

Chemical and Physical Behavior of Phenolic Resins in Air-Dried Films of Phenolic Varnishes

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Synopsis

Chemical and physical behavior of the oil soluble phenolic resins in phenolic varnish films were investigated by means of dynamic-mechanical measurement, infrared spectra, and \bar{M}_c measurement. The viscoelastic property of phenolic varnish films or increase in $(T_g)_d$ due to the addition of resin is the same regardless of the types of phenolic resin (oil-reactive or oil-nonreactive) employed, and despite the lower reactivity of the oil-nonreactive phenolic resin in the cooking stage. A reaction takes place between the oil-nonreactive phenolic resin and drying oil in the course of autoxidation and proceeds in aging, resulting in a network in which the phenolic resin is the backbone. Both the crosslinking and filling of resin were effective in increasing the $(T_g)_d$ of the films; crosslinking is the better method as it results in films having a smaller acetone-extractable portion.

INTRODUCTION

There are two types of oil-soluble phenolic resins—oil-reactive (resol) and oil-nonreactive (novolak)—used for varnishes; in the cooking process for preparing the varnish, the former bubbles, while the latter does not.

Early in 1941, Turkington and Allen¹ applying practical tests to the various phenolic varnishes, concluded that varnish prepared from a base-catalyzed phenol-formaldehyde condensate was superior to that prepared from an acid-catalyzed phenol-formaldehyde condensate with respect to drying, as well as durability and color stability of the film. Shortly thereafter it was suggested that the base-catalyzed phenol-formaldehyde condensate reacts with drying oils with the formation of chroman derivatives.²⁻⁴ However, the physicochemical effects of these oil-soluble phenolic resins in air-dried films have not been studied yet.

This aim of the present report is to elucidate the physicochemical effects of oil-reactive and oil-nonreactive phenolic resins in the films. For this purpose, the reaction of oil and resin, and its effect on film properties were considered. The following items were examined: (1) reactivity of oil-soluble phenolic resins on the drying oil in the cooking process; (2) physical properties of phenolic varnish films; (3) confirmation of the reaction between oil-soluble phenolic resins and drying oil in the course of film

formation; (4) the increase of $(T_g)_d$ of drying oil films by crosslinking and filling effects of resins.

The results obtained offer information on the effect of the mode of network formation: crosslinking, filling, and blending, on the physical properties of films prepared from blended prepolymers (drying oil-natural resin, styrenated drying oils, and alkyd-melamine resins, etc.).

EXPERIMENTAL

Materials

Drying Oil (O). A mixture of tung oil (iodine value 168) and linseed oil (iodine value 187), (1:1) was used.

Phenolic Resins. *p*-tert-Butyl phenol-formaldehyde resins were prepared by the conventional method. The oil-reactive resin (R), had a molecular weight of 650, as measured by a vapor pressure osmometer (Mechrolab Inc.), m.p. 65–72°C.; the oil-nonreactive resin (N), had a molecular weight of 375, m.p. 55–62°C.

Acetylated Phenolic Resins. These were prepared by acetylation of the phenolic resins. The oil-reactive acetylated resin (R - Ac) had a molecular weight of 622, m.p. 14–18°C.; the oil-nonreactive acetylated resin (N - Ac) had a molecular weight of 505, m.p. 4–8°C.

Ester Gum (EG). This was a glycerol ester of rosin supplied by Japan Reichhold Chem. Inc., molecular weight 880, m.p. 83–93°C.

Rosin-Modified Phenolic Resin (RP). This was a product commercially available as Beekacite 1100, from Japan Reichhold Chem. Inc., having a molecular weight of 1300, m.p. 125–142°C.

Preparation of Prepolymers. Oil only or a mixture of oil and resin (6:4) was heated in air at 210°C. The heating was stopped near gelation, and the mixture was dissolved in an equal weight of mineral turpentine. The reaction times were 8 hr. for the oil-nonreactive resin (N-O), 3 hr. for the oil-reactive resin (R-O), and 5½ hours for the oil (PO), respectively. In addition to these varnishes, six other varnishes were prepared by dissolving a mixture of polymerized oil and resin (6:4) in an equal weight of mineral turpentine containing 2–3% of methyl ethyl ketone at room temperature (N+PO, R+PO, N-Ac+PO, R-Ac+PO, EG+PO, and RP+PO). The chemical change involved in the cooking process was examined by measuring the molecular weight, the infrared spectra near 3 μ , and the iodine value (Wijs method).

Preparation of Films. The varnishes containing drying agents (Co 0.02%, Mn 0.02%) were coated on tin plates. For air drying, application of varnish followed by standing one day at room temperature was repeated 10 times (20°C., 68% R.H.). For baking, coating with varnish and heating at 80°C. for 2 hr. was repeated 10 times. The films were then stripped off by an amalgam method.

Methods

Gelation Time. The variation in gelation time with the composition (oil/resin ratios of 5/5, 6/4, 7/3, and 10/0, termed "oil length" of 50, 60, 70, and 100, respectively) was examined. The gelation time was taken as the time of heating of the mixture at 210°C. required for gelation to occur.

Dynamic Mechanical Measurements on Films. The temperature (t) dependence of shear modulus (G) and logarithmic decrement (λ) of the films were measured by the torsional pendulum method.⁵ The data obtained from the $G-t$ and $\lambda-t$ curves were the glass transition temperature measured by dynamic-mechanical method (T_g)_d (the temperature whose λ is maximum, λ_{\max}) and the shear modulus obtained from the plateau region at high temperatures G_h (a measure of degree of crosslinking⁶⁻⁸).

Infrared Spectra. An infrared method was employed for examining the chemical reaction. The change in functional groups is reflected in changes in optical density D .

Film Extraction. The films were subjected to Soxhlet extraction with acetone for 50 hr. The extractable and nonextractable parts were dried in vacuum at room temperature.

Determination of \bar{M}_c . \bar{M}_c (the number-average molecular weight between crosslinks) was determined from results of stress-strain measurements on swollen crosslinked polymers.^{9,10}

RESULTS AND DISCUSSION

Reactivity of Oil-Soluble Phenolic Resins with Drying Oil in the Cooking Process

The gelation time was shortened as the content of the oil-reactive resin increased, while in the case of the oil-nonreactive resin, gelation time was prolonged (Fig. 1).

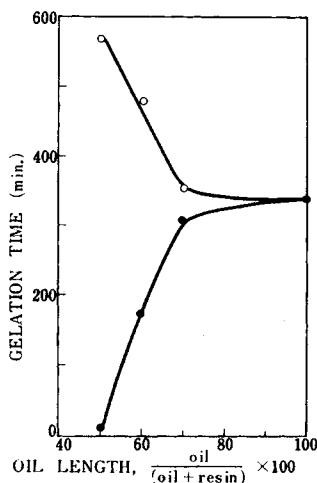


Fig. 1. Gelation time vs. oil length: (○) oil-nonreactive resin; (●) oil-reactive resin. Heating temperature 210°C.

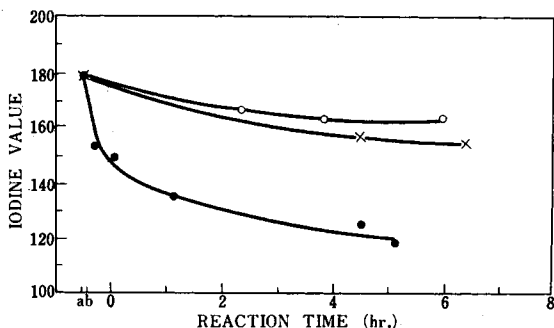


Fig. 2. Iodine value vs. reaction time in cooking process for preparing phenolic varnishes: (O) oil-nonreactive; (●) oil-reactive resin; (X) drying oil. Reaction temperature 210°C.; oil length 70; *a* and *b* are, respectively, the time at which heating is begun and the time at which resin is added.

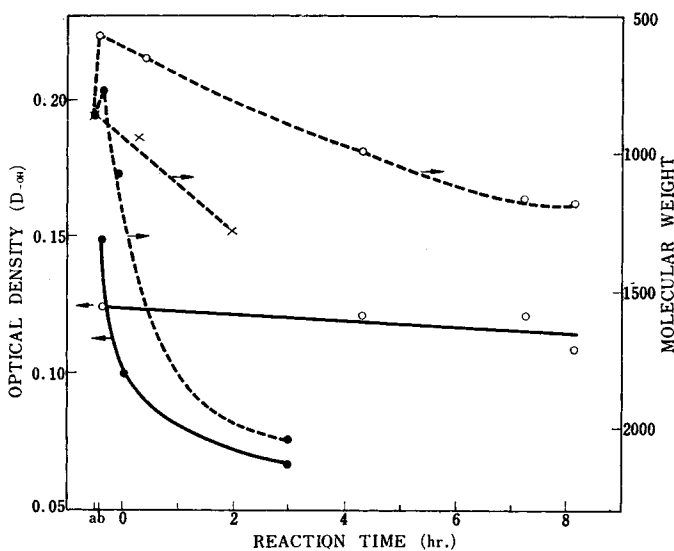


Fig. 3. Plots of (---) molecular weight and (—) optical density D_{OH} vs. reaction time in cooking process for preparing phenolic varnishes: (O) oil-nonreactive resin; (●) oil-reactive resin; (X) drying oil. Reaction temperature 210°C.; oil length 60; *a* and *b* denote, respectively, the time heating is begun and the time at which resin is added.

The iodine value, the molecular weight, and the D_{OH} versus the reaction time (Figs. 2 and 3) were less affected by the oil-nonreactive resin than the oil-reactive resin in the cooking process.

Physical Properties of Phenolic Varnish Films

The $G-t$ and $\lambda-t$ curves of the films are shown in Figures 4 and 5, and the results are summarized in Table I. The $G-t$ and $\lambda-t$ curves of the

films of both the oil-nonreactive resin and the oil-reactive resin were similar, i.e., values of $(T_g)_d$ and G_h were about the same in spite of the structural difference of the varnishes. It is also noticed that the $(T_g)_d$

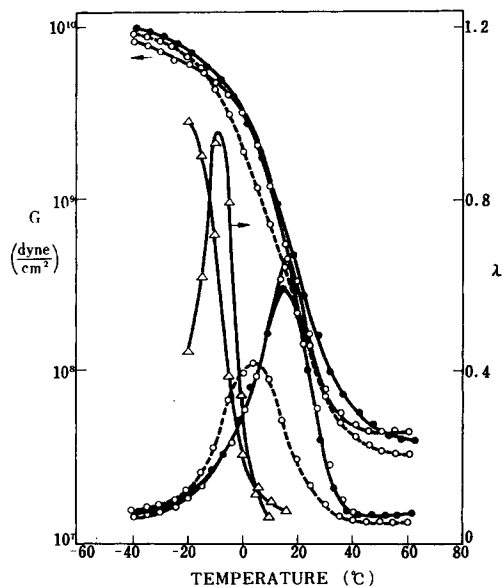


Fig. 4. G vs. t and λ vs. t curves of films of phenolic varnishes (air drying): (—○) N—O; (—●) R—O; (-○) N + PO; (Δ) R-Ac + PO.

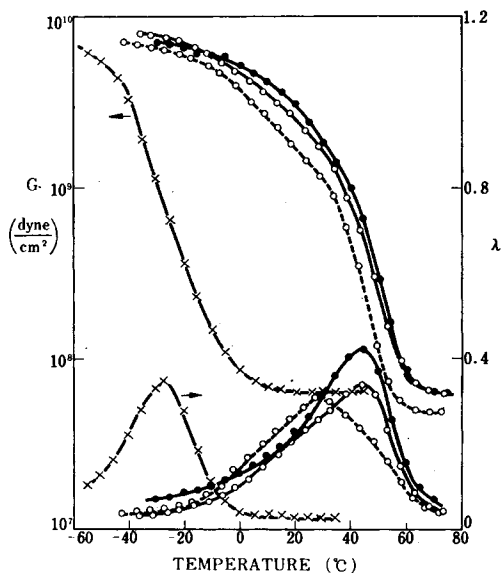


Fig. 5. G vs. t and λ vs. t curves of films of phenolic varnishes (baking): (—○) N—O; (—●) R—O; (-○) N + PO; (\times) PO.

of the phenolic varnish film was 70°C. higher than that of the drying oil film prepared under the same drying conditions. It is obvious from this fact that the resins were quite effective in raising $(T_g)_d$ of the drying oil films, i.e., in increasing the hardness of the films.

TABLE I
Physical Properties of Films of Phenolic Varnishes

Film	Drying method	$(T_g)_d$, °C.	$G_h \times 10^{-7}$, dyne/cm. ²
N - O	Air drying	15	4.3
N - O	Baking	45	6.0
R - O	Air drying	15	3.8
R - O	Baking	45	6.0
N + PO	Air drying	5	2.8
N + PO	Baking	30	4.8
PO	Baking	-27	

Therefore, despite the fact that the films prepared from the oil-reactive phenolic resins were superior in use to those from oil-nonreactive resins, as reported by Turkington and Allen;¹ no difference was observed between the films from the oil-nonreactive resin and those from the oil-reactive resin with respect to viscoelastic properties as measured by dynamic-mechanical measurement. However there arises the question of whether the increase in $(T_g)_d$ of the films of oil-nonreactive phenolic varnish is due to the reaction between resin and oil or to the filling effect of resin with formation of a network structure of polymerized oil, as predicted from the free volume concept.^{11,12}

Confirmation of the Reaction between Oil-Nonreactive Resin and Drying Oil in the Course of Air Drying

The reaction involved in the process of film formation, has been shown by the study of infrared spectra and the viscoelastic properties of the films¹³ to be due to a reaction between the phenolic resin and the drying oil hydroperoxide.

This is supported by other data. Air-dried film of varnishes from R - O, N - O, and N + PO were acetone-extracted as described before, and the infrared spectral analysis was applied to the nonextractable portions of the films. It was found that the infrared spectra of the original films and those of the nonextractable parts were almost the same (Figs. 6-8), namely, the absorptions of benzenoid carbon-hydrogen deformation at 887 and 822 cm.⁻¹ were observed in the spectra of the nonextractable portion. When the same extraction procedure was applied to films prepared from blends of acetylated resin and oil (N - Ac + PO and R - Ac + PO) (Figs. 9 and 10) absorptions of benzenoid carbon-hydrogen deformation at 900 and 832 cm.⁻¹ were not observed in the spectra of the nonextractable parts. The spectra of the nonextractable parts were similar to that of a film of

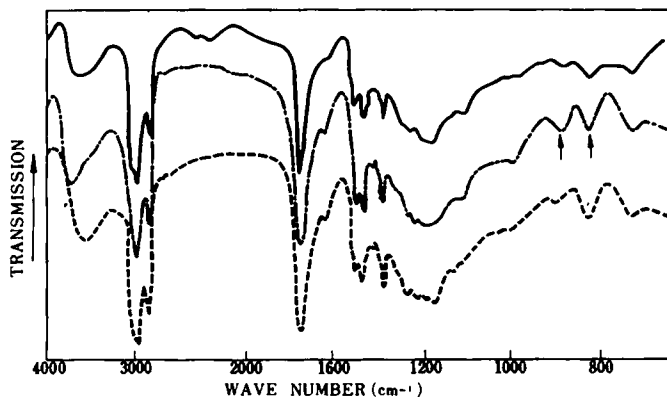


Fig. 6. Infrared spectra of films of oil-nonreactive phenolic varnish (air drying): (—) original film (film); (---) acetone-extractable material (capillary); (- - -) nonextractable portion (KBr disk).

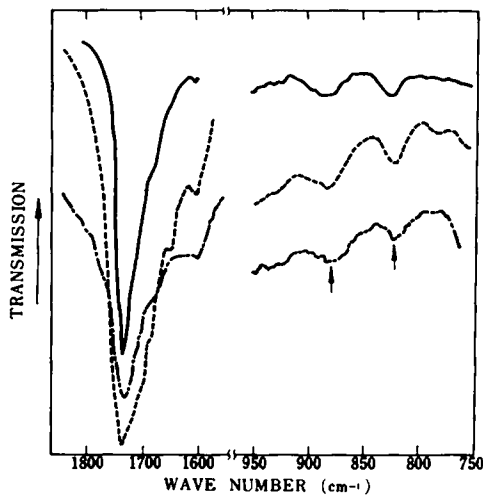


Fig. 7. Infrared spectra of films of oil-reactive phenolic varnish (air drying): (—) original film (film); (---) acetone-extractable material (capillary); (- - -) nonextractable portion (KBr disk).

polymerized oil, showing that the resin was removed from the films by the extraction.

This therefore confirms the reaction between the oil-nonreactive resin and drying oil in the course of air drying.

Degree of Crosslinking of Phenolic Varnish Films Compared to that of Polymerized Oil Films

As crosslinking took place between the oil-nonreactive resin and drying oil, a comparison of the degree of crosslinking of the films of phenolic

varnish and that of films of polymerized oil was carried out. The degree of crosslinking was determined from G_h and \bar{M}_c . The G_h and \bar{M}_c values for films dried under different conditions are shown in Table II.

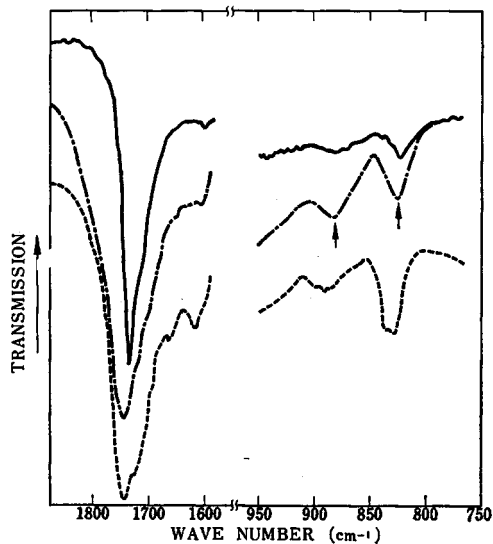


Fig. 8. Infrared spectra of film of oil-nonreactive phenolic varnish (cold mixing, air drying): (—) original film (film); (---) acetone extractable material (capillary); (- - -) nonextractable portion (KBr disk).

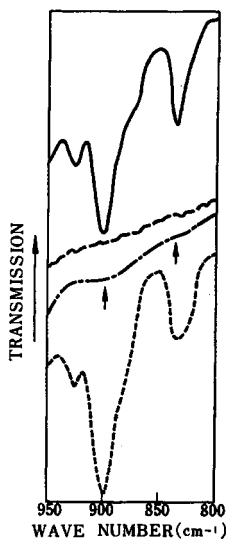


Fig. 9. Infrared spectra of films of acetylated phenolic varnish (oil-reactive resin, air-drying): (—) original film (KBr disk); (---) acetone-extractable material (capillary); (- - -) nonextractable portion (KBr disk); (- - -) nonextractable portion of film of polymerized linseed oil (KBr disk).

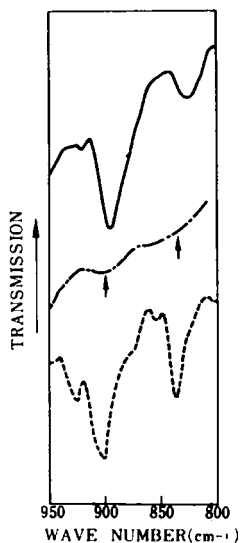


Fig. 10. Infrared spectra of films of acetylated phenolic varnish (oil-nonreactive resin, air drying): (—) original film (KBr disk); (--) acetone-extractable portion; (capillary); (- - -) nonextractable portion (KBr disk).

The G_h values of the phenolic varnish films were smaller than those of films of polymerized oil dried under the same conditions. The \bar{M}_c values were also in agreement with this trend.

TABLE II
 G_h and \bar{M}_c of Films of Phenolic Varnish Dried under Various Conditions

Film	Ratio resin/oil	Drying agent	Drying time, hr.	Temperature, °C.	Times of coating	$G_h \times 10^{-7}$, dyne/cm. ²	\bar{M}_c
PLO	0/100	Co (0.08%) +Mn (0.08%)	2	80	4	7.5	
PLO + N	10/100	Co (0.08%) +Mn (0.08%)	2	80	4	6.2	
PLO	0/100	Co (0.08%) +Mn (0.08%)	28	80	4	8.0	2420
PLO + N	10/100	Co (0.08%) +Mn (0.08%)	28	80	4	7.8	3160
PLO + N	67/100	Co (0.08%) +Mn (0.08%)	28	80	4	5.2	3640
PTO	0/100	None	8	80	4	3.9	
PTO + N	67/100	None	8	80	4	3.0	
PTO	0/100	Co (0.02%) +Mn (0.02%)	24	20	4	6.0	
PTO + N	67/100	Co (0.02%) +Mn (0.02%)	24	20	4	5.2	

* PLO = polymerized linseed oil, prepared by heating in air at 210°C., \bar{M}_n 1730; PTO = polymerized tung oil, prepared by heating in air at 210°C., \bar{M}_n 1990.

Therefore, the degree of crosslinking of films of phenolic varnish was smaller than that of films of polymerized oil; this suggests a steric effect of phenolic resin on crosslinking in the autoxidation of drying oil.

Aging of Films of Phenolic Varnishes

Generally, the autoxidation of oxidative polymerized films proceeded as time elapsed.¹⁴ The change of $(T_g)_d$ and G_h at various time intervals was determined for air-dried and baked films of phenolic varnishes. The results are shown in Table III, results for alkyd resin films being included for comparison. The $(T_g)_d$ increased as the oil length decreased (i.e., as the resin content increased) in the case of baked phenolic varnish films at both early and later stages; such a relation was found for air-dried phenolic varnish films when they were allowed to stand in air for a certain time. As the $(T_g)_d$ of air-dried film increased, G_h did also, showing the progress of the crosslinking.

TABLE III
Changes in $(T_g)_d$ and G_h on Aging of Films of Phenolic Varnishes

Film	Oil length	Drying method	$(T_g)_d$, °C.			$G_h \times 10^{-7}$, dyne/cm. ²	
			2-3 weeks	3 months	8 months	2-3 weeks	3 months
Phenolics*	70	Air drying	12	20	22	5.3	6.6
	70	Baking	22	38			10.0
	60	Air drying	15	28	28	5.5	5.8
	60	Baking	45	58			6.0
	50	Air drying	10	26	28	0.9	5.5
	50	Baking	60	62			7.8
Alkyds	60	Air drying	1				
	60	Baking	8				
	50	Air drying	4				
	50	Baking	16				
	40	Air drying	18				
	40	Baking	26				

* Prepared by cooking the oil-nonreactive resin and drying oil.

The relation of $(T_g)_d$ and oil length for films of alkyd resins was found to be similar to that for phenolic varnishes in the early stage of drying in both air drying and baking. This result could be reasonably explained by considering that the phthalate group exists as the polyester backbone of alkyd resin prior to film formation, namely, in the prepolymer stage.

The crosslinking of phenolic resin and drying oil proceeded with aging, the phenolic resin being the backbone of the network.

Increase in $(T_g)_d$ of Drying Oil Films Resulting from Crosslinking and from Filling Effects of Resins

It is useful to compare the increase of $(T_g)_d$ of drying oil films by crosslinking and that obtained as a result of filling effect of resins; the former is

TABLE IV
Increase in $(T_g)_d$ of Drying Oil Films by Crosslinking and Filling Effect of Resins

Films	Method of mixing	Method of drying	Melting point of resin, °C.	Molecular weight	T_g , °C.	Extractable film, %	Method of increasing $(T_g)_d$
N - O	Cooking	Air drying	55-62	375	15	32	Crosslinking
		Baking	55-62	375	45	11	"
R - O	Cooking	Air drying	65-72	650	15	34	"
		Baking	65-72	650	45	14	"
N + PO	Cold blend	Air drying	55-62	375	5	40	"
		Baking	55-62	375	30	13	"
R + PO	Cold blend	Baking	65-72	650	15	29	"
EG + PO	Cold blend	Air drying	83-93	880	8	80	Filling*
		Air drying	83-93	880	25	61 ^b	"
		Baking	83-93	880	13	50	"
		Baking	83-93	880	35	38 ^b	"
RP + PO	Cold blend	Air drying	125-142	1300	11	52	Crosslinking
		Baking	125-142	1300	15	25	"
N - Ac + PO	Cold blend	Air drying	4-8	505	-10	71	Filling*
		Baking	4-8	505	-5	50	"
R - Ac + PO	Cold blend	Air drying	14-18	622	-15	67	"
		Baking	14-18	622	-10	58	"
PO		Baking			-27	15	

* Examined by infrared spectral analysis. Absorption bands characteristic of resins were not found in the infrared spectra of nonextractable parts.

^b Films allowed to stand in air for 1 year.

of a chemical nature, the latter of a physical nature. Table IV shows the increase in $(T_g)_d$ of drying oil films obtained by crosslinking with phenolic resins and by filling by acetylated phenolic resins and ester gum. These resin-filled materials were obtained by mixing or cooking phenolic resins, acetylated phenolic resins, or ester gum with polymerized oil (6:4) and preparing the varnishes and films by the usual way. The films were then subjected to the dynamic-mechanical measurement and extraction.

It was found that both crosslinking and filling of resins were effective on increasing the $(T_g)_d$ of drying oil films. The extractable portion of crosslinked films was smaller than that from filled films under the same drying condition. In this respect, the crosslinking type is better as the greater solvent resistance of film may be expected.

The present study provides some results on correlation of structure and physical properties, but additional data, such as the change of specific volume by temperature, for evaluating the free volume in the films are necessary for further discussion.

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Résumé

Le comportement chimique et physique des résines phénoliques solubles dans l'huile, contenues dans les films de vernis phénoliques, a été étudié au moyen de mesures dynamo-mécaniques, par spectrographie infrarouge, par mesure de \bar{M}_c . On a trouvé que: la propriété viscoélastique des films de vernis phénolique, ou l'augmentation de $(T_g)_d$ due à l'addition de résine, est la même quelles que soient les différents types de résine phénolique employée (réactionnelle vis-à-vis de l'huile ou non-réactionnelle), ou malgré le fait que la résine phénolique non-réactionnelle vis-à-vis de l'huile soit moins réactionnelle pendant la période de chauffage. La réaction a lieu entre la résine phénolique, non-réactionnelle vis-à-vis de l'huile, et l'huile pendant la réaction d'autooxydation, et se poursuit pendant le vieillissement, la résine phénolique formant la chaîne principale du réseau. La pontage et le remplissage de la résine sont efficaces pour augmenter le $(T_g)_d$ des films, et le pontage est favorable en ce sens qu'il réduit la partie extractible des films.

Zusammenfassung

Das chemische und physikalische Verhalten von öllöslichen Phenolharzen in phenolischen Lackfilmen wurde mittels dynamisch-mechanischer Messung, Infrarotspektren, \bar{M}_v -Messung untersucht. Es wurde gefunden: Die Viskoelastizität phenolischer Lackfilme oder die Erhöhung von $(T_g)_d$ durch den Zusatz von Harz ist gleich, ungeachtet der Unterschiede zwischen den verwendeten Phenolharztypen (ölreaktiv und ölnichtreaktiv) und ungeachtet der Tatsache, dass das ölnichtreaktive Phenolharz in der Kochphase weniger reaktiv ist. Die Reaktion findet zwischen dem ölnichtreaktiven Phenolharz und trocknendem Öl im Verlauf der Autoxydation statt, schreitet bei der Alterung fort und führt schliesslich zu einem Netzwerk mit dem Phenolharz als Hauptkette. Sowohl Vernetzung als auch Füllen des Harzes führte zu einer Erhöhung von $(T_g)_d$ des Films; die Vernetzung ist günstig für die Herabsetzung des extrahierbaren Teils des Filmes.

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