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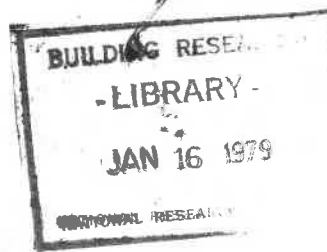
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WATER VAPOR PERMEATION THROUGH CLEAR COATINGS

ANALYZED

by M. Yaseen and H.E. Ashton



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SOMMAIRE

La perméabilité à la vapeur d'eau est l'un des facteurs les plus importants influant sur le rendement des revêtements extérieurs. Les changements relatifs à la perméabilité et causés par des hausses d'humidité relative ou de température sont aussi importants, non seulement parce qu'ils indiquent le rendement réel d'un revêtement mais aussi parce qu'ils donnent un aperçu de sa structure moléculaire.

L'article traite des effets de l'humidité relative et de la température dans le cas des finis phénoliques et alkydes transparents ainsi que des coefficients de perméabilité de ces finis. Les changements entraînés par chaque variante sont reliés à la composition des revêtements et aux caractéristiques de leurs composants.



Water Vapor Permeation Through Clear Coatings

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Permeability of exterior coatings to water vapor is one of the more important properties affecting their performance. Changes in permeability with increasing relative humidity or temperature are also important, not only because they indicate how a coating may behave in practice but also because they give an insight into the molecular structure.

The effects of relative humidity and temperature upon permeation through and the permeability coefficients of clear phenolic and alkyd finishes are studied. Changes caused by each variable are related to the composition of the coatings and the characteristics of the components.

INTRODUCTION

The protection provided by an organic coating depends on many factors, one being its resistance to permeation by gases, vapors, liquids, and ions.¹ The phenomenon of permeation begins when a diffusant in contact with the coating gets imbibed in it. Depending on the forces of interaction between the diffusing molecules and the components of the coating, the diffusant moves within the coating in the sorbed state. This process results in gradual absorption of vapor until a state of dynamic equilibrium is reached. At this stage the difference in vapor pressure between the two sides of the coating causes the permeation of vapor through it. Hence, permeation through a coating occurs in three steps: absorption of vapor on the surface, followed by its diffusion through the film, and then desorption or evaporation at the lower vapor pressure side.²

Generally, protective coatings are used because they act as barriers to the free access of gases, vapors, and liquids to surfaces and of ions to metal surfaces. While it is believed that no organic coating is completely impervious, coatings provide the substrate with considerable protection from corrosive agents.^{3,4} Hence, the permeability characteristics of coatings are important in assessing their performance in practical use. Permeability properties of coatings also affect their adhesion to

metallic substrates by controlling the changes in osmotic pressure at the interface.⁵

Permeation is basically governed by the vapor pressure and temperature of the surroundings while permeability of a material depends chiefly upon the molecular structure and nature of chemical groups present in the material and their affinity towards the diffusant. Change in permeability with increasing relative humidity or temperature, as well as being a practical importance, provides evidence of the molecular structure of the material.

Although the permeability of plastic films has been studied in great detail because of their use as vapor barriers, the permeability of organic coatings, and its change with temperature and relative humidity, has not received as much attention. This paper describes permeability studies made with clear finishes intended for exterior wood. The effects of the two variables on permeation and on the permeability coefficient are reported.

THEORETICAL

Equations for Permeation

At a steady rate of permeation the quantity of vapor (Q) transmitted through a coating of thickness (l) and area (a) in time (t) at vapor pressure differential (Δp) is expressed by:

$$Q = P \cdot \frac{at}{l} \Delta p \quad \text{or} \quad P = \frac{Ql}{a t \Delta p} \quad (1)$$

where P is a proportionality constant known as the permeability coefficient.

Effect of Temperature and Vapor Pressure On the Permeability Coefficient

Rate dependent phenomena are naturally affected by changes in temperature. A rise in the temperature activates the molecules and creates voids by the movement of polymer segments which in turn are occupied by

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Table 1—Composition of Clear Finishes

NRP Formula No.	Oil Content			% Volatile Content		Varnish Properties	
	Type	Approx. Length	% on Solids	Aromatic Solvent	Mineral Spirits	% Solids	G - H Viscosity
Para-Phenylphenolic Varnishes							
1020	Tung	15	58.3	85.3	14.7	51	A-B
893	Tung	20	66.7	33.3	66.7	50	C
894	Tung	30	75	10.0	90.0	50	D
901	Tung	40	80	—	100.0	50	B-C
1021	Linseed	15	58.3	49.4	50.6	49.5	D
902	Linseed	20	66.7	30.6	69.4	51	B-C
903	Linseed	30	75	20.2	79.8	49.5	D
905	Linseed	40	80	10.0	90.0	50	C-D
1022	Soya	20	66.7	28.6	71.4	50	B
1023	Soya	40	80	34.7	65.3	50	C-D
1024	DH Castor	20	66.7	33.3	66.7	50	C
1025	DH Castor	40	80	2.6	97.4	49	E

NRP Formula No.	Oil Content		% Phthalic Content		Solution Characteristics	
	Type	% on Solids	Isomer	% on Solids	% Solids	G - H Viscosity
Alkyds						
912	Soya	59.4 ^a	Ortho	25	50	A-B
913	Soya	62.5 ^a	Ortho	24	50	A-B
914	Soya	56 ^a	Ortho	30	50	D-F
915	Soya	48 ^a	Ortho	35	42	E
916	Soya	39.6 ^a	Ortho	39	40	G-H
1055 ^b	Linseed	54	Ortho	35	50	A-B
1056 ^b	Soya	56.5	Ortho	31	50	A-B
E1	Safflower	70	Ortho	17	60	A ₁
E2	Safflower	83	Iso	9	60	A ₁
E3	Linseed-Soya	85	Iso	13	60	A ₁
E4	Soya	75	Iso	18	50	C-D
E5	Soya	72	Iso	20	50	C-D
E6	Soya	67	Iso	28	50	C-D

(a) Percent oil content calculated from reported fatty acid content. Other commercial alkyds are reported as oil content.

(b) Prepared in laboratory.

diffusant in the vicinity, thus providing the vapor with an easy means of movement.⁶ Permeation of vapors through polymers is a thermally activated process and the temperature dependence over small changes can be given by an Arrhenius type equation.⁷

$$P = P_0 e^{-E_p / RT} \quad (2)$$

P_0 , the pre-exponential factor, can be related to the openness of the polymer structure and the appearing-disappearing and reforming of voids due to movements of segmental chains in the activated state. E_p is the apparent energy of activation for permeation.

The concentration dependence of the permeability coefficient of a polymer for a vapor is governed basically by the size and shape of the penetrating molecule and also by its activity and solvent power. Ideal gases, because of their low activity and solvent power, do not cause swelling, strain, or other rearrangements in the structure of polymers. Consequently, permeability coefficients of polymers for such gases are not affected by concentration at a constant temperature. This is not the case with water vapor. Although water is not a good

solvent for most organic polymers, it does interact physically with polar groups present in the polymer and is absorbed. The activity of the sorbed water increases with concentration, thus affecting permeation. Hence, water permeation through polymers departs from Fickian behavior with changes in concentration or vapor pressure. The effect, however, is not large, as shown by the small change in permeability coefficients of polymers with increasing relative humidity.⁸

EXPERIMENTAL

Materials

Twelve paraphenylphenolic resin varnishes previously described⁹ were used. The proportion of oil, resin, and solvents in each varnish is summarized in Table 1. Five commercial short, medium, and long orthophthalic alkyds, plus two laboratory-prepared medium ones, and six isophthalic long and very long alkyds were also tested. The compositions of the commercial alkyds listed in the Table are based upon infor-

Table 2—Composition of Modified Phenolics, Oils and Alkyds

NRP Formula No.	Content of Varnish Oil or Alkyd		Content of Hexamine Condensate		Solution Characteristics	
	Type	% on Solids	Type	% on Solids	% Solids	Gardner-Holdt Viscosity
Phenolic Varnishes						
1057	20-gal D.H. Castor (1024)	60.0	Cardanol	40.0	50	B
1058	20-gal D.H. Castor (1024)	60.0	CNSL	40.0	50	B
1059	20-gal Soya (1022)	60.0	Cardanol	40.0	50	A-B
1060	20-gal Soya (1022)	60.0	CNSL	40.0	50	A-B
1061	40-gal D.H. Castor (1025)	50.0	Cardanol	60.0	50	C-D
1062	40-gal Soya (1023)	50.0	Cardanol	60.0	50	B-C
Oils						
1063	Dehydrated Castor Oil —	66.7	Cardanol	33.3	50	A-B
1064	Soybean Oil —	66.7	Cardanol	33.3	50	A-B
Alkyds						
1065	67% Soya Isophthalic (E6)	58.8	CNSL	41.2	50	B-C
1066	83% Safflower Isophthalic (E2)	58.8	Cardanol	41.2	50	A
1067	62.5% Soya Orthophthalic (913)	58.8	CNSL	41.2	50	A-B
1068	39.6% Soya Orthophthalic (916)	58.8	Cardanol	41.2	50	D

mation given by the manufacturers in the technical literature.

Some of the materials were modified as follows. Commercial cardanol and cashew nut shell liquid (CNSL) were first condensed, individually, with hexamine. One of the reaction products, cardanol-hexamine condensate or CNSL-hexamine condensate, was incorporated in some of the oils, phenolic resin varnishes, and commercial alkyds. The compositions of the modified coatings are described in Table 2.

Free Films

Coatings of uniform thicknesses were drawn down by a machine-driven film applicator on tin foil and air dried for three weeks in a dust-free room, controlled at $50 \pm 5\%$ RH, and $73.5 \pm 3.5^\circ\text{F}$ ($23 \pm 2^\circ\text{C}$). The free films obtained by amalgamation of the tin were dried in the same room for at least another three weeks before use.

Permeability Measurements

The steady rate of permeation of water vapor through free films of the clear finishes was determined using a modification of the well-known cup method. Film samples cut to the size of the cup were placed carefully on thin cardboard rings soaked in molten wax. They were first equilibrated with vapor at the desired RH and temperature and then placed over the cup which had been filled to the top with anhydrous magnesium perchlorate, taking care that the granules did not touch the film. The cup was sealed with wax in such a way that a known area of film covering the desiccant in the cup was exposed for the transmission of vapor.¹⁰ Sealing of the cups with the films was carried out at the temperature of the experiment so that the films would not bulge or contract due to changes in the temperature of the surroundings. Triplicate specimens were prepared for each type of film and separate sets were used for the variation of temperature and of RH.

Table 3—Effect of Relative Humidity on Rate of Permeation Through Phenolic Varnish Films at 73°F Rate of Permeation of Water Vapor - $\text{g/m}^2/\text{h}/\text{mil}$ ($25\ \mu\text{m}$)^a

% RH	15-gal. Varnishes		20-gal. Varnishes				30-gal. Varnishes		40-gal. Varnishes			
	1020 Tung	1021 Linseed	893 Tung	902 Linseed	1022 Soya	1024 DH Castor	894 Tung	903 Linseed	901 Tung	905 Linseed	1023 Soya	1025 DH Castor
50.0	0.54	0.58	0.67	0.75	1.16	0.93	0.80	0.79	1.13	1.22	1.46	1.20
57.5	0.62	0.67	0.78	0.86	1.27	1.07	0.92	0.92	1.31	1.39	1.69	1.39
70.0	0.76	0.82	0.94	1.06	1.57	1.30	1.12	1.13	1.59	1.71	2.06	1.70
80.0	0.92	0.98	1.07	1.21	1.86	1.50	1.35	1.38	1.85	2.02	2.41	2.05
87.0	1.02	1.08	1.20	1.33	2.09	1.67	1.55	1.57	2.10	2.28	2.65	2.37
97.0	1.17	1.27	1.39	1.60	2.37	1.93	1.79	1.83	2.38	2.61	3.05	2.73

(a) Thickness of film.

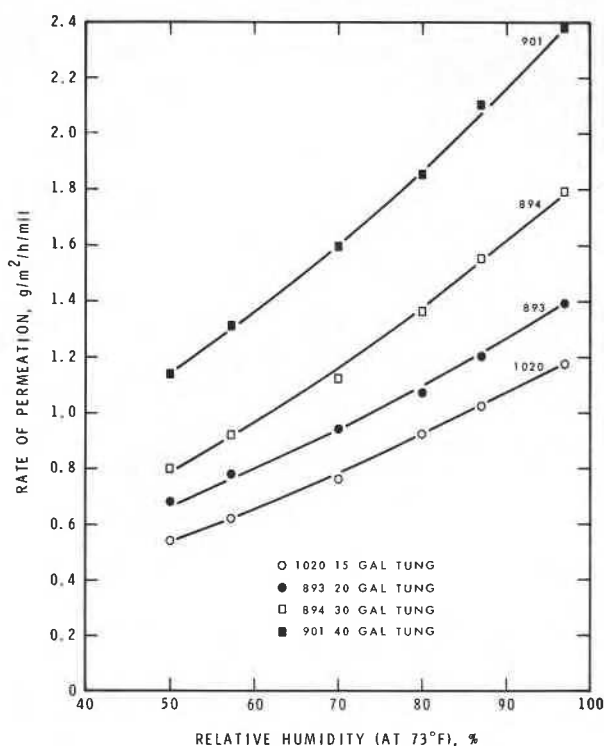


Figure 1—Relative humidity vs. permeation rate through phenolics with different oil contents

The sealed cups were placed in a specially designed humidity cabinet which can be adjusted to any desired RH at temperatures between 30 and 160°F (−1 and 71°C). The transmission of water vapor was determined by weighing the cup inside the humidity cabinet, the gain in the weight being followed as a function of time. In most cases a steady rate of vapor transfer was attained in 48 hr.

The rate of water vapor permeation through the free film was determined under steady flow conditions at different relative humidities with a constant temperature of 73°F (23°C) and at different temperatures with a constant humidity of 50%. Rates were calculated in terms of the quantity of vapor (g) permeating in one hour (h) through a film of unit area (m²) and unit thickness, 1 mil (25 μ m).

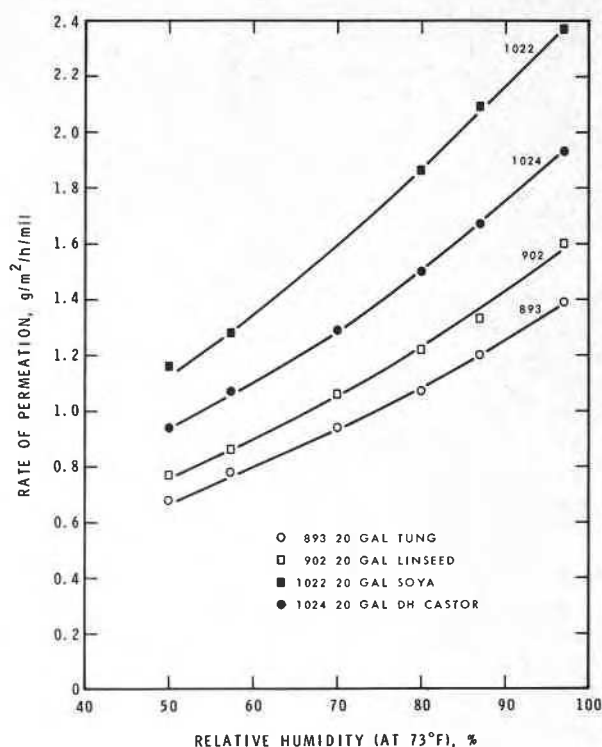


Figure 2—Relative humidity vs. permeation rate through phenolics with different oil types

RESULTS

Treatment of Results

The space in the cup under the film was filled with the desiccant to the extent that only a small volume between the film and desiccant was left. In such a system the vapor permeating through the film is mostly absorbed by the desiccant thus having negligible pressure in the cup. For the purpose of calculating the coefficient of permeation, the vapor pressure inside the cup was considered to be zero and the pressure differential, Δp , across the film equal to the vapor pressure corresponding to the RH of the experiment.

The permeability coefficient of each coating formu-

Table 4—Effect of Relative Humidity on Rate of Permeation Through Alkyd Films at 73°F

Rate of Permeation of Water Vapor - g/m²/h/mil														
Ortho-phthalic Alkyds														
Commercial						Lab Prepared			Iso-phthalic Alkyds - Commercial					
% RH	912 Soya	913 Soya	914 Soya	915 Soya	916 Soya	E1 Saf-flower	1055 Lin-seed	1056 Soya	E2 Saf-flower	E3 Lin-Seed Soya	E4 Soya	E5 Soya	E6 Soya	
50	0.99	1.42	1.03	0.86	0.73	1.46	0.52	1.07	2.05	1.82	1.87	1.55	1.30	
65	1.38	2.00	1.41	1.19	1.01	2.04	0.73	1.46	2.94	2.49	2.52	2.12	1.76	
80	2.10	3.11	2.17	1.85	1.57	3.19	1.17	2.19	4.21	3.72	3.75	3.20	2.40	
90	2.47	3.67	2.54	2.21	1.85	3.81	1.40	2.51	5.05	4.33	4.36	3.72	2.88	
97	2.86	4.26	2.97	2.55	2.13	4.43	1.66	2.90	5.74	4.91	4.96	4.17	3.31	

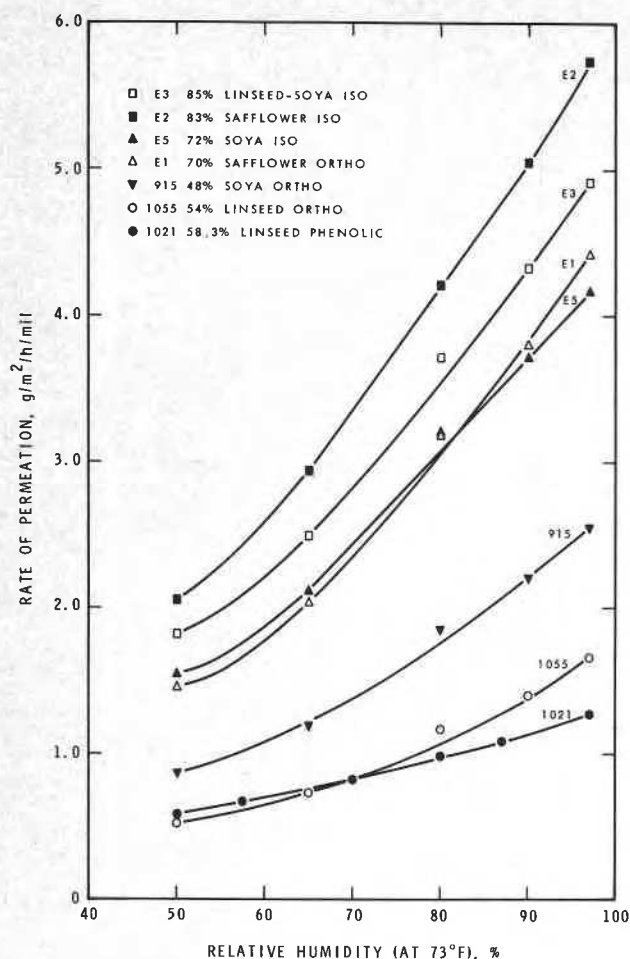


Figure 3—Relative humidity vs. permeation rate through alkyds

lation for water vapor was calculated using equation (1) and expressed in the following units:

$$P = \frac{Q \times l}{a \times t \times \Delta p} \quad \frac{\text{gm cm}}{\text{cm}^2 \text{ sec mm Hg}} \quad (3)$$

Effect of RH on Permeation

The permeation rates through phenolic varnishes are given in Table 3 with representative curves plotted in Figure 1 for different oil contents and in Figure 2 for different oils types. It can be seen that at lower RH the rates increase linearly with vapor pressure but at higher RH the increase is somewhat more than linear.

Permeation rates through alkyds (Table 4) are more affected by water vapor pressure than through phenolics. For example, at 50% RH and 73°F the permeation of water vapor through a medium linseed alkyd (NRP 1055) is 10% lower than through a linseed phenolic (1021), whereas at 97% RH it is 31% more. It is evident in Figure 3 that in the one comparable case the permeation rate through an orthophthalic alkyd is affected more by higher RH than an isophthalic alkyd (E1 vs. E5). Because in the case of alkyds the permeation rates increase markedly with RH, it is concluded that the sorbed vapor has a greater plasticizing action on the internal structure of alkyds than phenolics.

Of the phenolic varnishes, those prepared from semi-drying soya oil are, relatively, the most permeable to water vapor. Upon modification with the condensate of either cardanol or CNSL this property is changed considerably (Figure 4). Modified dehydrated castor oil phenolics also show lower permeation than the unmodified ones. The results also indicate that the CNSL condensate with hexamine reduces the permeability of phenolics more than the cardanol condensate.

It is evident from Table 5 that modification of the long and very long oil alkyds reduced their permeability significantly (E2 vs. 1066, E6 vs. 1065, and 913 vs. 1067). With a short alkyd there is not the same degree of change in permeability (916 vs. 1068) (Figure 5). This is considered to be confirmation that in long and very long alkyds, the oil is not fully reacted with the resin¹¹ so the cardanol or CNSL hexamine condensate forms crosslinks with the partially reacted oil and improves the properties of the composition. In a short alkyd the degree of reaction is limited hence the modification can have less effect.

Effect of Temperature on Permeation

A certain amount of energy is needed to generate thermal motion in coating molecules so that they are separated sufficiently to allow the diffusant molecules to move through the spaces created. The fairly low permeation rates of some varnishes at 63°F (17°C) show that the movement of water vapor through the coatings is very low due to the low state of molecular activity. On the other hand, a temperature increase of 40°F (22°C) activates the coating molecules so that the permeation rates of some phenolics are found to be more than seven times faster (Table 6). These results indicate that a

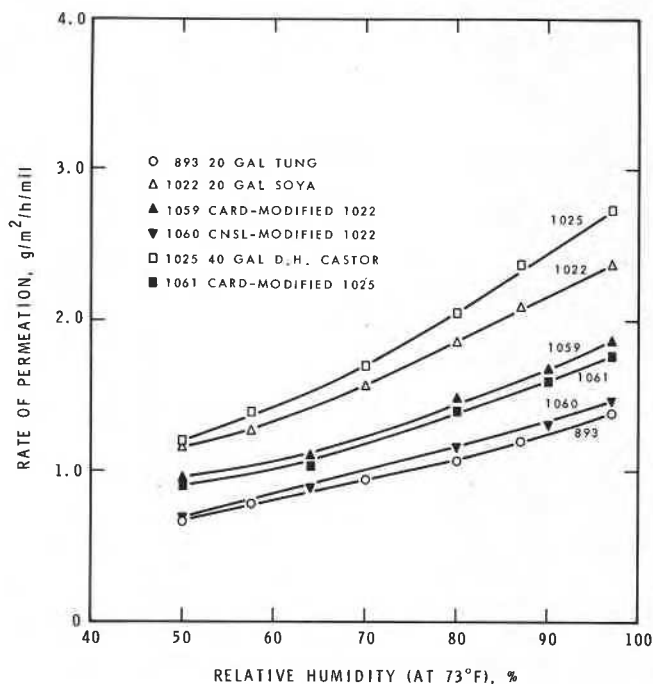


Figure 4—Relative humidity vs. permeation rate through phenolics and modified phenolics

Table 5—Effect of Relative Humidity on Rate of Permeation Through Modified Phenolic, Oil, and Alkyd Films at 73°F

Per-Cent R.H.	Rate of Permeation of Water Vapor - g/m ² /h/mil											
	Modified Phenolics				Modified Oil				Modified iso-phthalic Alkyds	Modified o-phthalic Alkyds		
	20-gal.	40-gal.	20-gal.	40-gal.	20-gal.	40-gal.	20-gal.	40-gal.	1066 Card. Very Long Saf-flower	1067 CNSL Long Soya	1068 Card. Short Soya	
	1057 Card. ^a DH Castor	1958 CNSL ^b DH Castor	1059 Card. Soya	1060 CNSL Soya	1061 Card. DH Castor	1062 Card. Soya	1063 Card. DH Castor	1064 Card. Soya	1065 CNSL Long Soya			
50	0.76	0.61	0.86	0.69	0.80	0.95	0.93	1.51	0.96	1.51	1.02	0.85
64	0.98	0.78	1.11	0.89	1.03	1.22	1.20	1.98	1.25	1.96	1.43	1.10
80	1.25	1.01	1.48	1.16	1.40	1.63	1.55	2.61	1.69	2.62	1.98	1.46
90	1.45	1.16	1.68	1.31	1.60	1.84	1.80	3.02	1.94	3.04	2.32	1.71
97	1.61	1.29	1.87	1.47	1.77	2.06	2.01	3.38	2.19	3.42	2.62	1.93

(a) Card. = Cardanol

(b) CNSL = Cashew Nut Shell Liquid

change in the environmental temperature has a marked influence on permeation rates of vapors through certain coatings. It is useful, therefore, to know the temperature dependence of permeation rates if the selection of coatings is to be made on the basis of permeability properties.

The results show that with phenolic varnishes the increase in permeation rates with temperature depends on the type of oil used because the increase is not

proportional in all cases (Table 6). For example, at 63°F and 50% RH, the rate through 20-gal soya phenolic (0.61 g/m²/h/mil) is one and one-half times that of the same oil length tung phenolic (0.405 g/m²/h/mil), whereas at 103.6°F (39.8°C) it is double (soya - 4.64; tung - 2.36). In the case of varnishes with the same oil but different oil contents, the permeation rates of coatings with high oil content increase relatively fast with temperature [linseed oil: 1021 vs. 903; soya: 1022 vs. 1023 (Figure 6)].

In the same Figure, comparison of plots for alkyds and phenolics (1055 vs. 1021, 1056 vs. 1022, and E4 vs. 1023) shows that the temperature dependence of permeation rates of alkyds is more than for phenolics even though the latter contain somewhat more oil. Among alkyds the increase in rates with temperature is greater in the case of orthophthalic alkyds than in the isophthalic ones (913 vs. E5 in Table 7). It is thought that the effect of temperature on permeation properties of alkyds is dependent upon the degree of crosslinking, the inter-molecular spacings, and the total free energy levels in their molecular structures.

The effect of temperature on permeation rates through modified alkyds and phenolics is presented in Table 8. After modification there is less difference between dehydrated castor and soya (1058 vs. 1060) than with the original varnishes. The large difference between a modified coating and its original counterpart shows the improvement in temperature resistance properties due to the reaction. Modification of the 40-gal soya phenolic results in lower permeability for 1062 than the unmodified 20-gal varnish, 1022. Even soya oil modified by cardanol condensate (1064) transmits less water vapor than unmodified very long oil alkyds at higher temperatures. The difference in temperature dependence between unmodified and modified alkyds is small for short oil lengths (916 vs. 1068) but increases with increasing oil content (913 vs. 1067 and E2 vs. 1066).

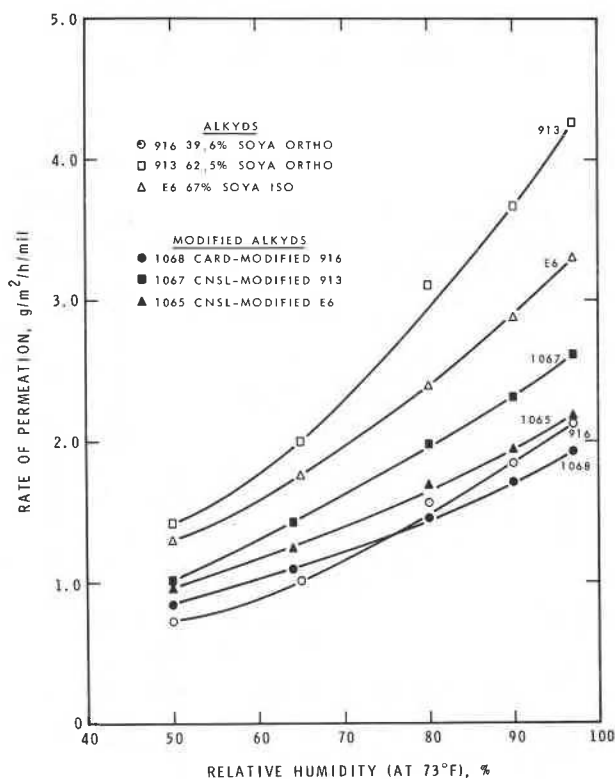


Figure 5—Relative humidity vs. permeation rate through alkyds and modified alkyds

Table 6—Effect of Temperature on Rate of Permeation Through Phenolic Varnish Films at 50% RH

Temperature °F	Rate of Permeation of Water Vapor - g/m ² /h/mil											
	15-gal. Varnishes		20-gal. Varnishes				30-gal. Varnishes		40-gal. Varnishes			
	1020 Tung	1021 Linseed	893 Tung	902 Linseed	1022 Soya	1024 DH Castor	894 Tung	903 Linseed	901 Tung	905 Linseed	1023 Soya	1025 DH Castor
63.0	—	—	0.40	0.41	0.61	0.50	—	—	0.61	0.68	—	—
73.0	0.54	0.58	0.67	0.75	1.15	0.93	0.80	0.79	1.13	1.22	1.46	1.20
84.0	0.88	0.84	1.01	1.15	1.91	1.46	1.39	1.38	1.76	1.92	2.28	2.10
94.6	1.41	1.36	1.59	1.89	3.04	2.33	2.28	2.14	2.83	3.04	3.84	3.52
103.6	2.26	2.28	2.38	2.91	4.70	3.56	3.35	3.41	4.36	4.75	6.27	5.46

Effect of RH on Permeability Coefficient

Permeability coefficients at different RH are illustrated in Figure 7. While higher humidities had a relatively large effect on permeation rates (Figures 1 and 2) the phenolic permeability coefficient plots are almost flat with respect to the RH axis except at humidities above 85% or for varnishes containing large proportions of semi-drying oils. Although the deviation

away from the axis indicates some dependence on moisture content, it is concluded that the permeability coefficients of phenolics for water vapor are little affected by an increase in moisture content. Modification of the longer oil varnishes reduced the effect of RH on the permeability coefficient to close to that of the short oil varnishes.

The permeability coefficients of alkyds increase with RH rather more than phenolics, with the isophthalic alkyd being less affected than an ortho alkyd of slightly lower oil content. A remarkable decrease in the RH dependence of the permeability coefficient of very long isophthalic alkyd E2 can be seen after its modification (1066).

Effect of Temperature on Permeability Coefficient

The change in permeability coefficient with temperature provides an insight into the mechanism of permeation and the nature of the coating. Owing to the low activity of ideal gases towards polymers, log P is a linear function of 1/T over a wide temperature range above the glass transition temperature. By contrast, the permeation of water vapor through any amorphous polymer, such as a coating, is affected by temperature because of the increased activity of water. Nevertheless, the logarithmic values of permeability coefficients of coatings for water vapor are linearly related to the inverse of temperature over small temperature changes.

While the permeability coefficients of phenolics were almost independent of RH at lower relative humidities, Figure 8 shows that they increase with temperature. As before, the increase is greater with varnishes containing soya oil or larger amounts of tung and linseed.

The increase in permeability coefficients of alkyds with temperature is relatively higher than phenolics unless the alkyd contains much less oil (916 vs. 1022). The temperature dependence of orthophthalic alkyds is greater than that of iso alkyds at comparable oil lengths.

Modification of phenolics reduces both the magnitude of the permeability coefficient and its change with temperature. The coefficient of the short oil alkyd is affected more by temperature than is its modification (916 vs. 1068).

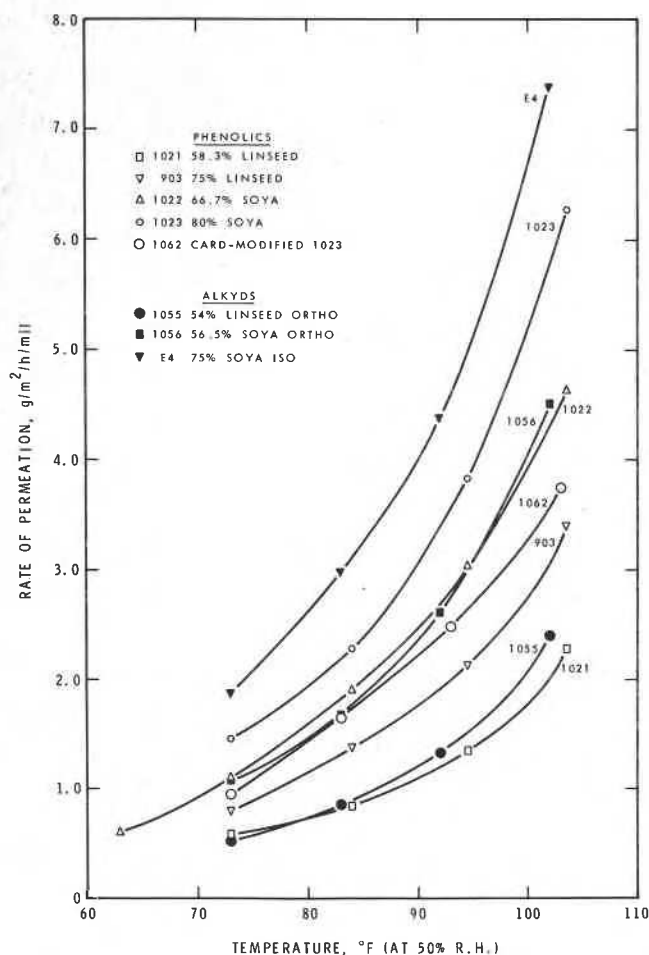


Figure 6—Temperature vs. permeation rate through phenolics and alkyds

Table 7—Effect of Temperature on Rate of Permeation Through Alkyd Films at 50% RH

Rate of Permeation of Water Vapor - g/m ² /h/mil													
Temperature °F	Ortho-phthalic Alkyds						Lab. Prepared		Iso-phthalic Alkyds—Commercial				
	Commercial												
	912 Soya	913 Soya	914 Soya	915 Soya	916 Soya	E1 Saf- flower	1055 Lin- seed	1056 Soya	E2 Saf- flower	E3 Lin- seed Soya	E4 Soya	E5 Soya	E6 Soya
73	0.99	1.42	1.03	0.86	0.73	1.46	0.52	1.07	2.05	1.82	1.87	1.55	1.30
83	1.64	2.39	1.68	1.45	1.24	2.41	0.86	1.71	3.22	2.93	2.98	2.51	2.12
92	2.47	3.63	2.64	2.41	2.00	3.65	1.33	2.62	5.22	4.32	4.38	3.71	3.15
102	4.32	6.46	4.35	3.79	3.44	6.29	2.41	4.51	—	—	7.39	6.27	5.44

Effect of Composition of Permeation Of Water Vapor

From the results presented, it can be seen that, in general, the higher the oil content in either phenolic varnishes or alkyds the greater the permeability and the more permeation rates and coefficients are affected by temperature and RH.

In phenolic varnishes, the rate of permeation decreases with increasing resin content in all four oils studied. Also the changes in permeability and permeability coefficient with both increasing RH and temperature are smaller with varnishes containing less oil (Figures 1, 4, 6, and 8). It is also evident that tung oil varnishes are less permeable to water vapor than those containing linseed oil. Dehydrated castor and soya varnishes are, in turn, more permeable. Again, the effect of RH and temperature on permeation rate and permeability coefficient is in the same order.

Alkyds are more permeable to water vapor than phenolics. To obtain the same permeation rate at 73°F as the 20-gal soya varnish which contains 67% oil, it is necessary to use a soya alkyd with an oil content of less

than 60%. Within the alkyd group there is the same relationship between oil content and permeability, although NRP 914 appears to be out of line. There are not enough resins containing the same amount but different types of oil to reach firm conclusions about the effect of oil type. It appears, however, that as with the phenolics, linseed alkyds are less permeable than soya or safflower alkyds. Isophthalic alkyds are less permeable than orthophthalic resins of comparable oil content; e.g., E6 with 67% soya transmits 1.3 g/m²/hr/mil while 913 with 62.5% oil transmits 1.4 g at 73°F.

The effect of modification with cardanol or CNSL hexamine condensate is to reduce the permeation rate at a given set of conditions and the effect of RH and temperature on permeation and permeability coefficients. CNSL causes a greater change in permeability characteristics than cardanol.

Permeability and Its Relation to Durability

In natural^{12,13} and accelerated weathering studies of many of these phenolics and alkyds applied to red cedar, the phenolics have generally performed better

Table 8—Effect of Temperature on Rate of Permeation Through Modified Phenolic, Oil, and Alkyd Films at 50% RH

Rate of Permeation of Water Vapor - g/m ² /h/mil												
Tempera- ture °F	Modified Phenolics						Modified Oil		Modified iso-phthalic Alkyds		Modified o-phthalic Alkyds	
	20-gal.			40-gal.								
	1057 Card. ^a DH Castor	1058 CNSL ^b DH Castor	1059 Card. Soya	1060 CNSL Soya	1061 Card. DH Castor	1062 Card. Soya	1063 Card. DH Castor	1064 Card Soya	1065 CNSL Long Soya	1066 Card. Very Long Saf- flower	1067 CNSL Long Soya	1068 Card. Short Soya
	73.0	0.76	0.61	0.86	0.69	0.80	0.95	1.13	1.51	0.96	1.54	1.02
83.0	1.31	1.06	1.50	1.20	1.46	1.67	2.23	2.44	1.65	2.71	1.76	1.54
93.0	1.93	1.55	2.22	1.83	2.19	2.49	4.11	3.84	2.40	4.03	2.78	2.23
103.0	2.95	2.45	3.36	2.81	3.25	3.76	6.91	6.14	3.51	6.03	4.24	3.43

(a) Card. = Cardanol

(b) CNSL = Cashew Nut Shell Liquid

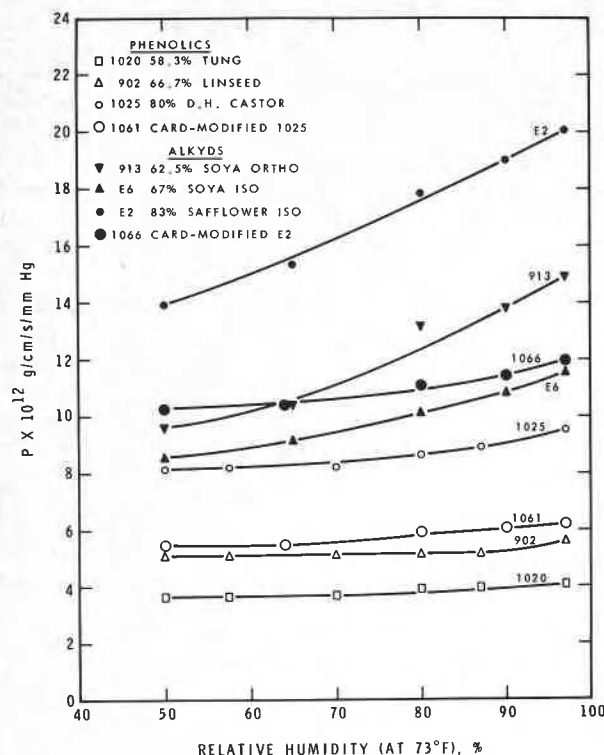


Figure 7—Relative humidity vs. permeability coefficient

than the alkyds. This difference in durability is related, in part, to the lower permeability of the phenolics. For example, both the 20-gal tung and linseed varnishes, which contain 67% oil, were superior to all the soya ortho alkyds, which vary in oil content from 39.5 to 62.5%. Only the short soya alkyd had a lower permeability at 50% RH and 73°F than the linseed phenolic, but permeability of the alkyd increased more rapidly with increasing temperature or humidity.

Within the phenolic group of coatings, for varnishes with the same oil type, the two shorter varnishes are the most durable, followed by the 30-gal varnish; the 40-gal is least durable. Thus, high durability correlates with the decreasing permeability shown in Figure 1. If oil content is decreased to 10 gal (50% oil), however, durability falls off while permeability should be similar to that of the 15-gal varnish. For varnishes containing the same quantity of different oils, durability is in the decreasing order of tung, linseed, DH castor, and soya, which corresponds exactly to the decrease in permeability and the effects of RH (Figure 2) and temperature (Figure 6).

For alkyds, only the ortho soya series and one iso alkyd were exposed in the exterior weathering studies. The durability results correlate with decreasing permeability only at the high oil content end because there is a peak in durability at 56 to 60% oil, while permeability decreases continuously with decreasing oil content.

The modified alkyds also illustrate that low permeability is not the only factor involved in durability of clear finishes. Cardanol and CNSL-hexamine modification reduced the permeability of all alkyds except 916, as well as the effect of RH or temperature on

permeability. It has not, however, been shown to improve durability of the alkyds.

DISCUSSION

The water molecule is relatively small and has a tendency to form hydrogen bonds with other water molecules in either the liquid or solid state, as well as with polar groups present in the material of contact. Hence, water vapor sorbed in a coating forms hydrogen bonds with hydrophilic or polar groups of the polymer, and permeation is followed by the spatial movement of the vapor from high to low pressure levels. Apart from the heat of solution the sorbed vapor needs energy for moving from one position to the other. This energy is principally supplied by the thermal motion of the polymer molecules. Structural configuration and inter-molecular forces contribute to a polymer's total free energy which, consequently, is of a different value for each polymer. Since a change in temperature generates different thermal motions in different polymers, a vapor with a definite amount of free energy faces different degrees of resistance in permeating through them.

This difference in energy requirement for the permeation of vapor is related to the degree of crosslinking in the polymer as well as to the size of the penetrating molecule. In a highly crosslinked product the randomness due to the movement of segmental chains and formation of spacings is restricted. In such a system the movement of the penetrant is impeded and the rate of diffusion and, consequently, the permeation is dependent upon the degree of crosslinking.¹⁴ The energy of

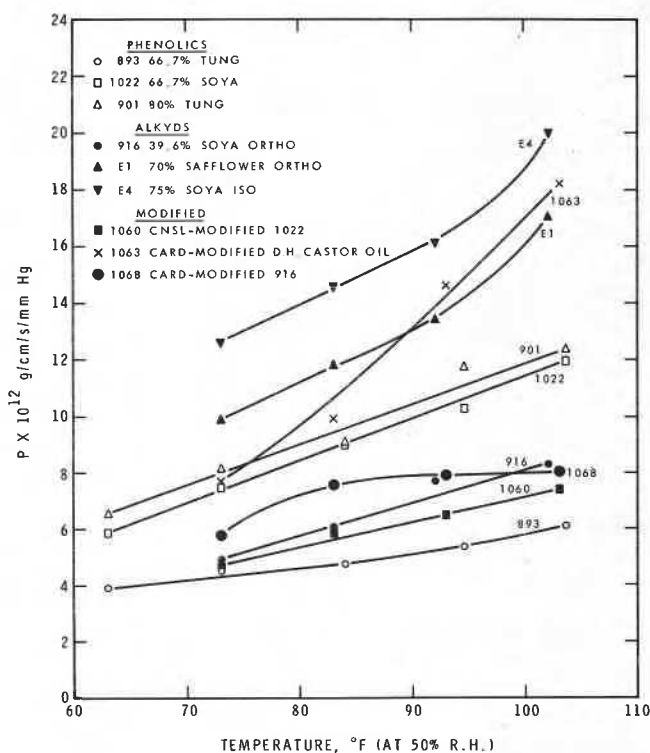


Figure 8—Temperature vs. permeability coefficient

activation required for the permeation of vapor through a coating can be correlated with the degree of crosslinking.

The results obtained on the permeation of water vapor through coatings containing semi-drying and drying oils qualitatively support the relation between permeation and the degree of crosslinking observed in polymers. Resin in the composition not only forms crosslinks with the oil but also physically reinforces the coating. This is illustrated by the differences between phenolics and alkyd coatings: phenolics have a more highly condensed structure which is reflected in the lower permeability and higher tensile strength of varnishes made with them.

Conversely, the oil portion of coatings has a much more open structure resulting in relatively low resistance to water transmission and low tensile properties. Tung oil, because of its high degree of conjugated unsaturation, forms more crosslinks with resins and with itself than do the other oils. Consequently, tung-based varnishes are not only less permeable to water but also stronger mechanically than varnishes made with other oils.

CONCLUSIONS

Permeability measurements correlate well with the durability ratings of phenolic varnishes containing 58 to 80% oil. The low oil content tung and linseed varnishes, which have lower permeabilities than soya or DH castor varnishes of the same oil content or tung and linseed varnishes of higher oil content, are the most durable on exterior wood. With alkyds, permeability is only a factor at higher oil contents because the shorter alkyds with lower permeabilities are also less durable than those containing intermediate quantities of oil.

Permeation rates and permeability coefficients of coatings for water vapor reported here differ greatly from each other in value. This feature of the permeability properties of coatings can be explained on the basis of the general characteristics of the materials used in the formulation and also their structural arrangement. Molecules with little or no regularity of structure do not pack closely together. Consequently, between such molecules there are openings with sufficient space for the permeating molecules to diffuse through easily, which results in high permeability. For this reason, amorphous polymers generally have higher permeation rates than crystalline ones.⁶

The low permeation rates and permeability coefficients that are less affected by RH and temperature of the lower oil content phenolic varnishes are related to the symmetry and greater crosslinking conferred by the phenolic resin. The decrease in permeability coeffi-

cients of the modified formulations is also due to molecular changes. The study of the RH and temperature dependence of permeability coefficients of coating materials for water vapor can be used as an index of the degree of crosslinking in their molecular structures when they are prepared from known components.

The results given here show that this type of study allows formulation of coatings on an engineering basis instead of on empirical relationships to generic classes. Where low permeability of the final product is important, the formulator should not select a resin the permeability of which is high or which increases markedly with temperature of RH. Conversely, for coatings intended to be permeable, selection of an impermeable resin or one relatively unaffected by temperature or humidity would necessitate greater pigmentation to obtain the desired permeability. This might adversely affect other properties such as weatherability.

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References

- (1) Funke, W., *Farbe Lack*, 73, No. 8, 707 (1967).
- (2) Bixler, H.J. and Sweeting, O.J., "Barrier Properties of Films," in "The Science and Technology of Polymer Films," O.J. Sweeting, ed., Vol. 2, Interscience, New York, 1968, p 5.
- (3) Sweeting, O.J. *ibid*, Vol. 1, p 596.
- (4) Yaseen, M., *Deut. Farben-Z.*, 27, No. 5, 213 (1973).
- (5) Rogers, C.E., "Permeability and Chemical Resistance," in "Engineering Design for Plastics," E. Baer, ed., Reinhold Pub. Corp., New York, 1964, p 609.
- (6) Van Amerongen, G.J., *J. Polymer Sci.* 2, No. 4, 381 (1947).
- (7) Meares, P., "Polymers: Structures and Bulk Properties," D. Van Nostrand Co. Ltd., London, 1967, p 324.
- (8) Long, F.A. and Thompson, L.J., *J. Polymer Sci.*, 15, No. 80, 413 (1955).
- (9) Yaseen, M. and Ashton, H.E., *J. Oil & Colour Chemists' Assoc.*, 53, No. 11, 977 (1970).
- (10) Joy, F.A. and Wilson, A.G., "Standardization of the Dish Method for Measuring Water Vapor Transmission," in "Humidity and Moisture," Vol. 4, P.N. Winn, ed., Reinhold Pub. Corp., New York, 1965, p 263.
- (11) Payne, H.F., "Organic Coating Technology," Vol. 1, J. Wiley and Sons, New York, 1954 p 279.
- (12) Ashton, H.E., *JOURNAL PAINT TECHNOLOGY*, 39, No. 507, 212 (1967).
- (13) Ashton, H.E., *Can. Paint & Finishing*, 48, No. 2, 13 (1974).
- (14) Sobolev, I., Meyer, J.A., Stannett, V., and Szwarc, M., *J. Polymer Sci.*, 17, No. 85, 417 (1955).