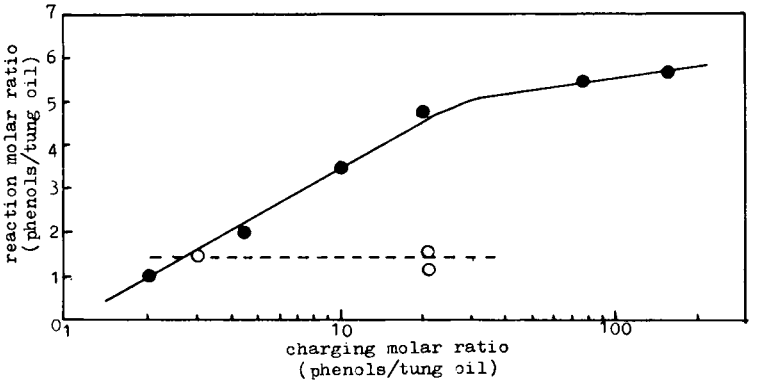

Fig. 4. Relationship between the charging molar ratio of the reaction molar ratio of 3-methyl phenol or phenol and tung oil: (●) 3-methyl phenol; (○) phenol.

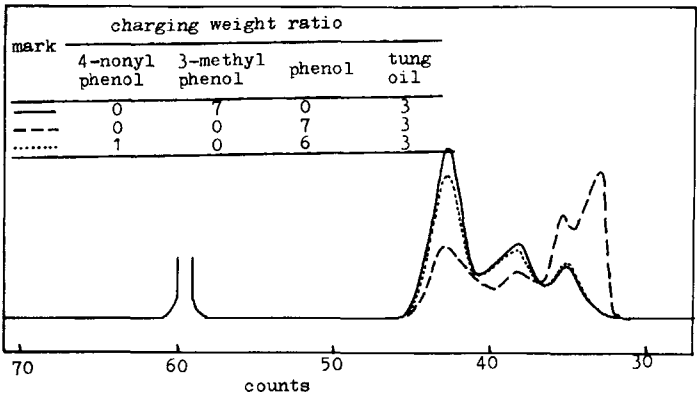

Fig. 5. HLC chromatograms of tung oil phenol reaction products prepared at varied phenols/tung oil.

It is apparent from the results that an increase in 3-methyl phenol charging molar ratio led to an increase in the amount of 3-methyl phenol reacted with 1 mol of tung oil and to a decrease in the average molecular weight of reaction product, and that an increase in phenol charging molar ratio neither increased so much the amount of phenol reacted with 1 mol of tung oil nor decreased so much the average molecular weight of reaction product. It is presumed that the good compatibility of 3-methyl phenol with tung oil may contribute to increased concentration of 3-methyl phenol present around the reactive points of tung oil molecules (tung oil cations) with an increase in the 3-methyl phenol charging molar ratio. By contrast, it is presumed that the poor compatibility of phenol with tung oil may not lead to increased concentration of phenol present around the reactive points of tung oil even with an increase in the phenol charging molar ratio. Adversely speaking, if the difference in reactivity with tung oil between phenol and 3-methyl phenol could be attributed to a difference in electron density on ring between them, the influence of concentration paragraph had to be observed also in the case of phenol. For confirming this, investigation on the reaction of phenol with tung oil was made using various kinds of third substance to be added for improving compatibility between phenol and tung oil. In Figure 5 and Table III are shown the results of HLC analysis of the reaction products and the amounts of phenol reacted with tung oil, respectively, in the case where nonyl phenol was added as an example of such a third substance. The SP value (δ) of nonyl phenol is 10–11 in the middle between that of tung oil (δ = 8.5) and that of phenol (δ = 14). Thus nonyl phenol must be good in compatibility with tung oil as well as phenol. As inferred from the results of Figure 5 and Table III, in the system where nonyl phenol was added to improve compatibility of

TABLE III
Relationship between the Type of Phenol and the Reaction Molar Ratio of Phenols and Tung Oil

Charging weight ratio				Reaction molar ratio of phenols to tung oil (mol/mol)
4-Nonyl phenol	3-Methyl phenol	Phenol	Tung oil	
0	7	0	3	3.5
0	0	7	3	1.1
1	0	6	3	3.3

phenol with tung oil, the amount of phenol reacted with tung oil was increased with the average molecular weight of reaction product lowered relatively.

The experimental results described above clearly indicate that the compatibility of phenol with tung oil explains the peculiar reactivity of phenol different from those of alkyl phenols. An alkyl group substituent on a phenol ring affects the compatibility of the alkyl phenol with tung oil, and serves as a factor of determining the reactivity of the alkyl phenol with tung oil. This needs to be further confirmed by examining the molecular forms, diffusion heats, and the like in solutions of tung oil and alkyl phenols by a birefringence measurement apparatus, a calorimeter, and so on.

CONCLUSION

The reactions of alkyl phenols with tung oil under acidic conditions were investigated. As a result, the following facts were observed:

(1) A nuclear substitution reaction occurs between an alkyl phenol and tung oil via the conjugated double bonds of it.

(2) Reactivity in the nuclear substitution reaction is in the following order: 2-methyl phenol > 3-methyl phenol > 4-methyl phenol.

(3) The nuclear substitution reaction occurs preferentially at the para position relative to the phenolic hydroxyl group.

(4) The higher the alkyl group attacked to the phenol ring, the higher the reactivity with tung oil. This has something to do with the compatibility of alkyl phenol with tung oil (the SP values of alkyl phenols approaching that of tung oil with heightening of the alkyl group).

(5) The nuclear substitution reaction occurs at more than one position of the alkyl phenol to polymerize tung oil via phenol nuclei.

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