

Polymerization of Tung Oil by Reaction of Phenols with Tung Oil

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Synopsis

Investigation was made on the mechanism of polymerization in reactions of tung oil and phenols in the presence of an acid catalyst. It was made by means of comparative HLC and NMR analyses of the products of tung oil self-polymerization, other varied vegetable oil-various phenol reactions, and tung oil-various-in-functionality phenol reactions under given conditions. As a result, it was confirmed that polymerization in reactions of tung oil and phenols is attributed not to tung oil self-polymerization but to di- or trialkylation, with tung oil, of phenols, which can serve as crosslinking agents of tung oil.

INTRODUCTION

Phenolic resins¹ used in industry are frequently modified with tung oil so as to have flexibility. A number of papers²⁻²⁰ have reported on reactions between tung oil and phenols.

The author previously reported on reactions of tung oil and phenols under acidic conditions.^{21,22} It was confirmed in the theses that phenols react with tung oil by nucleophilic substitution via the conjugated trienes of tung oil, that up to two molecules of a phenol are addition-reacted with one conjugated triene group contained in glycerol trieleostearate which is the main component of tung oil, and that the substitution occurs preferentially at the para position of the phenol relative to its—OH group. However, it was only presumed that a polymer (molecular weight: 2000–5000) formed in reactions of tung oil and phenols may be due to di- or trialkylation of phenols. This article reports on investigation into tung oil polymerization in those reactions, in which possible self-polymerization of tung oil, reactions of various vegetable oils other than tung oil and phenols, and reactions of various phenols with varied functionalities of 0–3 and tung oil were examined.

EXPERIMENTAL

Reagents

Various vegetable oil of an industrial grade from China was used. Phenol, 2-methyl phenol, 3-methyl phenol, 4-methyl phenol, 2,4-dimethyl phenol, 2,6-dimethyl phenol, 2,4,6-trimethyl phenol, and 2,4,6-tribromo phenol used were of the first reagent grade. *p*-Toluenesulfonic acid used as catalyst was of the first reagent grade. Tetrahydrofuran (THF) used as HLC solvents were of the first reagent grade.

Analytical Method

Infrared Spectroscopic Analysis (IR). For IR analysis of samples, Hitachi Co., IR Model 285 was used.

Nuclear Magnetic Resonance Spectroscopic Analysis (NMR). NMR analysis of the reaction products, some of which were acetylated, were carried out by use of Hitachi Co., NMR Model R-24 or JEOL Ltd., NMR Model FX 270. Deutero chloroform and tetramethylsilan were used as solvent and internal standard, respectively. The procedure of acetylation was as follows: 0.1 g of the sample was dissolved in 0.2 mL of pyridine in a test tube and cooled to 0–5°C, and then 0.3 g of cooled acetic anhydride was dropped into it. The test tube was then allowed to stand for about 24 h. After that, 0.4 mL of chloroform was dropped into the test tube, followed by sufficient mixing, and the chloroform phase was washed with water several times. The chloroform phase finally obtained was heated under reduced pressure to remove the chloroform and the remaining water.

High-Speed Liquid Chromatographic Analysis (HLC). Toyo Soda Co., HLC Model HLC-802 in which one column of TSK G-3000H₈, three columns of TSK G-2000H₈, and an RI detector were employed was used, and THF was used as the elution solvent at flow rate of 1.5 mL/min. Samples were immersed in 1.1–2.2 wt % THF solution.

Reaction of Phenols with Tung Oil. The predetermined amounts of methyl α -eleostearate (ESA or E) were charged in a 100 mL four-necked flask equipped with a stirrer, a thermometer, a dropping funnel, and a reflux condenser. Then predetermined amounts of 20% aqueous solution of *p*-toluenesulfonic acid was added dropwise to the stirred mixture through the dropping funnel at 25°C. After completion of the dropwise addition of *p*-toluenesulfonic acid, the flask was heated at 80°C or 140°C for 1 or 2 h and then cooled.

RESULTS AND DISCUSSION

Reactions of Various Vegetable Oils and 3-Methyl Phenol

Investigation was made on reactions of 3-methyl phenol with tung oil having three conjugated trienes in the molecule, with dehydrated castor oil having two to three conjugated dienes in the molecule, or with castor or linseed oil having three nonconjugated double bonds in the molecule. The results are shown in Figure 1. Polymerization proceeded most in the case of tung oil with conjugated trienes and a little in the cases of dehydrated castor oil and linseed oil with conjugated dienes. On the other hand, castor oil and linseed oil did not react at all with 3-methyl phenol without occurrence of decomposition or degradation. In conclusion, the effect of kind of functional group on the advance of polymerization in the reactions of vegetable oils and 3-methyl phenol is in the order of conjugated triene > conjugated diene > nonconjugated double bond. As reported in the previous paper, one conjugated triene reacts with up to two molecules of a phenol. This will apparently indicate a presumption that a conjugated diene may react with one molecule of the phenol while a nonconjugated double bond may not react with a phenol. The above results are supportive of the presumption.

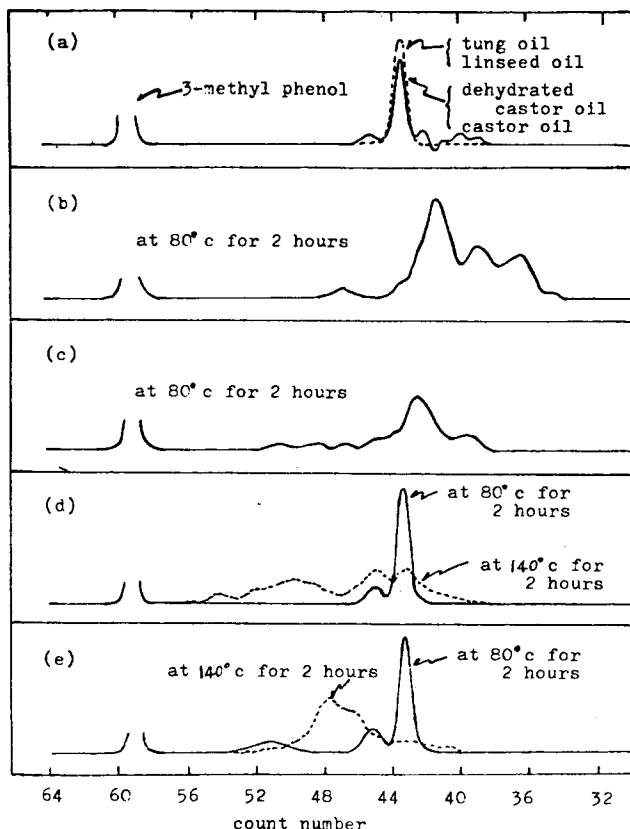


Fig. 1. HIC chromatograms of various vegetable oil-3-methyl phenol reaction products prepared at 3-methyl phenol/oil weight ratio of 7/3; (a) before reaction; (b) tung oil-3-methyl phenol reaction product; (c) dehydrated castor oil-3-methyl phenol reaction product; (d) castor oil-3-methyl phenol reaction products; (e) linseed oil-3-methyl phenol reaction products.

Self-Polymerization of Tung Oil

There is a possibility that a polymer of 2,000–5,000 in molecular weight formed in reactions of tung oil and phenols may be attributed to polymerization of tung oil molecules themselves. Investigation was made on this possibility.

The molecular weight distributions of self-polymerized products of tung oil obtained in the presence of NH_3 or *p*-toluene sulfonic acid (PTS) at 80°C or 140°C are shown in Figure 2. It is apparent from Figure 2 that the self-polymerization of tung oil in the presence of NH_3 occurs little at 80°C even with a reaction time of 1–2 h but proceeds a little at a high temperature of 140°C. On the other hand, it is apparent from Figure 2 that, although the self-polymerization of tung oil in the presence of PTS occurs little at 80°C similarly to that in the presence of NH_3 , tung oil decomposes and polymerizes at 140°C as substantiated by appearance of peaks which are to be assigned to eleostearic acid (count number: 50.5) formed by tung oil decomposition, to monohydrolyzed tung oil (count number: 45), and to polymerized tung oil (count number: below 42). Tung oil consumption was calculated to be 25% for a 1-h reaction and 40% for a 2-h reaction. It

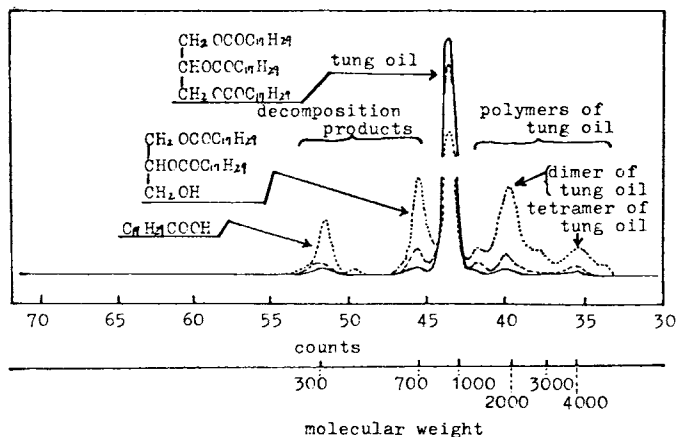


Fig. 2. HLC chromatograms of tung oil's self-polymerization products at varied conditions: (—) heated at 80°C for 2 h using PTS or NH_3 as catalyst; (---) heated at 140°C for 2 h using PTS as catalyst; (---) heated at 140°C for 2 h using NH_3 as catalyst.

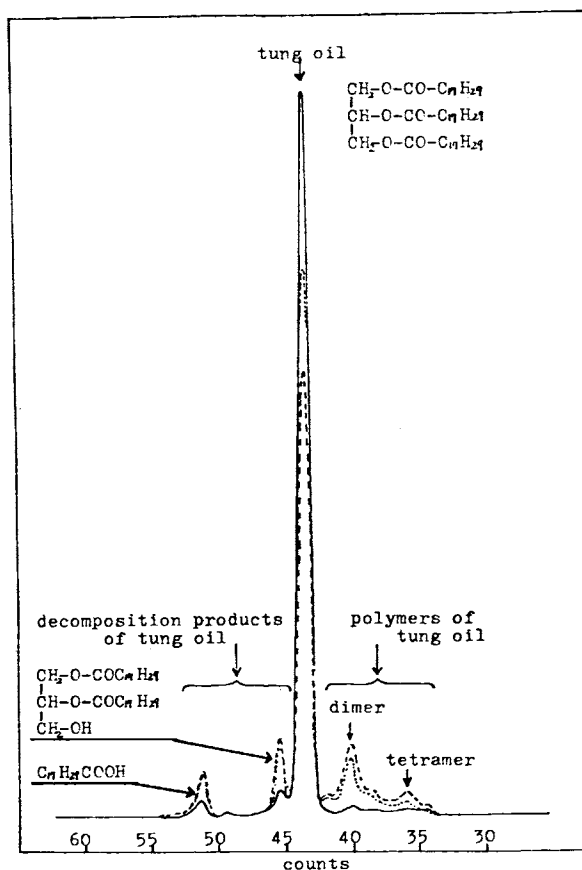


Fig. 3. HLC chromatograms of tung oil's self-polymerization products by using PTS as catalyst at 140°C for varied periods of time: (—) before reaction; (---) 1 h; (---) 2 h.

confirms that self-polymerization of tung oil easily proceeds in the presence of PTS at high temperatures (Fig. 3).

IR spectra of the reaction products are shown in Figure 4. The spectrum of the product obtained in the presence of PTS catalyst at 80°C is substantially the same as that of tung oil. The spectrum of the product obtained in the presence of PTS catalyst at 140°C has a lowered peak at 960 cm^{-1} assigned to double bonds indicating the occurrence of reaction via conjugated double bonds. Therefore, polymerization of tung oil can be attributed to reaction via its conjugated double bonds.

A hypothetical discussion will be given on the above results. Polymerization reactions are roughly classified into anion, cation, and radical mechanisms. A view of tung oil polymerization will be taken from the standpoint of anion polymerization. In general, the easiness of anion polymerization decreases in the order of $\text{K, Na, KR} > \text{RMgX} > \text{ROK, RONa} > \text{NR}_3$, weak alkali (R: alkyl group, X: halogen) for catalysts, and nitroethylene $>$ acrylo-

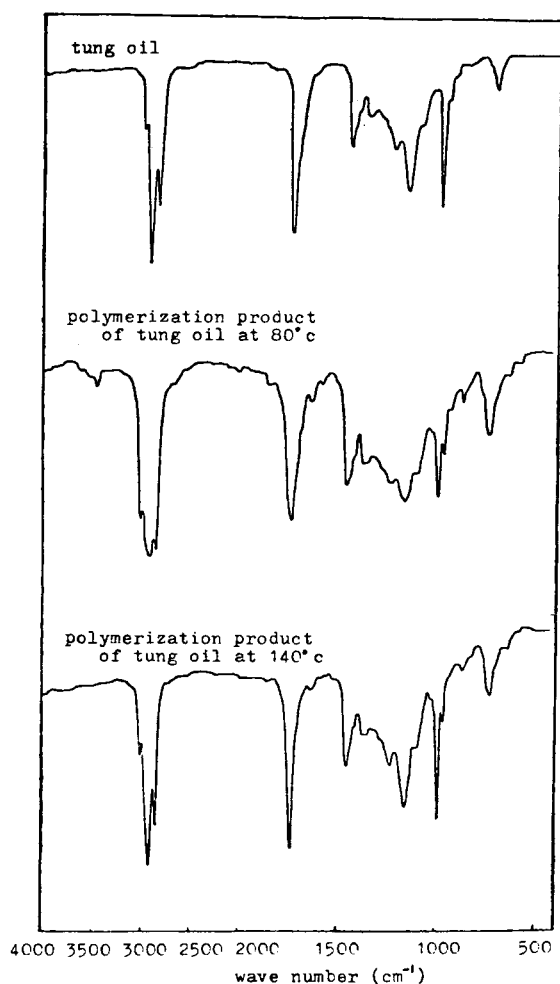
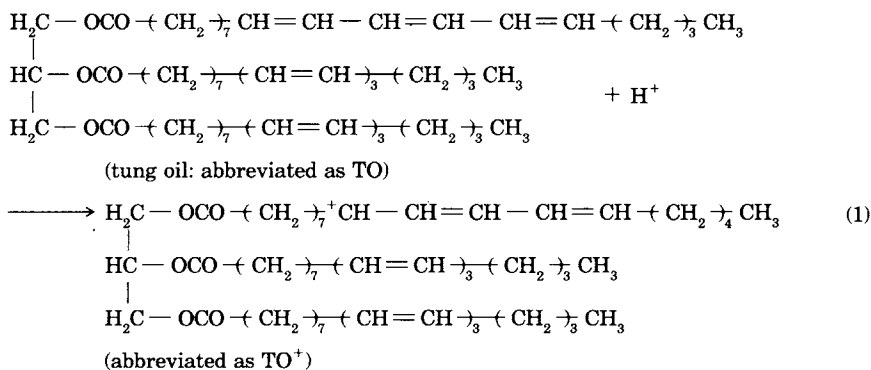


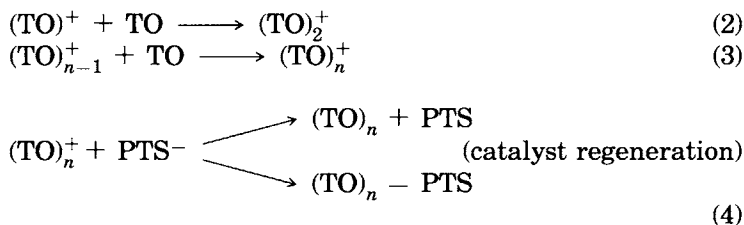
Fig. 4. IR spectra of tung oil and polymerization products of tung oil at 80°C and 140°C.

nitrile > methyl methacrylate > butadiene for monomers.²⁰ Thus, a weak alkali catalyst-butadiene system is lowest in reactivity. This may lead a conclusion that tung oil does not react in the presence of NH_3 catalyst.

A view of tung oil polymerization in the presence of acidic PTS catalyst will be taken from the standpoint of cation polymerization. At first a proton formed from PTS adds to a high electron density conjugated double bonds of tung oil:



TO^+ thus formed reacts with unreacted TO to form a dimer ion $(\text{TO})_2^+$ [eq. (2)]. TO molecules react in series with $(\text{TO}_2)^+$ to form $(\text{TO})_n^+$ [eq. (3)]. $(\text{TO})_n^+$ reacts with PTS^- to form polymers $(\text{TO})_n$ and $(\text{TO})_n - \text{PTS}$ [eq. (4)].



Additionally, a little formation of tung oil polymer at 140°C even in the presence of NH_3 , which is inactive as catalyst, may be caused by radical formation resulting from any interaction between the conjugated double bonds of tung oil, drying oil, and oxygen contained in air or dissolved in tung oil. Such interaction also will affect at least a little the polymerization under PTS acidic conditions according to the cation mechanism.

Tung oil decomposition is due to ester hydrolysis. In the molecular weight distribution of the product obtained in the presence of PTS at 140°C , the count number 50.5 is assigned to eleostearic acid, and, judging from the molecular weight, the count number 45 to the hydrolyzed product of tung oil from which one eleostearate group of the three eleostearate groups is hydrolyzed to allow eleostearic acid to leave from the tung oil molecule.

Reaction of Tung Oil and Mono-, Di-, or Tri-functional Phenol

As described above, little self-polymerization of tung oil occurs in reactions of tung oil and phenols under acidic conditions, particularly at relatively low temperatures of 80°C or so, on which reaction the investigation

of the author is centered. Therefore, polymer formation in the reactions must be caused according to other mechanism. For elucidating the mechanism, the manner of polymerization was observed in reactions of tung oil with respective varied-in-functionality phenols. Taking into account the facts reported in the previous report²² that the OH group of phenols is not involved in the reactions of tung oil with phenols and that the reactions occur at the ortho and para position of the phenol nucleus, phenol and 3-methyl phenol were used as trifunctional phenols, 2-methyl phenol and 4-methyl phenol as bifunctional phenols, 2,4-dimethyl phenol and 2,6-dimethyl phenol as monofunctional phenols, and 2,4,6-trimethyl phenol and 2,4,6-tribromophenol as nonfunctional phenols. Using these phenols, the reactivities of them with tung oil were examined.

HLC chromatograms of the reaction products are shown in Figure 5. The molecular weights of the reaction products were dependent on kinds of phenols in the following order: phenol > 3-methyl phenol > 2-methyl phenol \approx 4-methyl phenol > 2,4-dimethyl phenol \approx 2,6-dimethyl phenol > 2,4,6-trimethyl phenol \approx 2,4,6-tribromo phenol. This order corresponds to the order of functionalities of phenols: trifunctional > difunctional > monofunctional > nonfunctional. That is, the trend to polymerization decreases

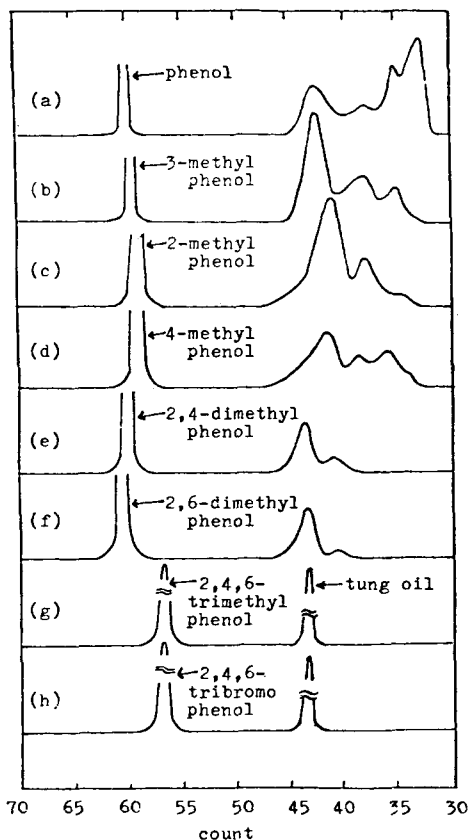


Fig. 5. HLC chromatograms of reaction products of various phenols with tung oil: (a) phenol; (b) 3-methyl phenol; (c) 2-methyl phenol; (d) 4-methyl phenol; (e) 2,4-dimethyl phenol; (f) 2,6-dimethyl phenol; (g) 2,4,6-trimethyl phenol; (h) 2,4,6-tribromophenol.

with a decrease in functionality of phenols. It should be particularly noted that little tung oil dimer (molecular weight: about 2000) was formed with formation of only tung oil-phenol adduct in the case of monofunctional phenols. It also should be noted that no reaction in the tung oil-phenol system occurs at all in the case of the use of nonfunctional phenols as is apparent from Figures 5(g) and (h) showing no decreases in peaks assigned to tung oil and phenols.

It can be confirmed from these results that tung oil reacts with phenols at only their ortho and para positions and does not react at all with phenols having ortho and para positions all occupied by substituents and that the phenolic —OH group is not involved at all in reaction itself.

The foregoing results will lead to the conclusion that, in view of the fact that tung oil polymerization occurs in the case of use of phenols having two or three reactive hydrogens at their ortho and para positions, but occurs little in the case of use of phenols having one or zero reactive hydrogen at their ortho or para positions, tung oil polymerization should be attributed to dialkylation or trialkylation with tung oil of phenols, which acts as crosslinking agents of tung oil.

Reaction molar ratios of phenols to tung oil are listed together with charging molar ratios of them in Table I. The reaction molar ratios were calculated from peak heights assigned to phenols and to tung oil in HLC chromatograms of reaction systems before and after the reactions.

Figure 6 is a set of graphs each showing the reaction molar ratios of 3-methyl phenol to tung oil, the numbers of substituted ring protons, and the average degree of tung oil polymerization plotted against the charging molar ratios of 3-methyl phenol to tung oil. The data in Figure 6 were obtained according to HLC and NMR analyses of the various reaction products of 3-methyl phenol and tung oil.

TABLE I
Relationship between the Kind of Phenols and the Reaction Molar Ratio of Phenols and Tung Oil

Kind of phenols	Charging molar ratio of phenols to tung oil (mol/mol)	Reaction molar ratio of phenols to tung oil (mol/mol)
Phenol	18.7	1.1
3-Methyl phenol	18.7	3.5
2-Methyl phenol	18.7	4.5
4-Methyl phenol	18.7	2.5
2,4-Dimethyl phenol	18.7	2.5
2,6-Dimethyl phenol	18.7	2.7
2,4,6-Trimethyl phenol	18.7	0
2,4,6-Tribromo phenol	18.7	0

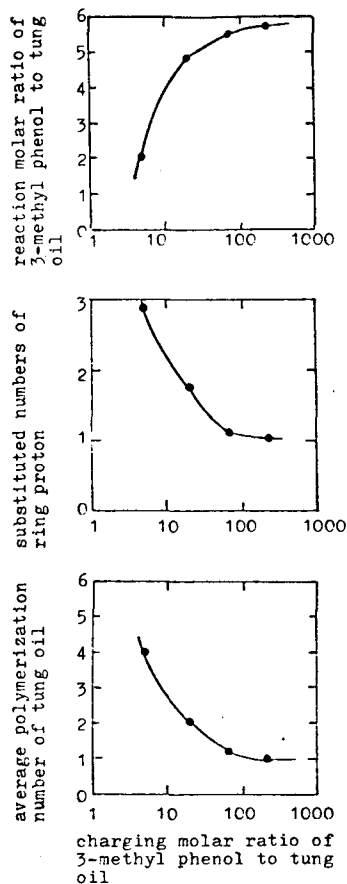


Fig. 6. Relationship between charging molar ratio of 3-methyl phenol to tung oil and reaction molar ratio, number of substituted ring proton, average degree of tung oil polymerization.

Figure 7 is a set of graphs each showing the number of substituted ring portions and the average degree of tung oil polymerization plotted against the reaction molar ratios of 3-methyl phenol to tung oil.

Figure 8 is a graph showing the average degree of tung oil polymerization plotted against the charging molar ratio of a phenol to tung oil as regards the reaction products of various phenols and tung oil.

It is apparent from these graphs that, with an increase in charging molar ratio of a phenol to tung oil, the number of phenol molecules reacted with one tung oil molecule increases while the average degree of tung oil polymerization decreases. This is supportive of the mechanism according to which proton substitution on the phenol ring contributes to tung oil polymerization.

Reaction of Tung Oil-Phenol Adduct

As described above, it is presumed that formation of tung oil polymer in reactions of tung oil and phenols be not caused by self-polymerization of

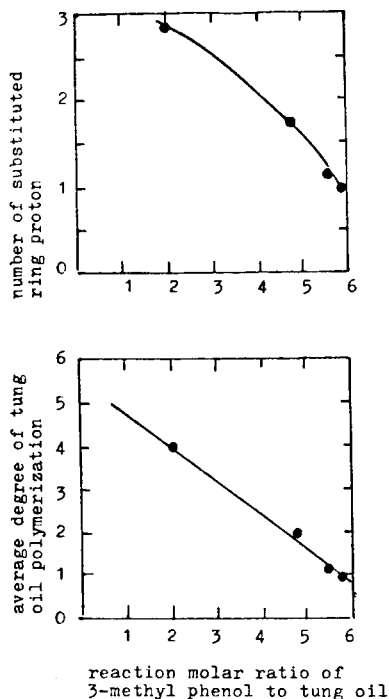


Fig. 7. Relationship between reaction molar ratio of 3-methyl phenol to tung oil and number of substituted ring proton, average degree of tung oil polymerization.

tung oil itself but by dialkylation or trialkylation with tung oil at the ortho and para positions of the phenol ring which serves as the crosslinking agent for tung oil.

For substantiating this, the following experiment was carried out. 1:6 tung oil-3-methyl phenol adduct¹⁷ and 1:6 tung oil-2,6-dimethyl phenol adduct as reported in the previous paper²² were synthesized, which are represented by the respective formulas

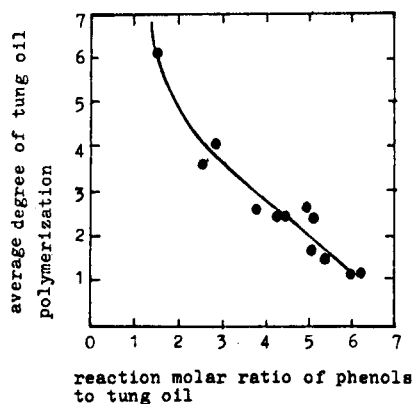
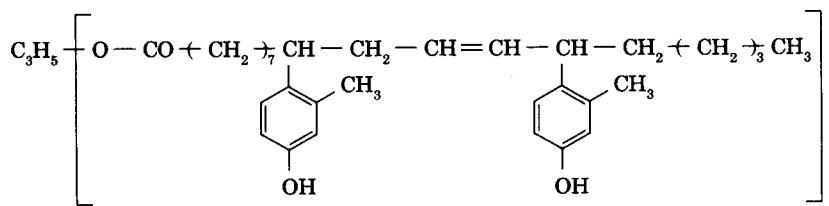
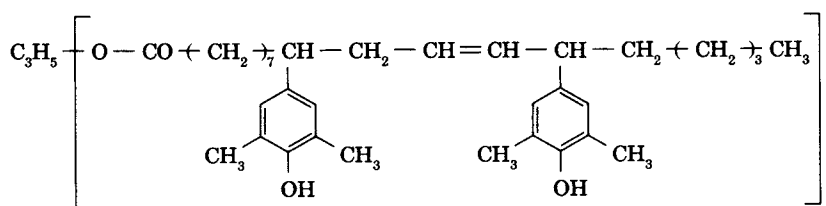


Fig. 8. Relationship between reaction molar ratio of phenols to tung oil and average degree of tung oil polymerization.



and



Subsequently, the following reactions were tried: (1) reaction of each 1:6 adduct itself; (2) reaction of each 1:6 adduct and 3-methyl phenol; and (3) reaction of each 1:6 adduct and tung oil.

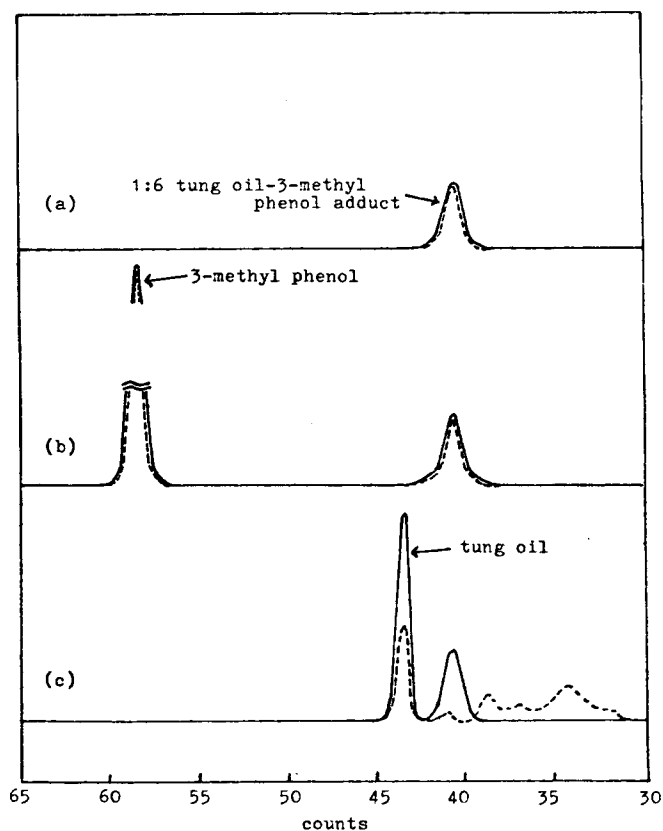


Fig. 9. HLC chromatograms of reaction products of 1:6 tung oil-3-methyl phenol adduct: (a) self-reaction; (b) reaction with 3-methyl phenol; (c) reaction with tung oil: (—) before reaction; (---) after reaction.

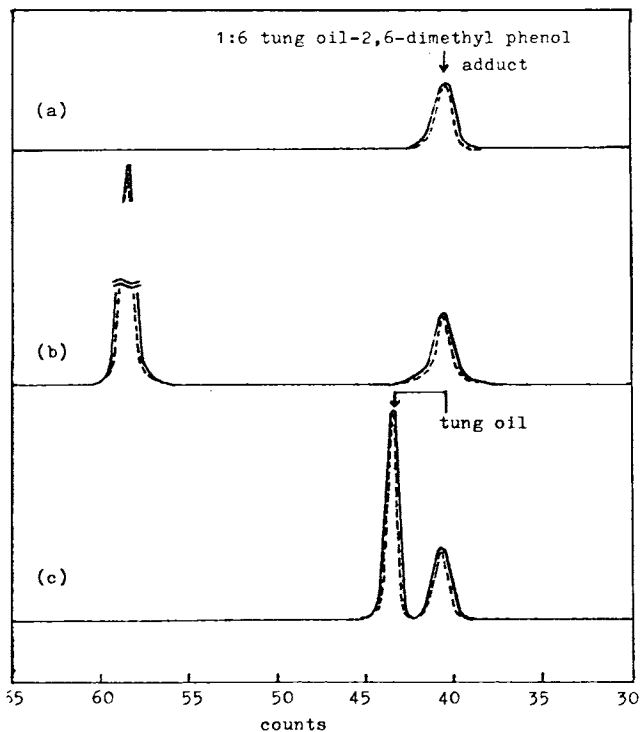


Fig. 10. HLC chromatograms of reaction products of 1:6 tung oil-2,6-dimethyl phenol adduct: (a) self-reaction; (b) reaction with 3-methyl phenol; (c) reaction with tung oil: (—) before reaction; (- -) after reaction.

HLC chromatograms of the products are shown in Figures 9 and 10. They indicate the following facts: (1) either 1:6 tung oil-3-methyl phenol adduct or 1:6 tung oil-2,6-dimethyl phenol adduct does not react at all by itself; (2) either 1:6 tung oil-3-methyl phenol adduct or 1:6 tung oil-2,6-dimethyl phenol adduct does not react at all with 3-methyl phenol; (3) 1:6 tung oil-2,6-dimethyl phenol adduct does not react at all with tung oil; and (4) 1:6 tung oil-3-methyl phenol adduct reacts with tung oil to form a polymer corresponding to a mixture of dimer, trimer, and tetramer of tung oil with disappearance of the peaks assigned to the adduct and tung oil.

It can be concluded from the above results that, in reactions of tung oil and phenols, a phenol molecule is addition-reacted at their ortho or para position with a conjugated triene of tung oil molecule according to the alkylation mechanism, followed by further alkylation with other tung oil molecule at another remaining reactive position on the phenol ring to form tung oil dimer.

CONCLUSIONS

Investigation was made on tung oil polymerization in reaction of tung oil with phenols. The following conclusions were drawn.

1. The trend to polymerization in reactions of various vegetable oils and phenols is dependent on kinds of unsaturated groups in vegetable oils in

the following order: conjugated triene > conjugated diene > nonconjugated double bond.

2. Intermolecular polymerization of tung oil itself occurs under high temperature conditions (e.g., 140°C), but does not occur under low temperature conditions (80°C) without being involved in reactions of tung oil and phenols.

3. The trend to polymerization in reactions of tung oil and phenols is dependent on functionalities of phenols in the following order: trifunctional > difunctional > monofunctional > nonfunctional. Little polymerization occurs in the case of monofunctional and nonfunctional phenols.

4. 1:6 Tung oil-3-methyl phenol adduct which contain two 3-methyl phenols on each fatty acid chain does not react by itself, but reacts with tung oil to be subjected to polymerization if tung oil is present, but 1:6 tung oil-2,6-dimethyl phenol adduct which contain two 2,6-dimethyl phenols on each fatty acid chain neither reacts by itself nor reacts with other tung oil.

5. In view of the above, tung oil polymerization in reactions of tung oil and phenols under acidic conditions at 80°C is caused by di- or trialkylation, with tung oil, of phenols which serve as the crosslinking agent of tung oil.

References

1. Carl Thurman, "Phenol," in *Encyclopedia of Chemical Technology*, Kirk-Othmer, Ed., 3rd ed., Wiley, New York, 1982.
2. H. Von Euler, *Angew. Chem.*, **54**, 458 (1941).
3. K. Hultzs, *Kunststoffe*, **37**, 43 (1947).
4. G. R. Sprengling, *J. Am. Chem. Soc.*, **1952**, **74**, (1952).
5. A. Greth, *Kunststoffe*, **31**, 345 (1941).
6. R. F. Bowles, *Chem. Ind.*, **60**, 345 (1941).
7. H. S. Lilly, *Paint Technol.*, **8**, 189 (1943).
8. V. H. Turkington and I. Allen, *Ind. Eng. Chem.*, **33**, 966 (1941).
9. Yamauchi, Jpn. Pat. 187873. (1951).
10. K. Hultzs, *Chem. Phenolharze*, **78**, (1950).
11. A. Zinke, *Ber.*, **77B**, 264 (1944).
12. T. Kuwata, *J. Chem. Soc. Jpn.*, **45**, 1320 (1942).
13. U. S. Pat. 2380307. (1945).
14. U. S. Pat. 2267390. (1941).
15. U. S. Pat. 3228899. (1966).
16. A. J. Kolka et al., *J. Org. Chem.*, **22**, 642 (1957).
17. R. Gomper, *Angew. Chem., Int. Ed.*, **3**, 560 (1964).
18. R. W. Planck, *J. Am. Oil Chem. Soc.*, **33**, 350 (1956).
19. J. S. Hoffman, *J. Am. Oil Chem. Soc.*, **34**, 338 (1957).
20. R. T. O'Connor, *J. Am. Oil Chem. Soc.*, **32**, 616 (1955).
21. Y. Yoshimura, *J. Appl. Polym. Sci.*, **28**, 1147 (1983).
22. Y. Yoshimura, *J. Appl. Polym. Sci.*, **29**, 1063 (1984).

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