THE EFFECT OF VARIOUS WOOD SUBSTRATES ON THE LIQUID WATER AND WATER VAPOR PERMEABILITY OF PIGMENTED ORGANIC COATINGS

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ABSTRACT

THE EFFECT OF VARIOUS WOOD SUBSTRATES ON THE LIQUID WATER AND WATER VAPOR PERMEABILITY OF PIGMENTED ORGANIC COATINGS

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In this study, five organic coatings, both free films and those applied on ten redwood and one series of hemlock substrate variables, were tested for permeability to water vapor. The eleven substrate variables were the result of machining differences, chemical and structural differences or varying grain directions. The same five coatings applied to metal substrates to simulate free films and to five different redwood substrate variables, were tested for permeability to liquid water. From this information it was hoped that knowledge may be gained concerning the effects of a standard redwood substrate on the permeability of various pigmented coatings, the effects of various substrates on the permeability of the coatings and the equivalence of liquid water permeation to water vapor permeation. It was also hoped that the effect of film thickness on the permeability coefficient could be determined and the feasibility of the experimental electrical method of measuring liquid permeation established.

The number of coatings and wood substrate variables tested did not enable the experimental design to fit a statistical analysis. Due to this limitation, trends were indicated but not statistically proven.

It was noted that with all of the paints, except the linseed oil undercoat (paint no. 1) and the one coat latex paint (paint no. 3), there was an increase in the coated substrates permeability, as compared to that of the free film and the substrate combined. Paint no. 1 applied on the wood substrate was consistently less permeable than the free film and the wood substrate combined. The permeability of the one coat latex paint was so large that no definite results were obtained.

The permeability of paint no. 1 coated on variable redwood substrates decreased as the amount of excised cell wall material increased. The permeability was directly related to the exposure time of the surface excised cells to the atmospheric conditions. The permeability was directly related to the roughness factor of the wood substrate surface and to substrate expansion, caused by an increase in moisture content. Extractives present in the redwood substrate decreased the permeability of the applied film system, while steam conversion of the extractives increased the system's permeability. No conclusions were drawn concerning the effect of film thickness on the permeability coefficient. However, with the exception of paint no. 3, the film thickness was inversely related to the weight loss per 24 hours.

The equivalence of liquid water permeation and water vapor permeation was indicated but not definitely proven. This was because of the difficulty of obtaining reproducible results and the lack of absolute values with the liquid study. Also, comparisons were limited since paint no. 1 was used in the vapor study and paint no. 3 was used as the standard in the liquid study.

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INTRODUCTION

Wood finishes are polymeric substances which serve a twofold purpose; protection and decoration. The coating affords the substrate protection from degradation by moisture, ultraviolet radiation, oxygen and micro-organisms. Moisture degradation is the dominant cause of defects due to the chemical and physical properties of the water molecule. The dipole moment of water creates a polar molecule with a great solvating force. The molecule is able to penetrate protective coatings and by random diffusional jumps, determined by the moisture gradient, the water molecule passes through the film. The film cannot prevent moisture penetration but rather retards the rate causing a steep moisture gradient across the film. Since water has a greater affinity for wood than do most organic finishes, the adhesive bond at the substrate-coating interface is decreased. This allows various film failures to occur.

There are four main categories of wood finishes that are used to protect wood; films that cure by solvent evaporation, films that cure by an oxidative mechanism, thermosetting resins, and two component systems. This study is concerned with the effect of wood substrates on the liquid and water vapor permeability of films that cure by solvent or diluent evaporation and by an oxidative mechanism.

STATEMENT OF THE PROBLEM

A great deal of research has been completed, determining the permeability of various free films to water vapor. These studies were concerned with the effects of coating composition and structure on permeability, while ignoring the effect of the substrates. Also, only limited work has been completed concerning the permeability of organic coatings to liquid water due to the absence of a standard test for liquid water permeation.

This investigation proposes to determine the wood substrate's effect on the permeability to liquid water and water vapor of various pigmented organic coatings. It is hoped that by the use of various redwood substrates, differing in the type of machined surface, chemical composition, structure or grain direction, the effect of the substrate variable on the permeability of applied coatings can be determined. The liquid water permeation is hoped to be measured by an unproven electrical method so that another object of this study is the evaluation of the feasibility of this method. If the liquid water permeation test is feasible, it is hoped to evaluate the equivalence of liquid water permeation and water vapor permeation.

It is hoped that this investigation will illustrate the necessity of testing a coating's permeability when it is applied on the in-use substrate rather than as a free film. This study, correlated with previous studies on permeability, can possibly indicate the coating-substrate combination required to obtain the necessary permeability for a durable film.

CHAPTER I

REVIEW OF LITERATURE

Methods of Measurement

There are two methods widely used to determine diffusion and permeability coefficients of water vapor. The first method employs a film of known dimensions suspended inside a vacuum chamber. The rate of absorption or desorption is measured gravimetrically by the extension of a calibrated quartz spring, followed with a cathetometer. After introducing a fixed water vapor pressure, the amount of water absorbed by the film is observed. The diffusion coefficient is obtained from this information using Fick's law for time independent diffusion coefficients. The solubility coefficient is obtained from the equilibrium solubility. Assuming Henry's law to be valid, Spencer (24) calculated the permeability coefficient.

The second method for obtaining the water vapor permeability coefficient uses an initially dry film through which water vapor is permitted to pass. Pressure increase or weight loss is measured as a function of time. A steady state permeation is achieved and the diffusion coefficient is calculated from the time needed to reach the steady state. The permeability coefficient is calculated from the steady state results in accordance with ASTM D1653-62 using a vapometer cup and measuring weight loss.

A variation of the second method is the time-lag method used by Yasuda and Stannett (4) to determine water vapor permeability. A film separates an area of high pressure from a low pressure area. The water vapor supply is connected to the side of high pressure causing the water to diffuse through the film. The difference in the initial and final pressure is plotted versus time when the steady state condition is achieved. If the diffusion process is Fickian, the relationship is linear and extrapolation to the time axis yields the commencement time of steady state permeation. From this data, the permeability and the diffusion coeffients can be obtained.

There is no standard procedure for the determination of the permeability coefficient of liquid water. Various experimental techniques have been used but the reproducibility and accuracy were limited. At present Subcommittee 52 of the ASTM is developing a means for determination of liquid water permeability through organic coatings on porous substrates.

The Polymer Penetrant System

The penetration of water or any other small molecule into a polymeric structure is a thermodynamic process. Browne (7) has stated that permeability and water absorption have no direct correlation to each other. Michaels (22) however, states that permeability is governed by the joint process of diffusion and water absorption. He concludes that absorption affects the solubility coefficient(S) and diffusion is the rate limiting step of permeation.

Permeation is controlled by external conditions, the chemical and physical properties of the polymer and the nature of the penetrant, but the penetrant once in the polymeric system alters the polymer's properties. The second order transition or the glass transition temperature is one of these altered properties.

Polymer molecules seldom move as an entity but rather segmental motion occurs where a group of adjacent atoms along the chain move as a single small molecule in Brownian motion. These segments are attached to neighboring segments by primary valence bonds so that the motion affects that of its neighbors. A long chain polymer can twist itself into many different configurations by means of these segmental motions.

Below the transition temperature, the polymer is in a quasi-crystalline state. Segmental motion has essentially ceased, the configuration is locked in the polymer and the entropy is close to zero. The only motion is caused by the chain ends due to their additional degree of freedom. As the temperature is increased, the amplitude of segmented vibration increases until above the glass transition temperature (Tg) the polymer is in a rubbery state. The crystal structure has not changed, but is free to move, and the configurational entropy has increased. In copolymers where different bonds exist along the chain allowing rotation at different temperatures, there may be an upper and lower transition temperature.

Stannett and Williams (27) found no change in the diffusion rate of gases above or below the Tg. This effect was attributed to the relative sizes of the gas molecules compared to the hole size of the polymer. An increased diffusion effect was found with the polymer above the Tg when water vapor was the penetrant. This was attributed to the greater size of the water molecule and a plasticizing effect of the water when the film is above its glass transition temperature.

The water penetrant acts as a plasticizer once inside the polymer. This effect lowers the Tg by separating the polymer chains and allowing greater segment mobility at any given temperature. Therefore, the diffusion rate of water after the initial absorption increases until the polymer film comes to equilibrium in an expanded state. At this point, the diffusion reaches a steady state and the permeability coefficient can be calculated.

Long and Thompson (19) found that water plasticization in organic coatings increased the permeability of acetone and carbon tetrachloride by a factor of 75. Kumins and Roteman (15) found that the minimum free volume necessary for diffusion of water vapor is less than expected due to the plasticization effect.

The glass transition temperature (Tg) varies with the composition of the polymer system. In paint formulations where pigments are added, this non-reinforcing solid may restrict the motion of the polymer chains by adsorbing segments of the chain on its surface. If there was a significant surface area present, determined by the pigment volume content, the polymer would be immobilized enough to effectively reduce the Tg. It was shown by Kumins and Roteman (15) that as little as .01 volume fraction of titanium dioxide caused a measurable lowering of the upper Tg of copolymers. The trend observed was that the upper Tg decreased to the lower Tg and then increased with the further addition of pigment.

Kwei and Arnheim (16) found that the activation energy for gas diffusion in poly (vinyl acetate) filled with 12 percent by volume of titanium dioxide was 56 percent of the corresponding value in the unfilled polymer. The authors also found that the activation energies for gas permeation in filled polymers were the same above and below the Tg due to the small size gas molecules.

The immobilization of polymer chains is only one effect caused by pigment incorporation in the polymer system. Kumins (15) lists other filler-polymer system properties that may affect water vapor permeability of the polymer. Among these are considered the volume concentration of filler, the chemical and physical nature of the filler, the type of adhesive bond between the filler and polymer and the polarity of the polymer. Combinations of these properties determine the effect of the solid particles on water vapor permeability.

Barrar (2) stated that the permeability is greater the more hydrophilic the film. Spencer (24) found differences in the permeability coefficients of hydrophilic and hydrophobic films to be small. It was also found that the permeability coefficient is constant over a range of water vapor pressures for hydrophobic films but increase rapidly with differences in pressure above and below the film for hydrophilic coatings.

The presence of crosslinks and crystallites in the polymer reduce the diffusion rate. Crosslinking has little effect on the solubility unless in excess as found by Stannett and Coauthors (26). The crystallite regions act as barriers since water is practically insoluble in the crystallite areas.

Water Vapor Permeation

Interest in water vapor permeability has been centered on protection of the substrate, not upon what effect the substrate has on permeation. Water vapor diffuses due to a moisture and at times a temperature gradient from the inside of a house through the wood siding and collects under the paint film at the substrate-coating interface. Unless the vapor readily permeates the film, a pressure due to osmotic forces will occur. If the pressure is greater than the paint adhesion or cohesion, blistering will occur. Previous work on water vapor permeability has been concerned mainly with the effect of polymer-penetrant variables in the permeation mechanism.

The temperature effect on permeability is indirect. Lowrey and Broome (20) state that temperature affects the solubility coefficient (S) and the diffusion coefficient (D). Therefore the permeability coefficient (P) is also related to temperature through the following Arrhenius relationships:

$$S = S_o \exp(-\Delta H/RT)$$
$$D = D_o \exp(-E_d/RT)$$
$$P = P_o \exp(-E_p/RT) \qquad E_p = E_d + \Delta H$$

Where S_o, D_o and P_o are the temperature independent constituents, ΔH is the heat of solution, E_d and E_p are the activation energies for diffusion and permeation respectively. The activation energy in a physical sense is the energy necessary for segmental movement of the required amplitude. Hunt, Huff and Spencer (12) state that part of the activation energy is for penetrant film separation in hydrophilic polymers. Michaels states that the rate of change of the diffusion coefficient with change in temperature is directly proportioned to the polarity and chain stiffness of the polymer molecules.

The solubility of water vapor decreases rapidly with increasing temperature at constant pressure due to a corresponding decrease in relative humidity. As the temperature is raised further, the rate of increase in diffusivity becomes greater than rate of decrease of solubility, so that permeability begins to increase as temperature increases. The greater the water sorptivity of the polymer, the higher will be the temperature where inversion of the permeability-temperature coefficient occurs as stated by Michaels (22).

When a polymer film is subjected to a temperature and a water partial pressure gradient, the direction of water movement depends on the difference in magnitudes of the gradients. Michaels (22) states that 'uphill diffusion', from cool and humid to warm and dry, is due to the fact that the driving force for permeation is not the pressure, but rather the activity or chemical potential of the penetrating compound.

Water present in the film affects the transport rate of the penetrant depending on the film and the concentration of water in the film. If the polymer-water interaction is slight, the result may only be an increase in solubility which remains independent of concentration. As the degree of interaction increases, the solubility and diffusivity become concentration dependent. Lowrey and Broome (20) concluded that as the interaction increased, the chain mobility and free volume were increased so that the diffusivity became concentration dependent

Water has the tendency to cluster at certain sites in hydrophilic polymers, thus affecting the water concentration. At low concentrations the clusters are localized. Mayne and Cherry (21) found that with an oil modified alkyd film, carboxyl groups may exist in clusters, which would become sites of water clusters. As the relative humidity and the polarity of the film increases, clustering increases, creating water filled voids and breaking hydrogen bonds. This increases the chain mobility and free volume, thus influencing the diffusion coefficient. A specialized case was encountered by Kumins and Roteman (14). It was determined that the water-polymer interaction affected both the solubility and the diffusivity of the water penetrant, but was concentration independent in the hydrophobic film. This was attributed to the breaking of acetate groups by the water molecules.

Lowrey and Broome (20) working with hardboard substrates found that weathering of an acrylic latex, a linseed oil paint minus protective pigments, and a solvent type vinyl toluene-butadiene paint with a 45 percent PVC caused a marked increase in the permeability coefficients. The authors, however, could not arrive at any definite conclusions concerning the effect of the paint film thickness on the coating permeability. Work with organic vapors by Li and Henley (17) has shown that thickness of polyethylene film ranging from one to 10 mils had no influence on the permeation constant at various pressures in a membrane separation process.

Browne (7) working with various pigments found that in oil or oleoresinous vehicles both white lead and zinc oxide cause a lower permeability to water vapor than do titanium dioxide, antimony oxide or magnesium silicate. Water absorption by the coating is increased with zinc oxide. It was concluded concerning the vehicles that phenolic resin varnishes favor both low permeability and absorption, while raw linseed oil caused high absorption and permeation. A bodied linseed oil developed an intermediate permeability and absorption while an alkyd-resin vehicle favored an intermediate permeability but a greater absorption than raw linseed oil.

Liquid Water Permeation

There have been numerous and varied research projects concerning the permeability of polymer films to liquid water. The majority of these projects involved protective coatings on wood and metal substrates. Recently a great deal of work has been concerned with the separation of liquid mixtures by permeation through polymer films. Commercial interest in the latter for separation of salt from sea water, helium from natural gas, caustic soda from viscose and others has furthered the research. Although this study was concerned with the permeability of protective coatings, some of the basic principles of membrane separation apply.

The major driving force of liquid water through a film if no bare metal is present is the moisture-content gradient. Water tends to move to a less concentrated area i.e. an area of lower moisture content. Osmotic pressure from a solute concentration gradient is another driving force of the water. Elm (9) has stated that osmotic pressure gradients are largely a result of the formation of water soluble or hydrophilic organic compounds in the film. Also contaminants on the substrate surface such as oil and salts from a fingerprint and wood extractives constitute solutes to promote osmosis. These two forces cause water to enter the paint coatings against opposing hydrophobic forces inherent in the film.

The equivalence of liquid water to 100 percent relative humidity has been illustrated on the basis of thermodynamics and recently it has been experimentally proven. Yasuda and Stannett (32) reported that transport rates for liquid water and 100 percent relative humidity were identical in polymers of varying polarity. Li, Long and Henley (18) also concluded from their literature review of membrane separation processes, that the permeability of liquid versus saturated vapor penetrants were identical. However, there is not a definite concensus favoring the equivalence of saturated vapor and liquid penetration.

A study by the Federation of Paint and Varnish Production Clubs (3) on liquid water permeability produced definite results. A commercial alkyd paint film and various alkyd resins were tested using an inverted Payne Cup in a desiccator. This method is theoretically feasible but when it was tested for use in this project the reproducibility was poor.

Browne (7) reports applying a coating over a thin layer of blue cobalt chloride in methyl cellulose on clean glass. The coated specimens were submerged in water and the time necessary for penetration of the water was indicated by a color change in the cobalt chloride.

An electrical resistance method for determining the water permeability of coatings on metal by Simon, Lalk and Weber (23) incorporated additional variables. For normal in-use conditions, a moisture and a solute concentration gradient are the driving forces for the water penetration. The additional variables were the attractive forces of the salt ions in the penetrant solution and the driving force caused by electroendosmosis. Permselectivity was not a factor as stated by Kumins (13) because the solution used was above .01N.

Elm (9) has stated that the substrate material is not likely to exert enough influence to affect the water absorption properties of the film. This was concerned mainly with metal and glass substrates and not with wood.

Elm concluded that differences in blistering in the study were mainly caused by variations in adhesion on different substrates.

The ASTM Committee D-1 (11), however, believes that the effect of the substrate is substantial. The committee is at present developing a method for determination of liquid water permeability through organic coatings on porous substrates. The procedure involves block flotation, where the coated surface is in contact with the water and the other sides in contact with the water are sealed. The techniques and materials have recently been established leaving the degree of reproducibility and utility of the proposed method for evaluation.

Use of Wood Substrates in Permeability Studies

The wood substrate is a porous material whose microstructure determines the rate of permeation. The path of water movement through wood above the fiber saturation point (fsp) depends on the degree of filling of the fiber cavities with water. According to Stamm (25) the liquid water either evaporates within the wood due to the internal and external vapor pressure or pit membranes collapse and liquid water diffuses due to the tensile force that is set up.

This project is concerned with wood below its fsp where the moisture movement involves the diffusion of water vapor through the voids of wood in combination with bound water diffusion through cell walls. The moisture diffuses due to a moisture gradient, through the transient capillary structure of the cell wall as bound liquid water. The water vaporizes at the cell wall-cell cavity interface and then condenses after passing across the lumen, when in contact with the other cell wall.

Brown, Panshin and Forsaith (4) state that water movement below the fsp increases with an increase in temperature, since diffusion is an activated process. Also liquid moisture diffusion increases with an increase in the moisture content, the density and the pit area of the wood. However, water vapor diffusion decreases as the density of wood increases.

Work by Choong (6) supports the statement that vapor movement through the cell lumens, in series with bound water movement in the cross walls predominates in both transverse and longitudinal directions. The relative importance of this diffusion method increases with an increase in moisture content and decreases with an increase in specific gravity. Choong also states that the combined path of vapor movement through cell lumens in series with pit pores is important at higher temperatures and lower moisture contents. This path is negligible at higher moisture contents and lower temperatures.

There is no specific information concerning the chemical interaction between the applied paint film and the wood substrate. Tarkow and Southerland (28) differentiate between the lumen walls composing the surface and the excised cell wall material created by the saw or plane. The lumen wall and exposed wood substance are involved with the initial interaction but the exposed wood surface is more reactive. The reactivity is based on the amount of polymer adsorbed on the surface. The adsorption increased linearly with exposed area, so that the authors concluded that adsorption was a surface phenomenon, not complicated by penetration into the wood.

Ward, Cote and Day (30) state that the excised cell walls should be a good site for adhesion, but that they undergo dimensional changes in use. The lumen wall, that represents most of the surface area, would not be expected to promote good adhesion. However, the unreactive lumen wall is dimensionally stable to changes in moisture content, thus, a high degree of adhesion between the wood and the coating is not required.

Van Loon (29) considered the interaction between paint and wood from a different approach. It was concluded that the micro-structure of wood is a variable in the interaction between paint and wood. For example, paint penetrates further into pine than spruce, due to the larger pit openings in pine. Also the larger cell cavities of springwood absorb more paint material than the smaller cavities of summerwood causing shiny, thicker paint layers on the summerwood bands. However, the penetration depth is not correlated to the increased adhesion.

There has only been the minimal amount of experimentation concerning the effect of the substrate on the applied finish. This may be due to the variable nature of wood, casting doubt on the validity of the results. Werthan (31) stated that the need of a substrate is recognized for validity but in the laboratory unsealed cellophane was used instead of wood. Lowrey and Broome (20) used hardboard for a permeability substrate, but specified the need of work using natural wood substrates.

CHAPTER II

EXPERIMENTAL MATERIALS, EQUIPMENT AND PROCEDURE

Materials

The permeability of five commercial organic coatings was tested. A linseed oil and a long oil alkyd paint† were the oil base paints used. Both of these paints dry by an oxidative mechanism, while the other three paints studied were a latex type that drys by coalescence and evaporation of water.

Straight grained all heart redwood {Sequoia sempervirens (D.Don) Endl.} veneer, sliced from the same cant, was used as the major substrate for the water vapor permeation studies. These redwood veneers were vertical grain, slow growth (19-28 rings/in.) samples. Redwood siding planed to the required thickness was used to obtain the substrate variable indicated by (o) in Table 1. Due to the need for a thicker veneer in the liquid water studies, redwood siding planed to the desired thickness was also used to obtain the desired substrate variables. Straight grained western hemlock {Tsuga heterophylla (Raf.) Sarg.} was used in only one series of vapor tests to contrast the effect of a more difficult finishing wood. The sapwood of redwood was planed to the correct veneer thickness and was used as a substrate

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†The linseed oil paint formulation used was Sherwin Williams #450 Undercoat, and the long oil alkyd paint was Rockcote #850 Low Lustre White House Paint. All of the paint formulations are found in Appendix I.

TABLE I

COATING -- SUBSTRATE SYSTEMS TESTED FOR WATER VAPOR PERMEABILITY

Variable		Sherwin Williams #450	Rockcote #850	Muralo #350 PVA	Rhoplex AC-34 #303	Rhoplex AC-34 #347
Free films	1.5 mm	X	X	X	X	X
	3.0 mm	X	X	X	X	X
	6.0 mm	X	X			
Standard Substrate	1.5 mm	X				
Standard Substrate	3.0 mm	X	X	X	X	X
Standard Substrate	6.0 mm	X	X	X		
Machining Variables						
Standard (planed)		X				
Sliced		X				
Sanded		X				
Chemical Variables						
Steamed $_o$		X				
Aged $_o$		X				
Sapwood $_o$		X				
Grain Variables						
Flat grain slow growth $_o$		X				
Flat grain fast growth $_o$		X				
Vertical grain fast growth $_o$		X				
Inverted Standard Substrate		X				
Hemlock		X				

variable to determine the effect of the redwood substrate without extractives on the permeability of the applied coating. A one coat latex film, vinyl acetate copolymerized with a high molecular weight acrylic, along with two different formulations of an acrylic emulsion[†] latex paint, were also used.

Equipment

Gardner 5 in. Draw Blade Applicator: This applicator was employed to apply films of uniform thickness. Various shim thicknesses resulted in the same dry film thickness depending upon the paint formulation. A Gardner Scratch Thickness Gage verified the dry film thickness and a micrometer verified the free film thicknesses.

Bird Vacuum Plate (9"x 12"): The plate was used to secure photographic paper and stainless steel panels during the paint application process.

Vapometer Cups: The aluminum flanged vapometer cups of 7.9 cm. effective inside diameter were utilized for the vapor permeability studies according to ASTM D96-53T.

Health Servo Recorder and Vacuum Tube Volt Meter: The VTVM supplied a variable D.C. voltage, maximum 1.5 v., and measured the circuit resistance in the liquid water permeability studies. The servo recorder was utilized to record the measured resistance.

[†] The one coat copolymer used was Muralo #350 One Coat Latex, and the acrylic emulsion paints were Rhoplex AC-34 #303 and #347. Formulations are in Appendix I.

TABLE 2

PAINT IDENTIFICATION AND PROPERTIES

Designation	Manufacturer	Commercial Name	Vehicle	Viscosity (Min) #4 Ford Cup	Use
Paint 1	Sherwin Williams	#450 Undercoat	Processed linseed and high polymer oil	1.336	Barewood undercoat
Paint 2	Rockcote	#850 Low Lustre White House Paint	Long oil linseed pure alkyd	2.322	Prime or topcoat for wood siding
Paint 3	Muralo	#350 One Coat Latex	Poly (vinyl acetate) copoly-high M.wt. acrylic	3.343	One coat house paint
Paint 4	Rohm & Haas	AC-34 #305 Acrylic Emulsion	Rhoplex AC-34	1.196*	Primer for non-staining wood ~~and~~ substrates
Paint 5	Rohm & Haas	AC-34 #347 Acrylic Emulsion	Rhoplex AC-34	1.2136*	Primer for staining woods substrates

* Applied after dilution with 15 ml. of distilled water for better application

The detailed formulations for the above paints are listed in Appendix I

Experimental Procedure

Preparation of Substrate Samples

The selected substrates for the vapor and liquid studies were planed to thicknesses of .167 cm. and .482 cm. respectively. A redwood substrate variable with the surface exposed to atmospheric conditions for over 1.5 years was planed to the required thickness on the underside, not marring the aged surface. The sanded redwood surface variable used in the liquid and water vapor study required sanding to the desired thickness. The steamed redwood substrate variable planed prior to treatment was treated in an autoclave for seven hours at atmospheric pressure.

All of the wooden substrate samples were then conditioned in a humidity cabinet at a relative humidity of 70 percent (dry bulb 85°F and wet bulb 77°F ± 2°F) until the time of coating. These conditions created a uniform E.M.C. of 12.5 percent in the wood substrates immediately prior to the coating application.

Coating Application

The correct shim thickness for the draw blade to achieve the desired dry film thickness was obtained by trial and error for each paint. All of the wooden substrates were coated immediately after removal from the humidity cabinet. Two coats of the film forming materials were necessary to obtain the desired film thickness because of variable penetration into the coarse grained redwood. The first coat was allowed to dry four days and the final coat for seven days. The film thickness was verified by a Gardner Scratch Thickness Gage.

The permeability to liquid water of free films was also tested. The paints were applied to stainless steel panels, cleaned according to ASTM D609-61 (e). For vapor studies on free films, oil paints were coated on Kodabromide photographic enlarging paper by the method of Harris (10). The water base films were applied to clean glass and both types of film were removed from the substrate by water which weakened the adhesive bond. The free films were allowed to dry for a period of eight days on the substrate and one day after removal. The film thickness was verified by a micrometer.

Testing of Vapor Permeability Samples

The coated substrates and the free films were cut into circular discs 9.3 cm. in diameter. Then 25 ml. of distilled water were placed in the vapometer cups which were previously coated with a marine varnish to prevent corrosion. The film or film-substrate system to be tested was placed in the cup, coated side down and pressed flat on the flange using a chilled template. A mixture of 60 percent microcrystalline and 40 percent paraffin wax was used to seal the edge of the sample in the cup. Whatman no. 1 filter paper was used as a support for 1.5 mm. films when necessary.

The vapometer cups containing the installed samples were weighted to the nearest tenth of a milligram, and placed in a rack fitted to a precision oil bath calibrated to 100°F. The cups rested one cm. above the surface of the oil. The baths were in a humidity chamber calibrated for a relative humidity of 50 percent (80°F dry bulb and 67°F wet bulb ±0.5°F) creating an E.M.C. of 9.1 percent at the exposed wood surface.

The tests were continued, where practical, until the diffusion reached a steady state, usually requiring four to seven days. During the first 48 hours, weighings were made every six hours and after the initial period, weighings were made every 24 hours.

Testing of Liquid Water Permeability Samples

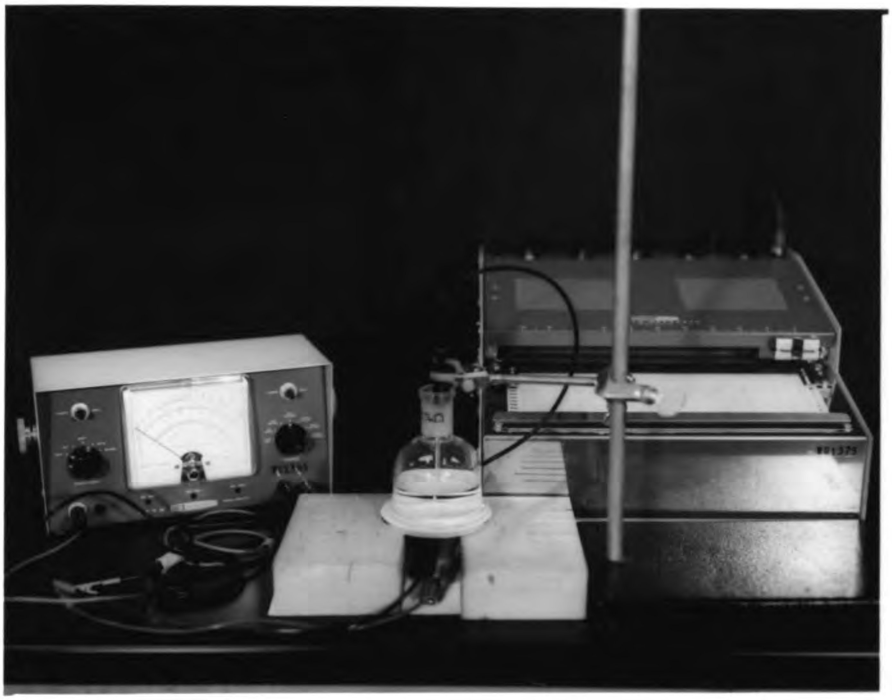
To eliminate the effect of the substrate on permeability, films were applied to stainless steel panels. The panel was used as one electrode completing a circuit through distilled water across a paint film. The apparatus is pictured in Figure 1a. and the diagramatic circuit is in Figure 1b.

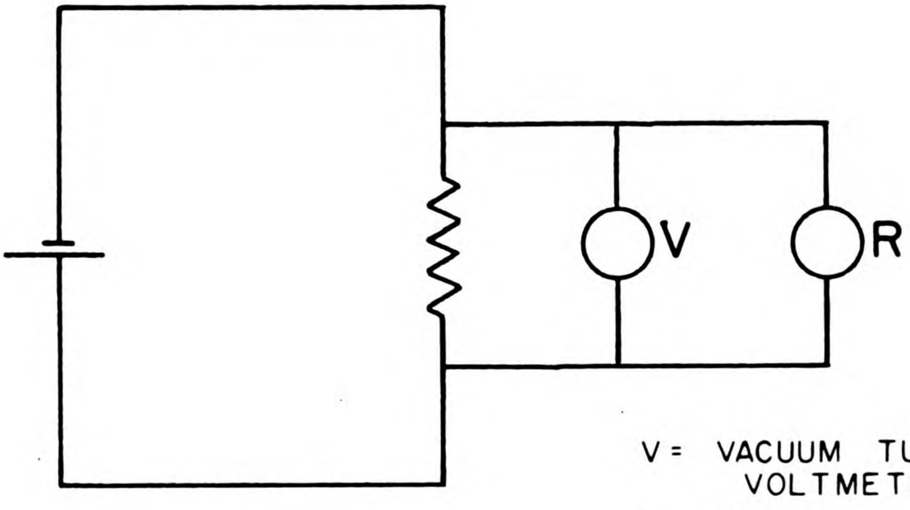
Vacuum stopcock grease was applied to the ground glass flange of the glass bulb of inside diameter 6.82 cm. The coated panel with the glass bulb fitted on it was connected to the negative terminal. One hundred milliliters of distilled water were added to the bulb and an aluminum strip, 1.82 cm^2 of water contact area serving as the positive electrode,was fitted into the water. A variable voltage, maximum 1.5 volts, was applied across the film by the VTVM. The resistance of the circuit was measured by the VTVM and recorded by the servo recorder as a function of time.

The films applied to wood substrates required a modified negative electrode since the metal panel was not used. Two moisture meter needles were forced into the underside of the panels by a micrometer modified to hold the probes, Figure 2. The electrodes were placed .5 mm. under the coating-substrate interface and were wired in parallel to decrease the resistance.

A plot of resistance versus time was obtained which describes the rate of permeation in relative quantities. During the water permeability studies, Fig 1a -- The liquid water permeability apparatus used in the study. Pictured is paint no. 3 on a redwood substrate with the two electrodes in the underside of the substrate 0.5 mils. below the coating -- substrate interface.

Fig. 1b -- A schematic diagram of the electrical circuit used in the liquid water permeation study.

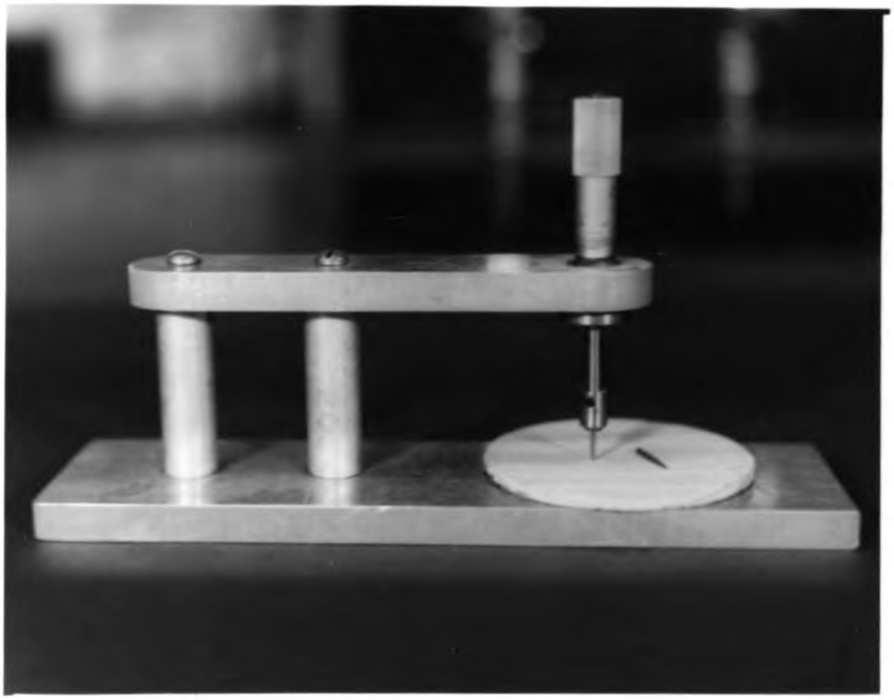




V = VACUUM TUBE VOLTMETER

R = RECORDER

Fig. 2 -- The mounted micrometer head used to force the electrodes (moisture meter needles) into the wood substrate .5 mm beneath the substrate-coating interface.



the external conditions were relatively constant: dry bulb range 71-74°F and wet bulb range 59-62°F.

CHAPTER III

TEST RESULTS

The results of the water vapor permeability studies on various combinations of coating and substrates are grouped in Figures 3 - 15 where weight loss is plotted versus time. The initial diffusion allows a more complete description of the results but only the steady state results were used in calculation of the permeability coefficients. The mean value of the coefficients are listed in column (C) of Table 3, as calculated from the formula derived according to Lowrey and Broome (20).

Solubility follows Henry's law where c is the

$$c = Sp \qquad (1)$$

concentration of water dissolved in the surface layer of the film expressed in g/cm^3, S is the solubility coefficient and p is the water vapor pressure in equilibrium with the surface expressed in mm. of Hg.

If diffusion occurs only by a random jump method due to segmental motion, diffusion will follow Fick's first law

$$q = -D\, dc/dx \qquad (2)$$

where q is the rate of permeation in g/cm^2 sec., dc/dx is the concentration gradient in g/cm^3/cm, and D is the diffusion coefficient.

Steady state diffusion produces

$$q = D\,\frac{(c_1-c_2)}{L} \qquad (3)$$

where the subscripts 1 and 2 refer to the wet and dry film surfaces and L is the film thickness in cm. Combining equations (1) and (3)

$$q = \frac{DS\ (p_1 - p_2)}{L} \tag{4}$$

The permeability coefficient (P) is defined by

$$q = \frac{P\Delta p}{L} \tag{5}$$

Therefore, following Henry's law for steady state conditions,

$$P = DS \tag{6}$$

and re-arranging equation (5), the following equation is obtained to conform to ASTM D1653-62

$$P = \frac{wL}{At\Delta p} \tag{7}$$

where w is the water in grams passed through the film of area A in time t.

The equation constants for this study were; $A = 56.94\ \text{cm}^2$, $t = 24$ hrs. and $\Delta p = 36.63$ mm. Hg. The film thickness and the substrate were separate independent variables and weight loss was the dependent variable. The units for the permeability coefficient are $\text{g cm/cm}^2\ \text{mm Hg } 24\ \text{hr}$.

The procedure for steaming of the standard redwood substrate to obtain the desired surface variable, and analyses of the extractives rendered insoluble, were modifications of ASTM D1110-56 and 1107-56 modified according to Anderson, Ellwood and Zavarin (1). The water soluble extractives were reduced 15 percent and the alcohol soluble extractives were reduced 20 percent based on the original extractive content.

Statistical analyses based on the Student t-test were used to determine the validity of the permeability coefficient differences.

Column (D) of Table 3 lists the t-values of the various systems compared to the corresponding standard. Free films of paint no. 1 are the standards of part I and paint no. 1 on the standard redwood substrate are the standards for part II. Column (E) lists the significance of the permeability differences in the same substrate-coating systems differing only in applied coating thickness.

Part III of Table 3 contains the permeability results of the various substrates that were coated with paint no. 1. Column (D) lists the t-values for permeability comparisons of the variable wood substrate systems in the standard substrate systems of part II. However, these permeability differences could have been due to the varying permeability of the uncoated redwood substrates listed in part IV. To alleviate this problem and to give a relative numerical value to the paint-substrate interaction effect on permeability, the following assumption was made. The resistance to the passage of water of the uncoated substrate plus the resistance of the free paint film is equivalent to the resistance of the coated substrate if no substrate-coating interaction is present. The following calculations based on this assumption were made:

Paint no. 1 and the standard substrate

The reciprocal of the weight loss per 24 hours for the free film plus the reciprocal of the weight loss through the uncoated substrates are summed similar to resistances in series.

$$\begin{array}{r} 4.0584 \\ + \underline{.2151} \\ 4.2735 \end{array}$$

The reciprocal of the sum is the weight loss per 24 hours of the redwood substrate and applied film if no interaction is present

$$\frac{1}{4.2735} = .2340 \text{ g/hr}$$

Subtracting the weight loss of the coated redwood substrate from the above sum, the difference is considered to be caused by the paint-substrate interaction which alters the water transport properties of the film and the substrate

$$\begin{array}{r} .2340 \\ - \underline{.1670} \\ .0670 \text{ g/hr} \end{array}$$

The values expressed in Column (F) of Table 3 are the interactions effects expressed as a percentage of the weight loss of the coated system. The interaction values are illustrated in bar-graph Figure 16. A 10 percent measurement error in the thickness of applied coatings was estimated due to limitations of the scratch thickness gage. Therefore any difference of 10 percent or less in permeability coefficients or interaction is not significant.

Liquid water permeation results of the five paints on metal and paint no. 3 on redwood substrates are in Table 4. There were no permeation results for paints 1, 2, 4 and 5 applied to wood substrates, due to the range limitation of the VTVM. The resistance of the coated system was too great to be measured by the voltmeter. Difficulty was encountered in achieving reproducible results for paint no. 3 on wood substrates. Therefore, the number of substrate variables was reduced and the testing intensity of the five remaining surface variables was increased.

The slopes of Figures 17 - 23, where electrical resistance was plotted versus time, were used as a relative measure of permeability. Also, a result of the permeation rate, the time needed for the system to read equilibrium, was used as a measure of the film's permeability. The significance of the permeability differences due to thickness variation are in column (G) and the t-value for comparison with the standards are in column (H). Other measurements were noted to give a more complete description of the results.

TABLE 3

THE RESULTS OF VARIOUS COATING SUBSTRATE SYSTEMS TESTED FOR WATER VAPOR PERMEABILITY

	A	B	C	D	E	F	G	H
System	Coating Thickness (Mil)	Wt. loss per 24 hr (g)	Perm. Coeff. x10^{-5}	t-value Compared to Standard	t-value Thickness Comparison	Percent Interaction	Density g/cc	Perm. Order 1=lowest
Part I - Free Films								
Paint 1	6.0	.1164	3.353		4.057**			
Paint 1	3.0	.2464	3.495		4.196**			
1	1.5	.4374	3.218					
Paint 2	6.0	.1766	5.051	65.06***	63.500***			
2	3.0	.2380	3.431	2.05	9.570***			
2	1.5	.9117	7.155	9.97***				
Paint 3	3.0	7.0256	98.140	12.65***	4.726**			
3	1.5	7.9840	59.670	17.00***				
Paint 4	3.0	1.9110	27.280	48.63***	.796			
4	1.5	3.7325	26.700	42.54***				
Paint 5	3.0	3.9059	56.650	35.20***	4.052**			
5	1.5	7.0110	50.450	165.72***				
Part II - On Standard Substrate								
Paint 1	6.0	.1270	3.712			- 9.84		
1	3.0	.1640	2.336		17.200***	40.12		
1	1.5	.4071	2.926		14.750***	2.87		
Paint 2	6.0	.7764	23.750	56.29***	5.160**	-76.83		
2	3.0	1.4149	20.180	29.77***		-84.00		
Paint 3	6.0	2.8920	83.200	41.40***	19.660***			
3	3.0	2.6850	38.570	35.52***		+ 3.20		

Table 3 -- continued

	A	B	C	D	E	F	G	H
System	Coating Thickness (Mil)	Wt. loss per 24 hr (g)	Perm. Coeff. x10^{-5}	t-value Compared to Standard	t-value Thickness Comparison	Percent Interaction	Density g/cc	Perm. Order 1=lowest
Paint 4	3.0	1.5062	21.660	121.96***	35.500***	-10.22		
Paint 5	3.0	2.6707	37.690	64.51***		-20.17		
Part III - Paint 1 on Various Substrates								
Standard	3.0	.1640	2.336			40.12		3
Sanded	3.0	.1677	2.421	1.872		39.35		4
Aged	3.0	.1897	2.713	9.921***		23.88		6
Sapwood	3.0	.1980	2.848	3.262*		22.88		8
Steamed	3.0	.2468	3.549	37.640***		- 3.93		10
Sliced	3.0	.2859	4.067	15.050***		-18.12		11
Hemlock	3.0	.2316	3.331	10.070***		2.20		9
Inverted	3.0	.1938	2.840	5.478**		18.83		7
Edge grain, Fast growth	3.0	.1788	2.571	2.578*		32.55		5
Flat grain, Slow growth	3.0	.1032	1.345	2.010		66.76		1
Flat grain, Fast growth	3.0	.1445	2.026	3.486*		64.64		2
Part IV Uncoated Substrates								
Standard		4.67					.35	2
Sanded		4.70					.35	3
Aged		5.10					.35	4
Sapwood		16.00					.33	9
Steamed		6.31					.36	7
Sliced		4.70					.35	3
Hemlock		6.02					.42	5

Table 3 -- continued

	A	B	C	D	E	F	G	H
System	Coating Thickness (Mil)	Wt. loss per 24 hr (g)	Perm. Coeff. x10^{-5}	t-value Compared to Standard	t-value Thickness Comparison	Percent Interaction	Density g/cc	Perm. Order 1=lowest
Inverted		4.70					.35	3
Edge grain, Fast Growth		6.12					.28	5
Flat grain, Slow growth		2.50					.48	1
Flat grain, Fast growth		6.90					.42	8

* Significance at the .05 level
** Significance at the .01 level
*** Significance at the .001 level

Fig. 3 -- The total water vapor permeation through three different free film thicknesses of the linseed oil paint (paint no. 1) plotted versus the elapsed time.

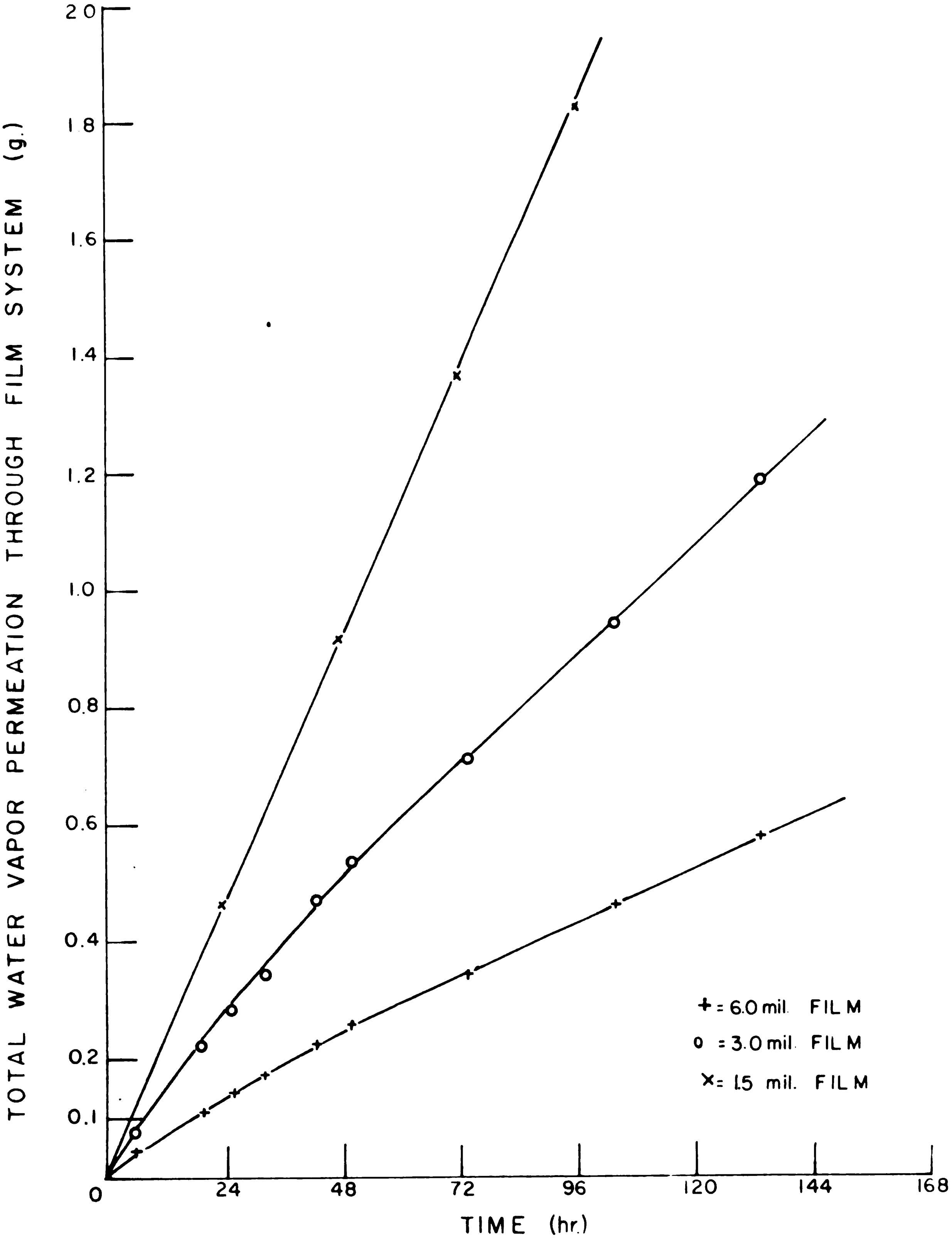

TOTAL WATER VAPOR PERMEATION THROUGH FILM SYSTEM (g.)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.1
0
24
48
72
96
120
144
168
TIME (hr.)
+ = 6.0 mil. FILM
o = 3.0 mil. FILM
×= 1.5 mil. FILM

Fig. 4 -- The total water vapor permeation through three different free film thicknesses of the long oil linseed pure alkyd paint (paint no. 2) plotted versus the elapsed time.

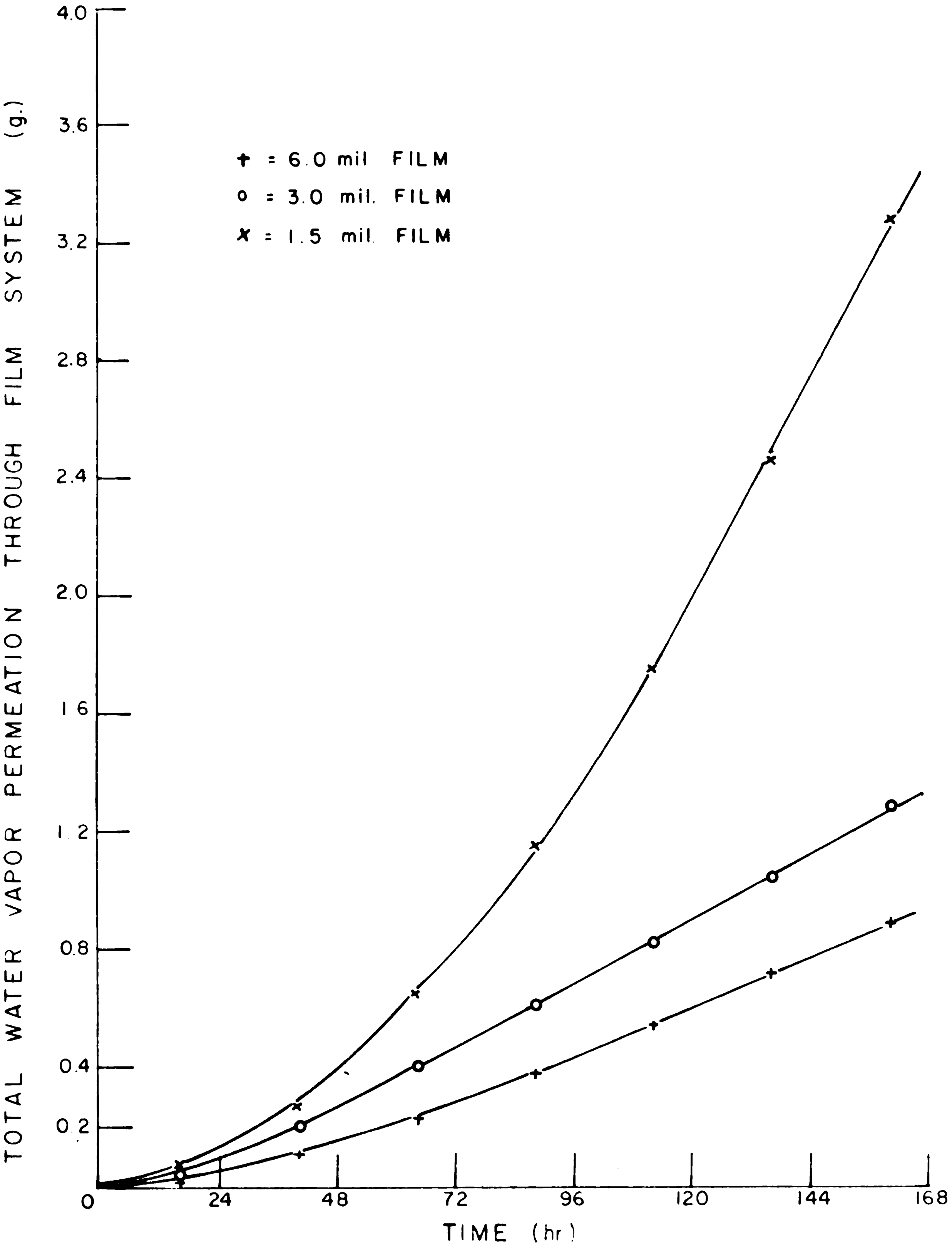

+ = 6.0 mil FILM
o = 3.0 mil. FILM
x = 1.5 mil. FILM
TOTAL WATER VAPOR PERMEATION THROUGH FILM SYSTEM (g.)
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.2
0
24
48
72
96
120
144
168
TIME (hr)

Fig. 5 -- The total water vapor permeation through two different free film thicknesses of the one coat latex paint (paint no. 3) plotted versus the elapsed time.

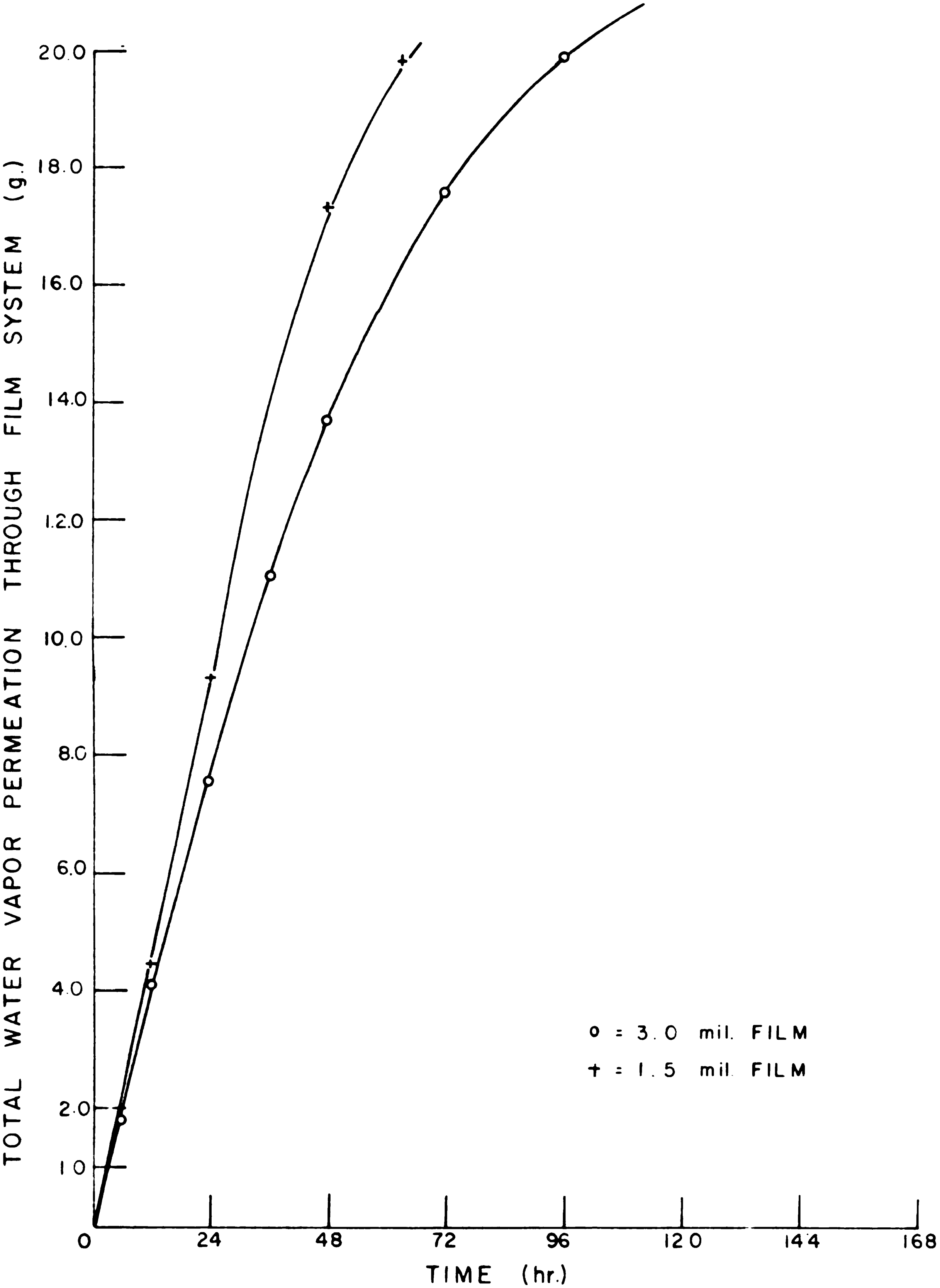

TOTAL WATER VAPOR PERMEATION THROUGH FILM SYSTEM (g.)
20.0
18.0
16.0
14.0
1.2.0
10.0
8.0
6.0
4.0
2.0
1.0
0
24
48
72
96
120
144
168
TIME (hr.)
o = 3.0 mil. FILM
+ = 1.5 mil. FILM

Fig. 6 -- The total water vapor permeation through two different free film thicknesses of the acrylic emulsion paint (paint no. 5) plotted versus the elapsed time.

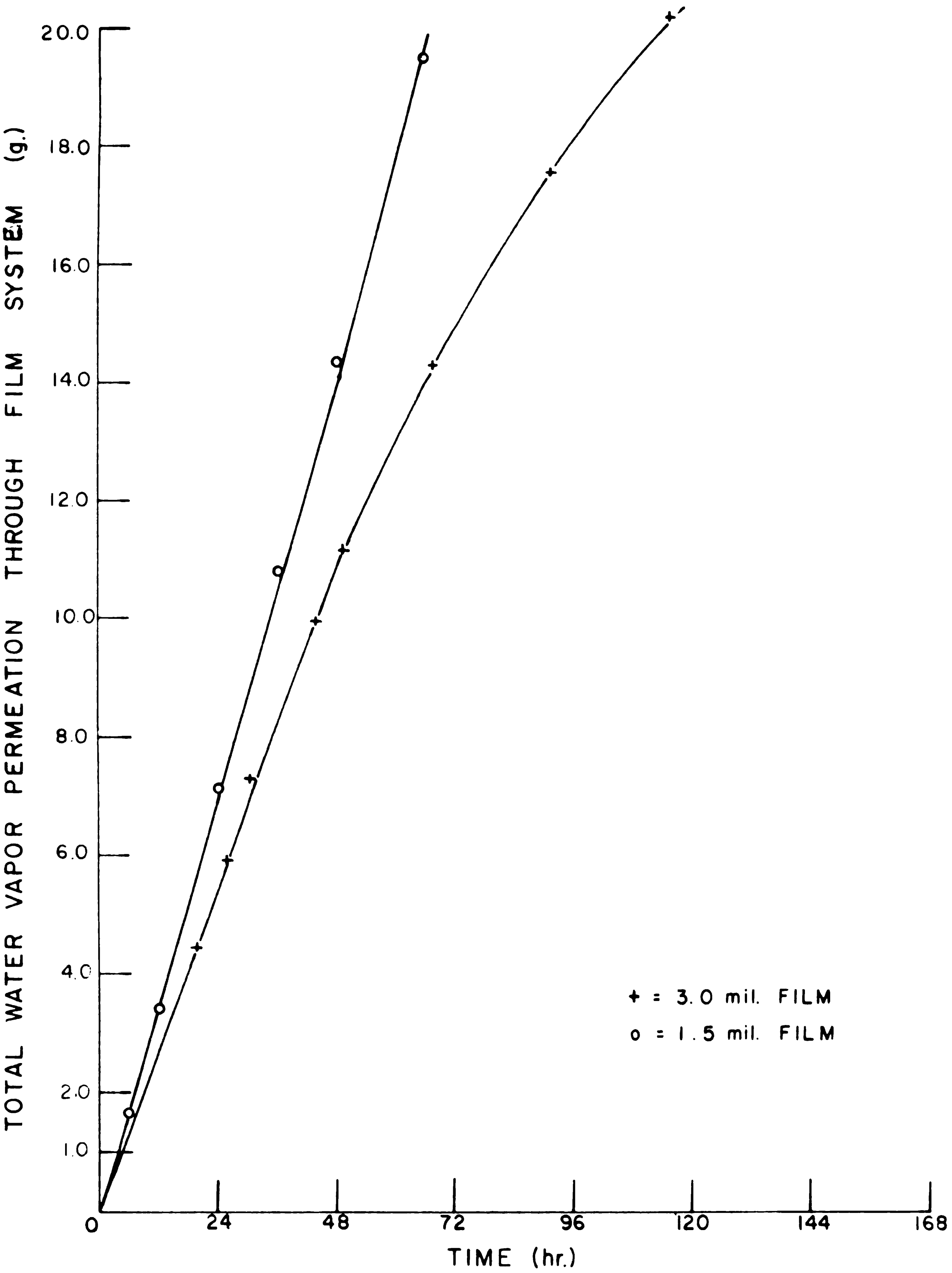

TOTAL WATER VAPOR PERMEATION THROUGH FILM SYSTEM (g.)
20.0
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
1.0
0
24
48
72
96
120
144
168
TIME (hr.)
+ = 3.0 mil. FILM
o = 1.5 mil. FILM

Fig. 7 -- The total water vapor permeation through three different thicknesses of the linseed oil paint (paint no. 1) on the standard redwood substrate plotted versus the elapsed time.

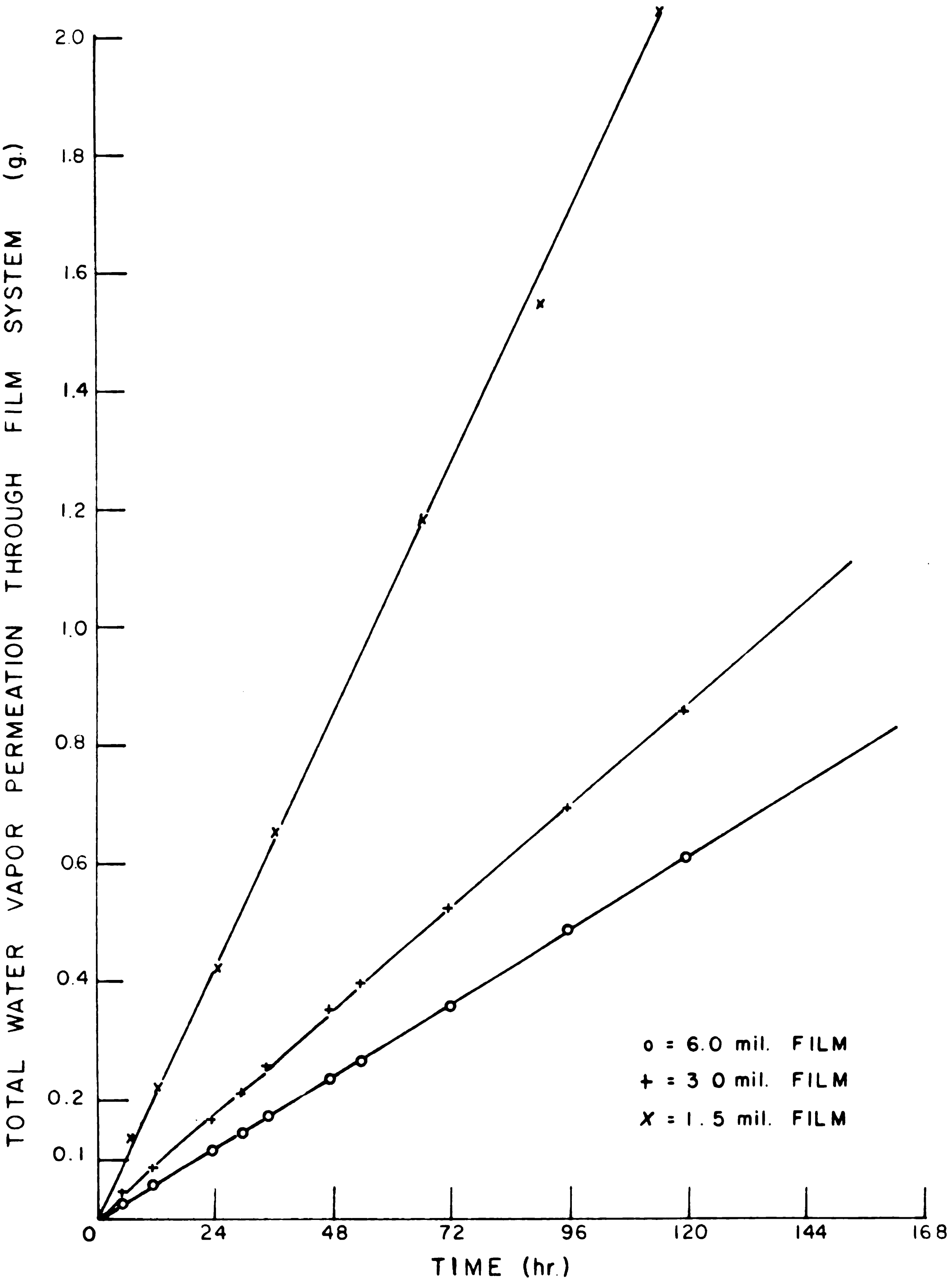

TOTAL WATER VAPOR PERMEATION THROUGH FILM SYSTEM (g.)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.1
0
24
48
72
96
120
144
168
TIME (hr.)
o = 6.0 mil. FILM
+ = 3.0 mil. FILM
X = 1.5 mil. FILM

Fig. 8 -- The total water vapor permeation through two different thicknesses of the long oil linseed pur alkyd paint (paint no. 2) on the standard redwood substrate plotted versus the elapsed time.

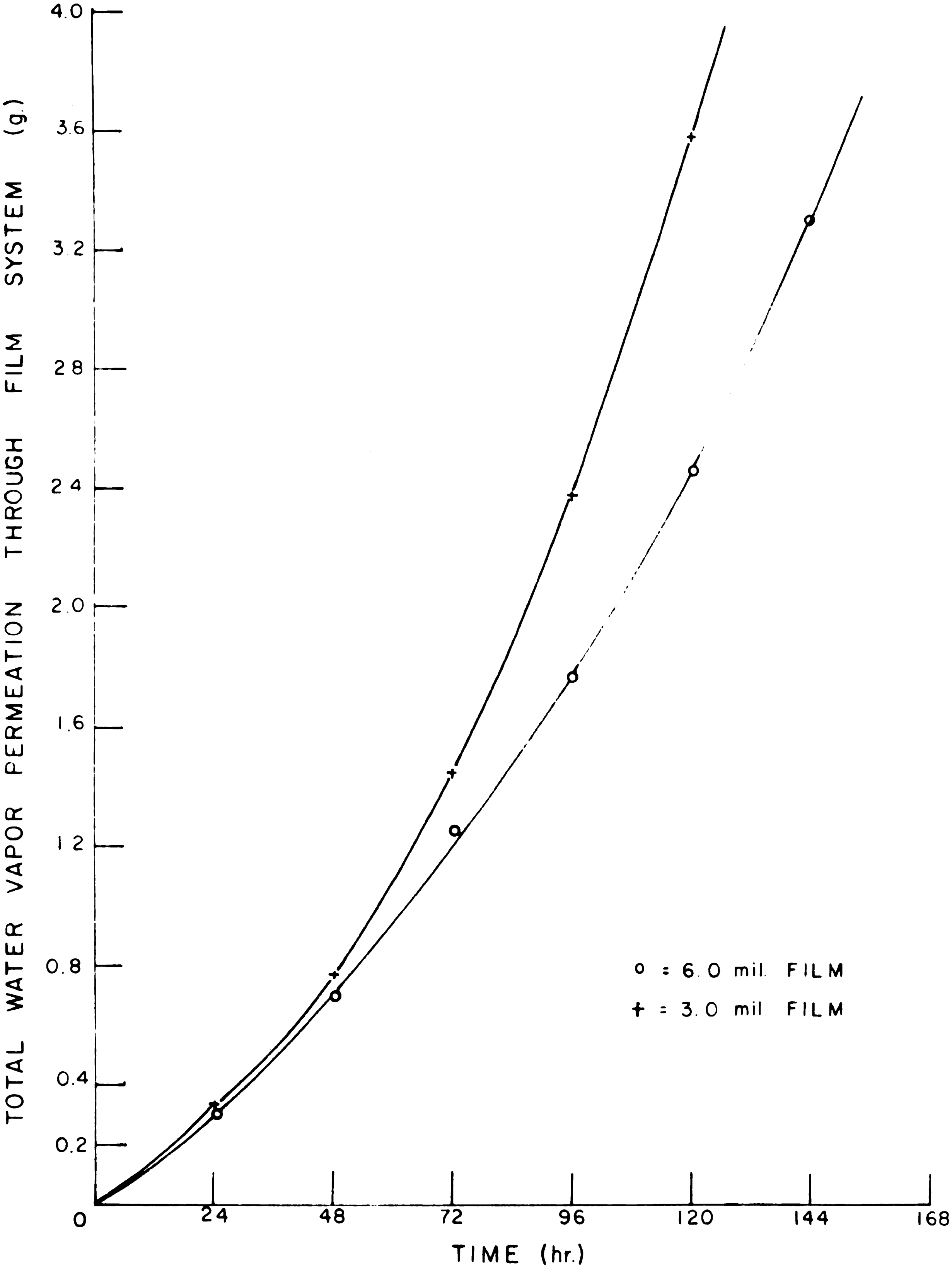

TOTAL WATER VAPOR PERMEATION THROUGH FILM SYSTEM (g.)
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.2
0
24
48
72
96
120
144
168
TIME (hr.)
o = 6.0 mil. FILM
+ = 3.0 mil. FILM

Fig. 9 -- The total water vapor permeation through two different thicknesses of the one coat latex paint (paint no. 3) on the standard redwood substrate plotted versus the elapsed time.

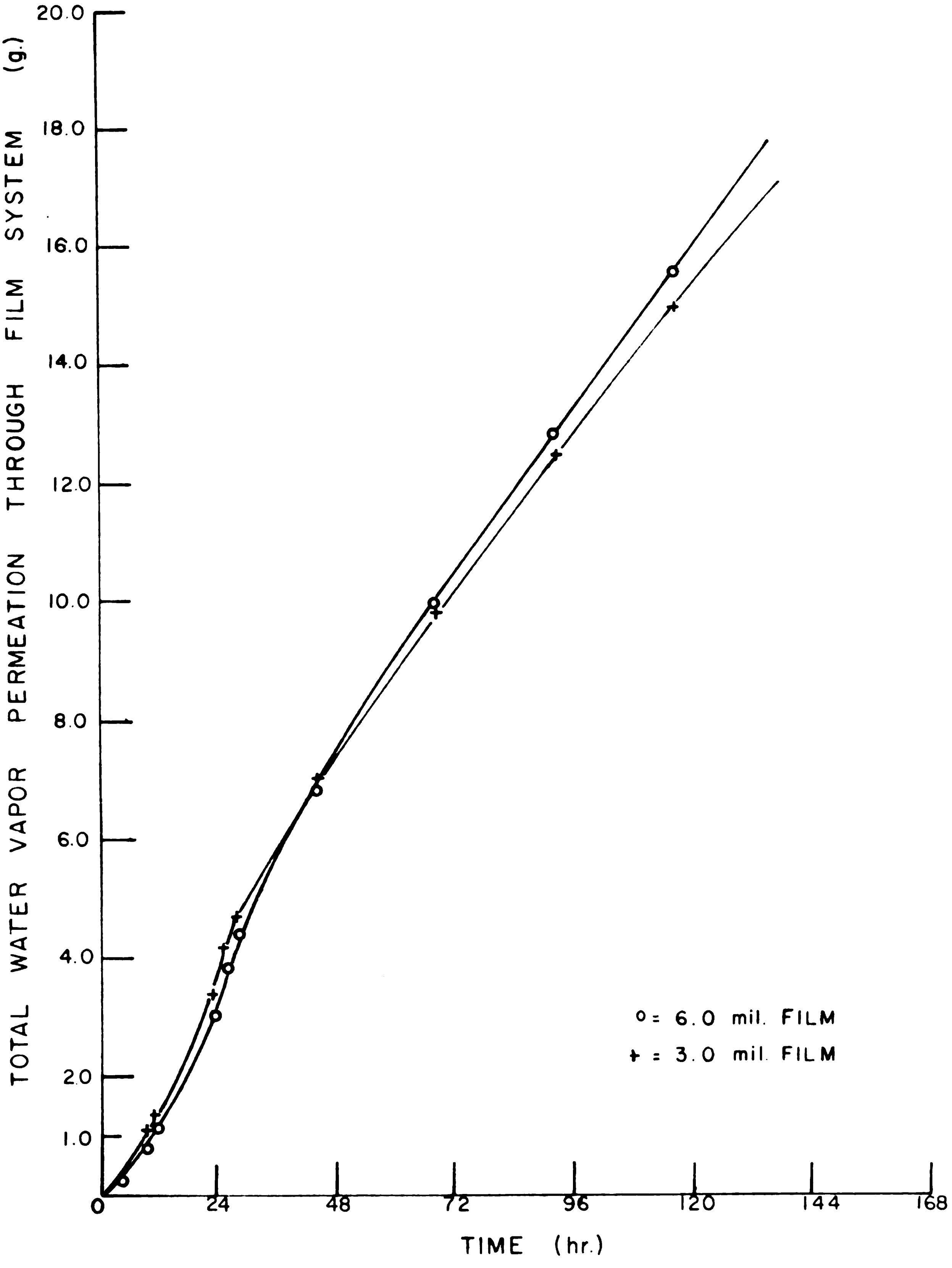

TOTAL WATER VAPOR PERMEATION THROUGH FILM SYSTEM (g.)
20.0
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
1.0
0
24
48
72
96
120
144
168
TIME (hr.)
o = 6.0 mil. FILM
+ = 3.0 mil. FILM

Fig. 10 -- The total water vapor permeation through 3.0 mil. films of the acrylic emulsion paints (paints nos. 4 and 5) on the standard redwood substrate plotted versus the elapsed time.

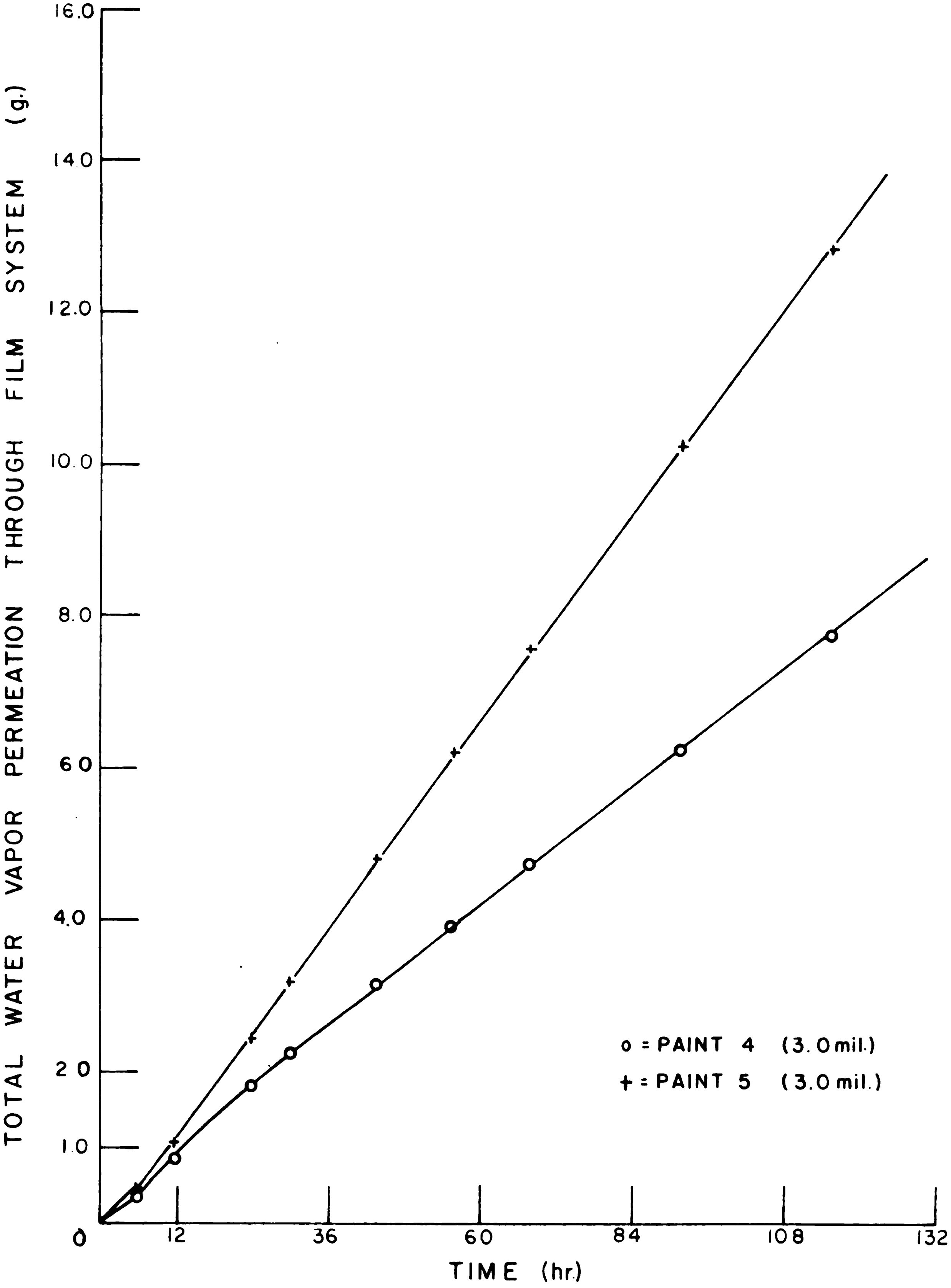

TOTAL WATER VAPOR PERMEATION THROUGH FILM SYSTEM (g.)
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
1.0
0
12
36
60
84
108
132
TIME (hr.)
o = PAINT 4 (3.0 mil.)
+ = PAINT 5 (3.0 mil.)

Fig. 11 -- The total water vapor permeation through 3.0 mil. films of the linseed oil paint (paint no. 1) on aged and sanded substrates plotted versus the elapsed time. Permeation through the standard system was plotted for comparison.

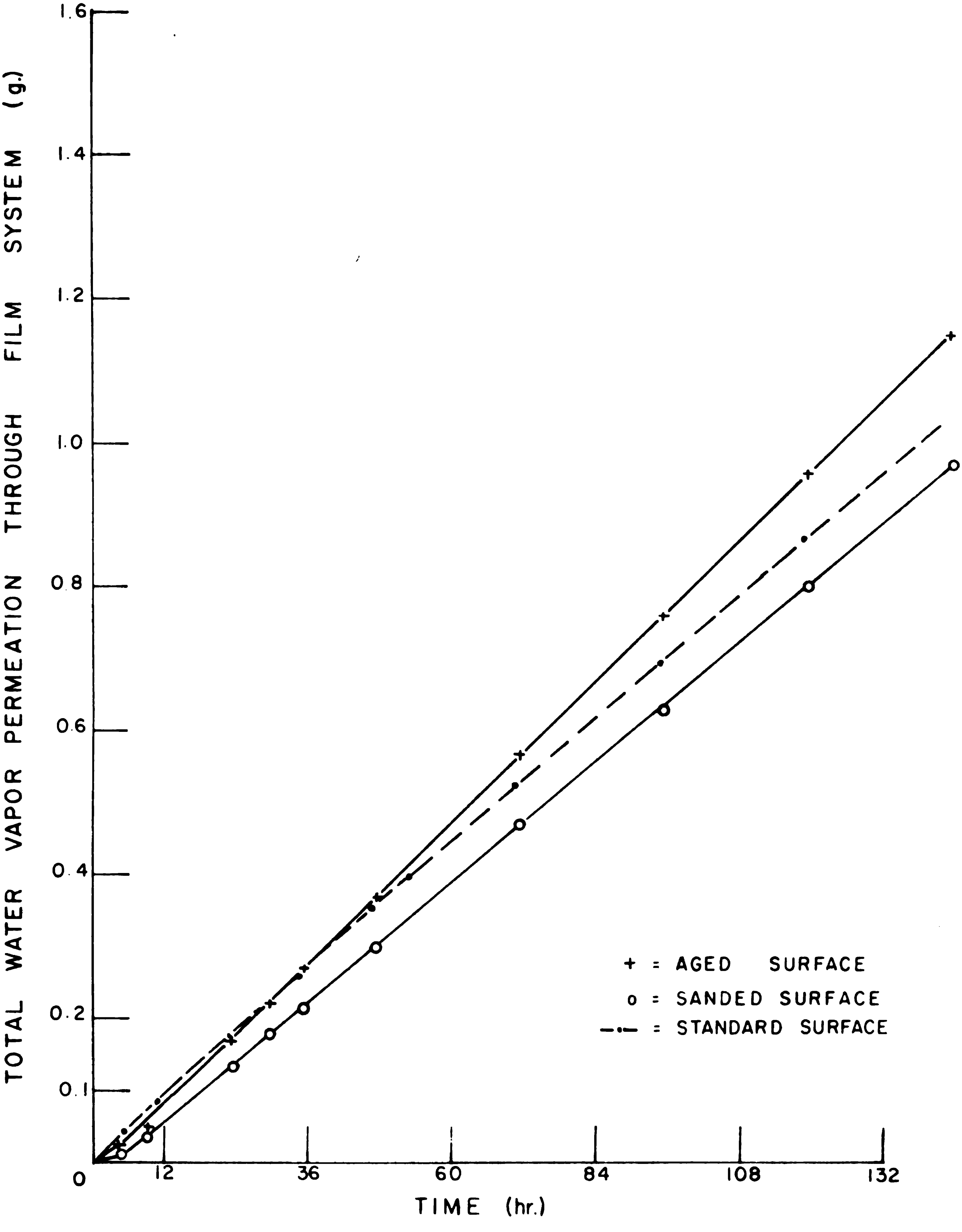

TOTAL WATER VAPOR PERMEATION THROUGH FILM SYSTEM (g.)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.1
0
12
36
60
84
108
132
TIME (hr.)
+ = AGED SURFACE
o = SANDED SURFACE
—·— = STANDARD SURFACE

Fig. 12 -- The total water vapor permeation through 3.0 mil. films of the linseed oil paint (paint no. 1) on steamed and sapwood substrates plotted versus the elapsed time. The permeation through the standard systems was plotted for comparison.

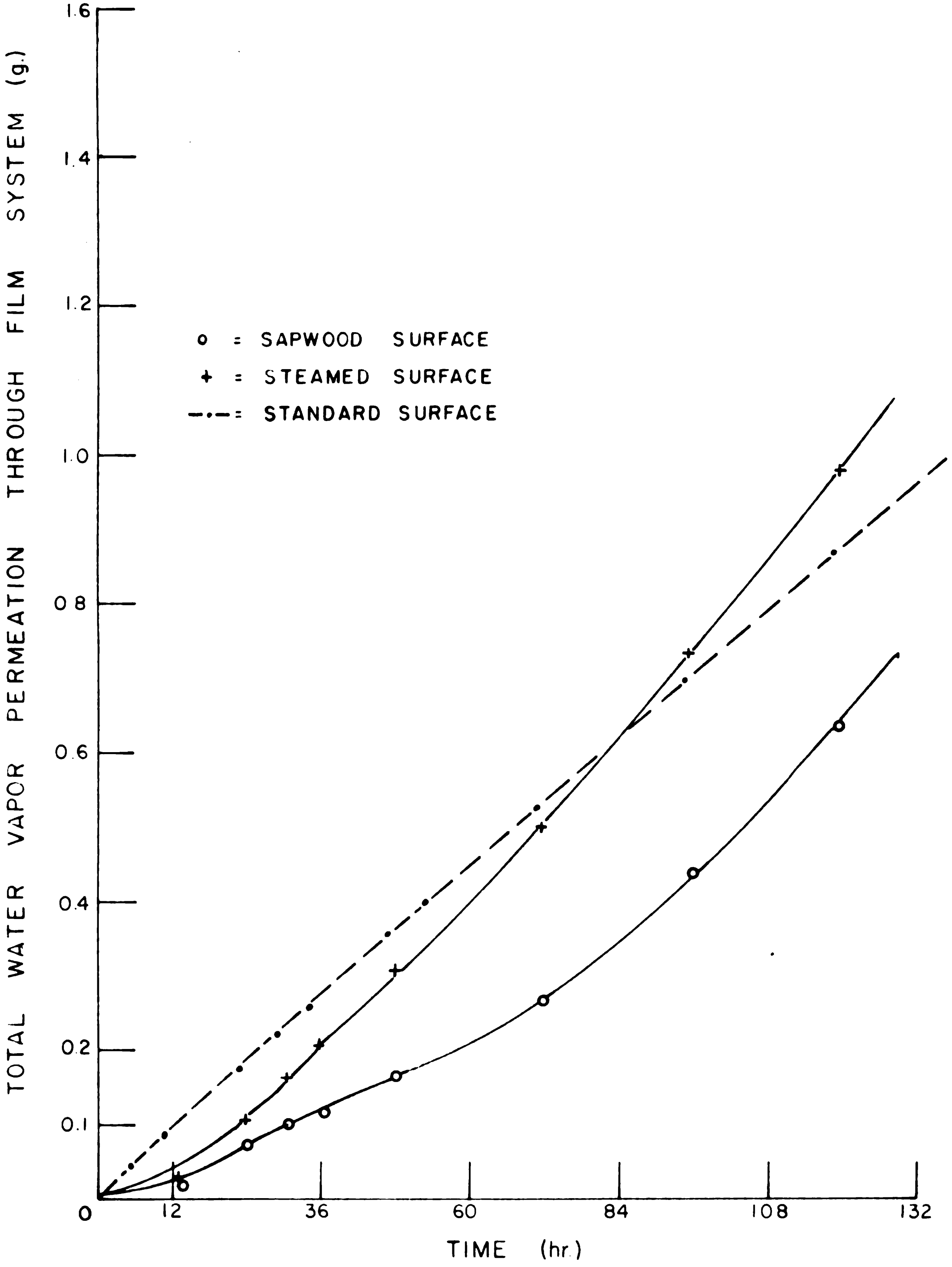
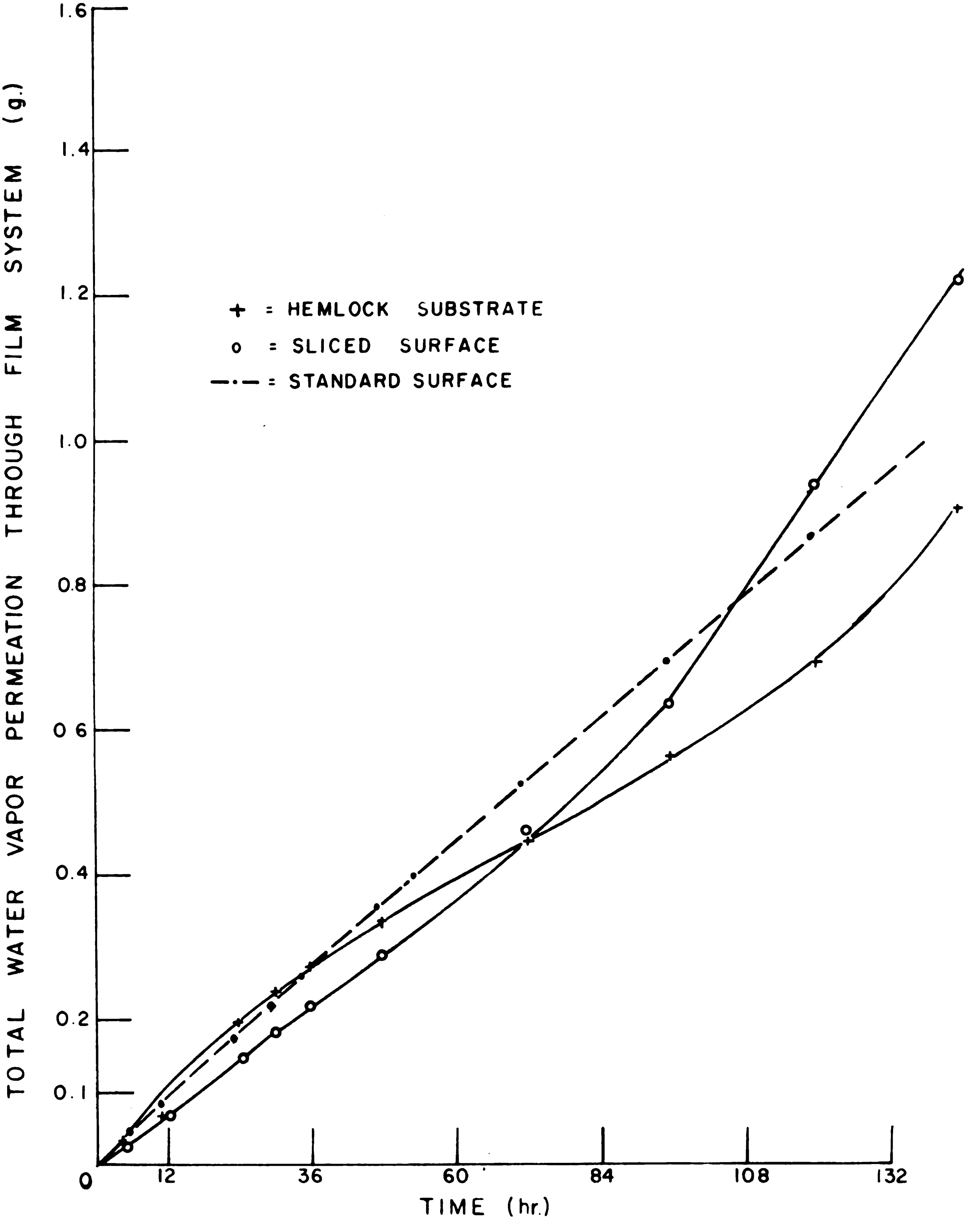

TOTAL WATER VAPOR PERMEATION THROUGH FILM SYSTEM (g.)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.1
0
12
36
60
84
108
132
TIME (hr.)
o = SAPWOOD SURFACE
+ = STEAMED SURFACE
—·—= STANDARD SURFACE

Fig. 13 -- The total water vapor permeation through 3.0 mil. films of the linseed oil paint (paint no. 1) on sliced redwood veneer and planed hemlock plotted versus the elapsed time. The permeation through the standard system was plotted for comparison.



TOTAL WATER VAPOR PERMEATION THROUGH FILM SYSTEM (g.)
1.6
1.4
1.2
1.0
0.8
0 6
0.4
0.2
0.1
0
12
36
60
84
108
132
TIME (hr.)
+ = HEMLOCK SUBSTRATE
o = SLICED SURFACE
—·— = STANDARD SURFACE

Fig. 14 -- The total water vapor permeation through 3.0 mil. films of the linseed oil paint (paint no. 1) on edge grain, fast growth substrates and inverted standard substrates plotted versus the elapsed time. The permeation through the standard system was plotted for comparison.

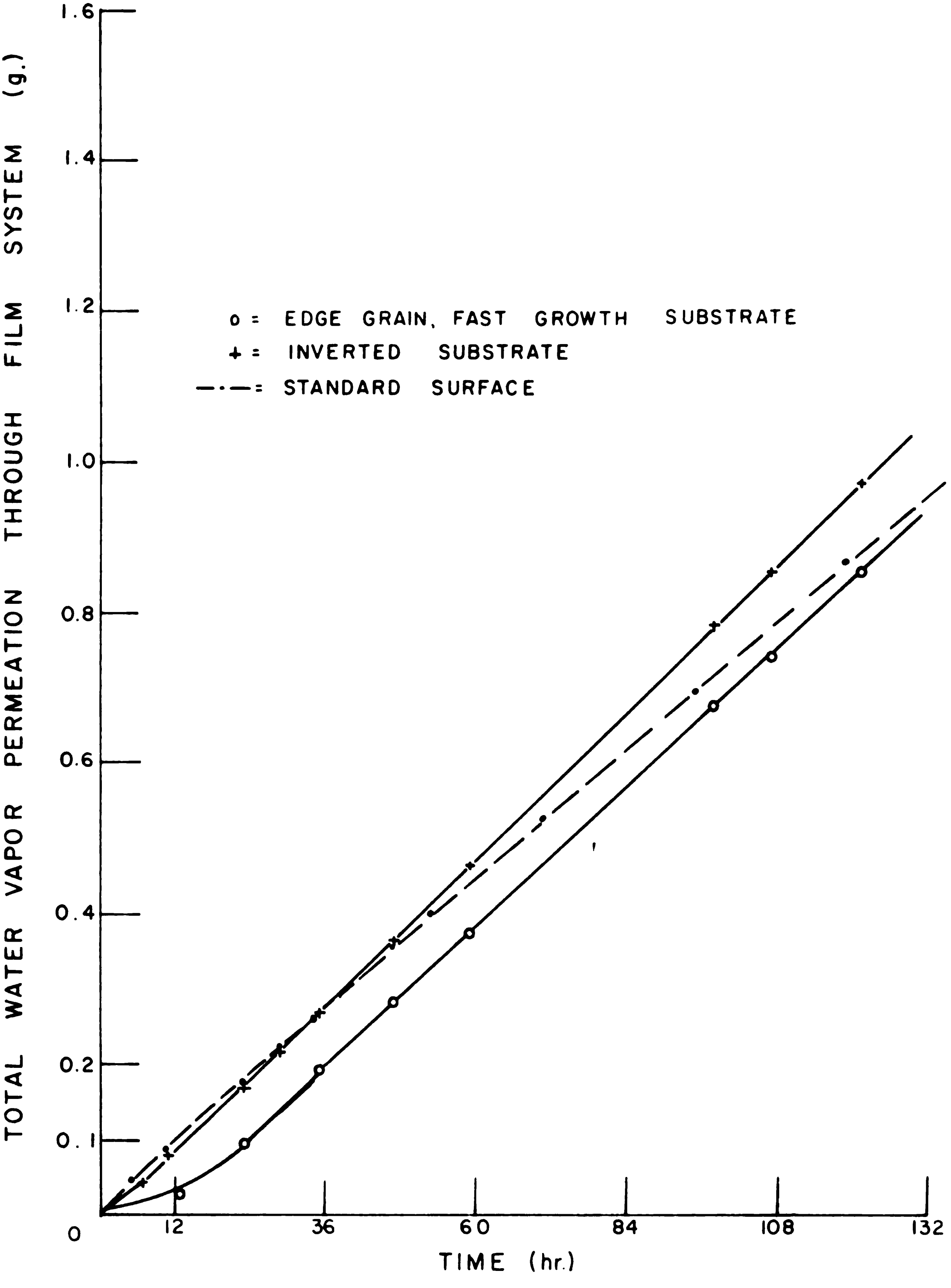

TOTAL WATER VAPOR PERMEATION THROUGH FILM SYSTEM (g.)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.1
0
12
36
60
84
108
132
TIME (hr.)
o = EDGE GRAIN, FAST GROWTH SUBSTRATE
+ = INVERTED SUBSTRATE
—·— = STANDARD SURFACE

Fig. 15 -- The total permeation through 3.0 mil. films of the linseed oil paint (paint no. 1) on flat grain, slow and fast growth substrates plotted versus the elapsed time. The permeation through the standard system was plotted for comparison.

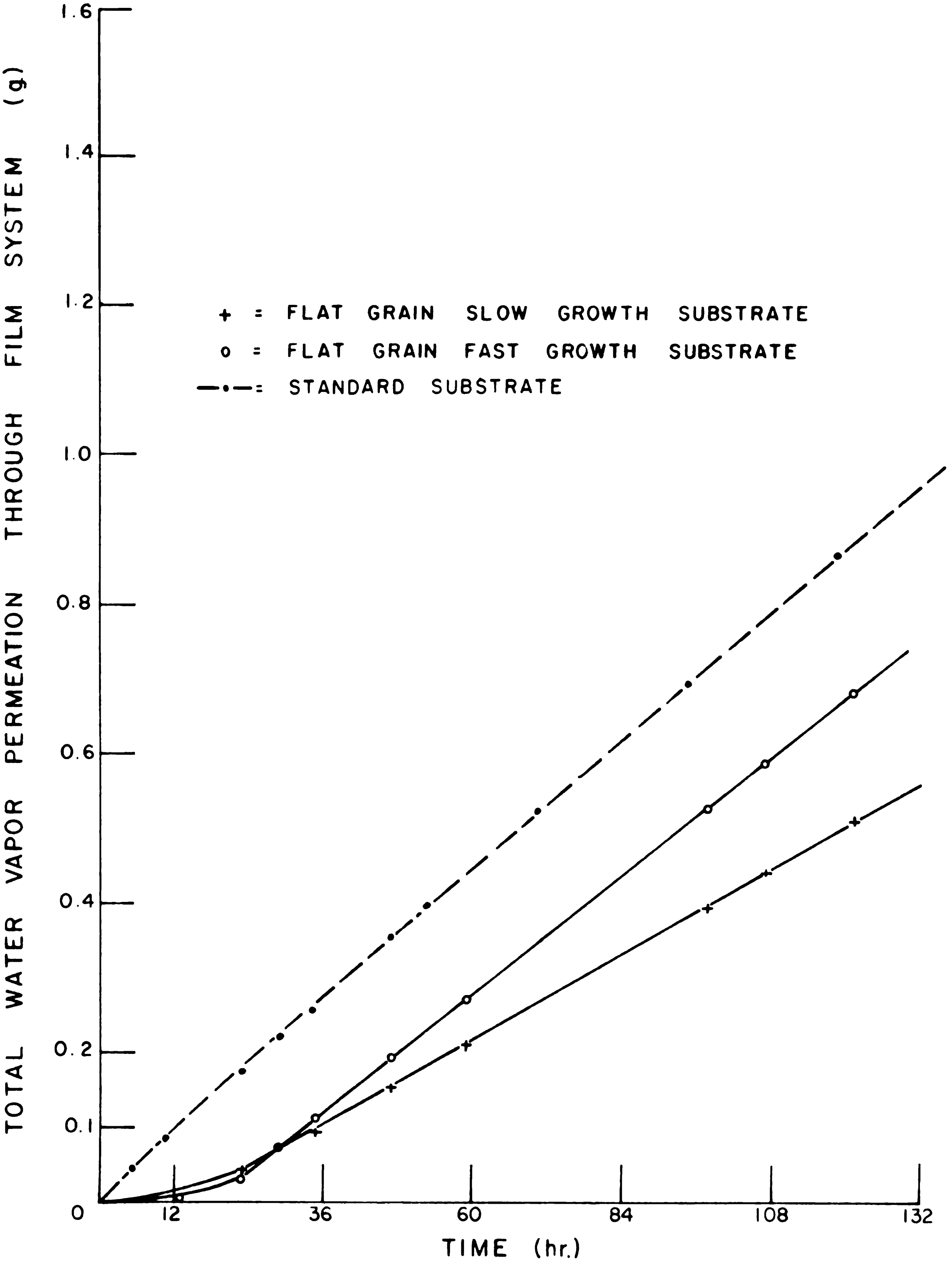

TOTAL WATER VAPOR PERMEATION THROUGH FILM SYSTEM (g)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.1
0
12
36
60
84
108
132
TIME (hr.)
+ = FLAT GRAIN SLOW GROWTH SUBSTRATE
o = FLAT GRAIN FAST GROWTH SUBSTRATE
—•—= STANDARD SUBSTRATE

Fig. 16 -- The percent of interaction between the applied coating and the substrates of the systems tested for water vapor permeability represented in bar-graph form. The percent was based on the value of the coated system.

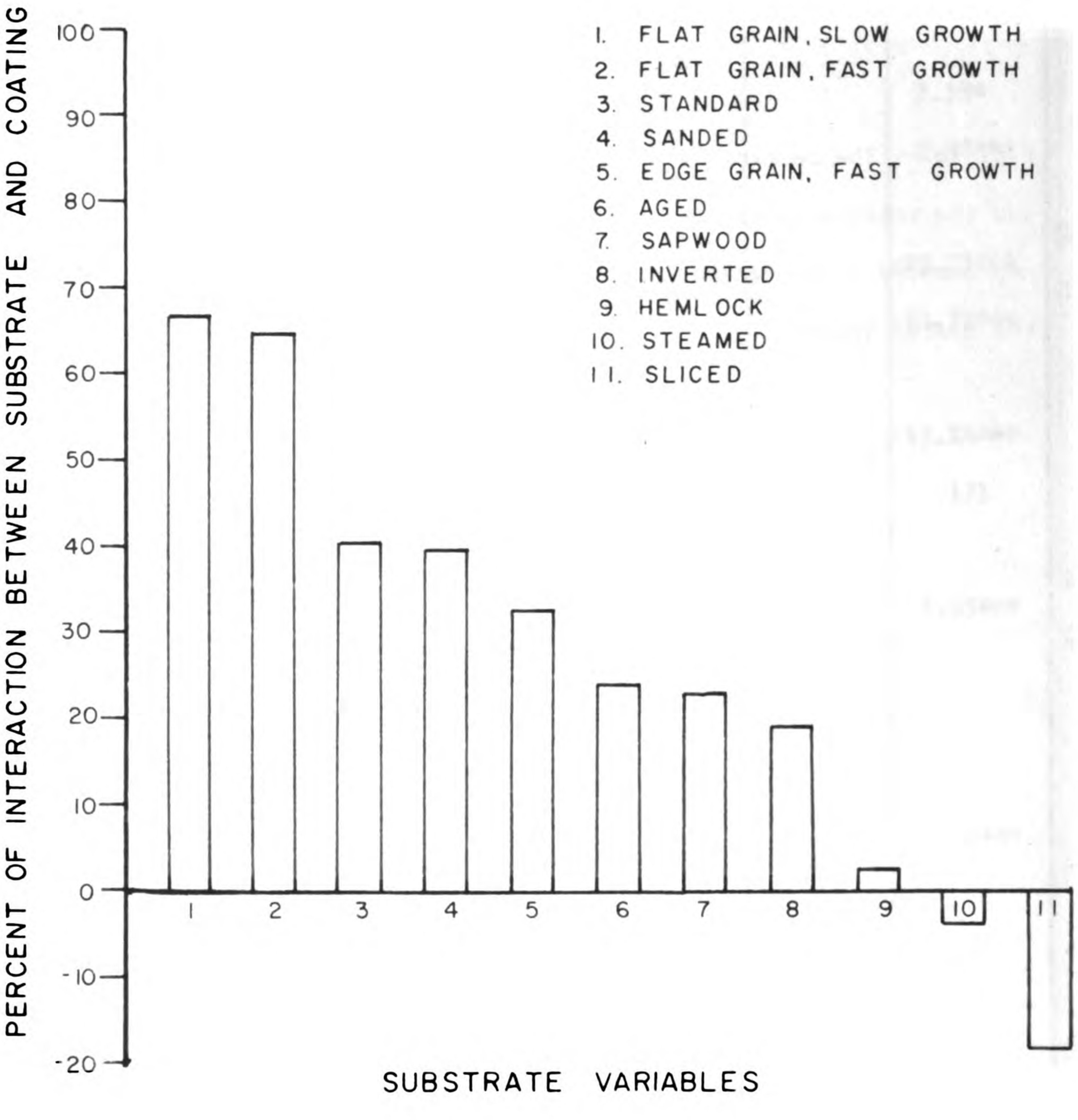

PERCENT OF INTERACTION BETWEEN SUBSTRATE AND COATING
100
90
80
70
60
50
40
30
20
10
0
-10
-20
1
2
3
4
5
6
7
8
9
10
11
SUBSTRATE VARIABLES
1. FLAT GRAIN, SLOW GROWTH
2. FLAT GRAIN, FAST GROWTH
3. STANDARD
4. SANDED
5. EDGE GRAIN, FAST GROWTH
6. AGED
7. SAPWOOD
8. INVERTED
9. HEMLOCK
10. STEAMED
11. SLICED

TABLE 4

THE RESULTS OF THE COATING SUBSTRATE SYSTEMS TESTED FOR LIQUID WATER PERMEABILITY

Film System	Film Thick-ness (mm)	Max R Ωx10^5	Minum R Ωx10^5	Time to Read Equilib (min)	Slope (Ω/min)x10^5	Order of Permea-bility	t-value Thickness	t-value Compound to Standard
Free films (on metal)								
Paint 1	6.0	450	26.0	123.0	6.03			
							3.39*	
1	3.0	230	10.0	39.5	7.63			
							9.38***	
1	1.5	150	9.5	34.0	14.95			
Paint 2	6.0	330	3.0	43.0	94.50			3.13***
							19.27***	
2	3.0	160	0.70	33.0	36.30			19.20***
							10.72***	
2	1.5	25	0.40	17.0	15.50			.38
Paint 3	6.0	7.4	0.41	37.0	1.84			7.94***
							15.24***	
3	3.0	7.0	0.52	17.5	7.13			1.88
							.173	
3	1.5	6.5	0.51	8.0	7.20			9.42***
Paint 4	3.0	105.0	26.0	51.0	135.50			21.30***
							6.55***	
Paint 5	3.0	100.0	18.0	34.0	202.50			23.39***
Paint on Wood								
Substrate	1							
Standard	6.0	850	26.0	56.5	82.50			
							14.52***	
Standard	3.0	800	18.0	41.0	167.80	4		
Flat grain fast	3.0	800	31.0	83.0	71.25	1		15.44***
Flat grain slow	3.0	800	100.0	74.5	91.75	2		16.11***
Sanded	3.0	800	18.0	39.0	143.80	5		2.83*
Steamed	3.0	800	18.0	44.0	130.00	3		5.54**

*** Significant at the .05 level**
**** Significant at the .01 level**
***** Significant at the .001 level**

Fig. 17 -- The total liquid water permeation through three different free film thicknesses of the linseed oil paint (paint no. 1) indicated by the electrical resistance decrease was plotted versus the elapsed time.

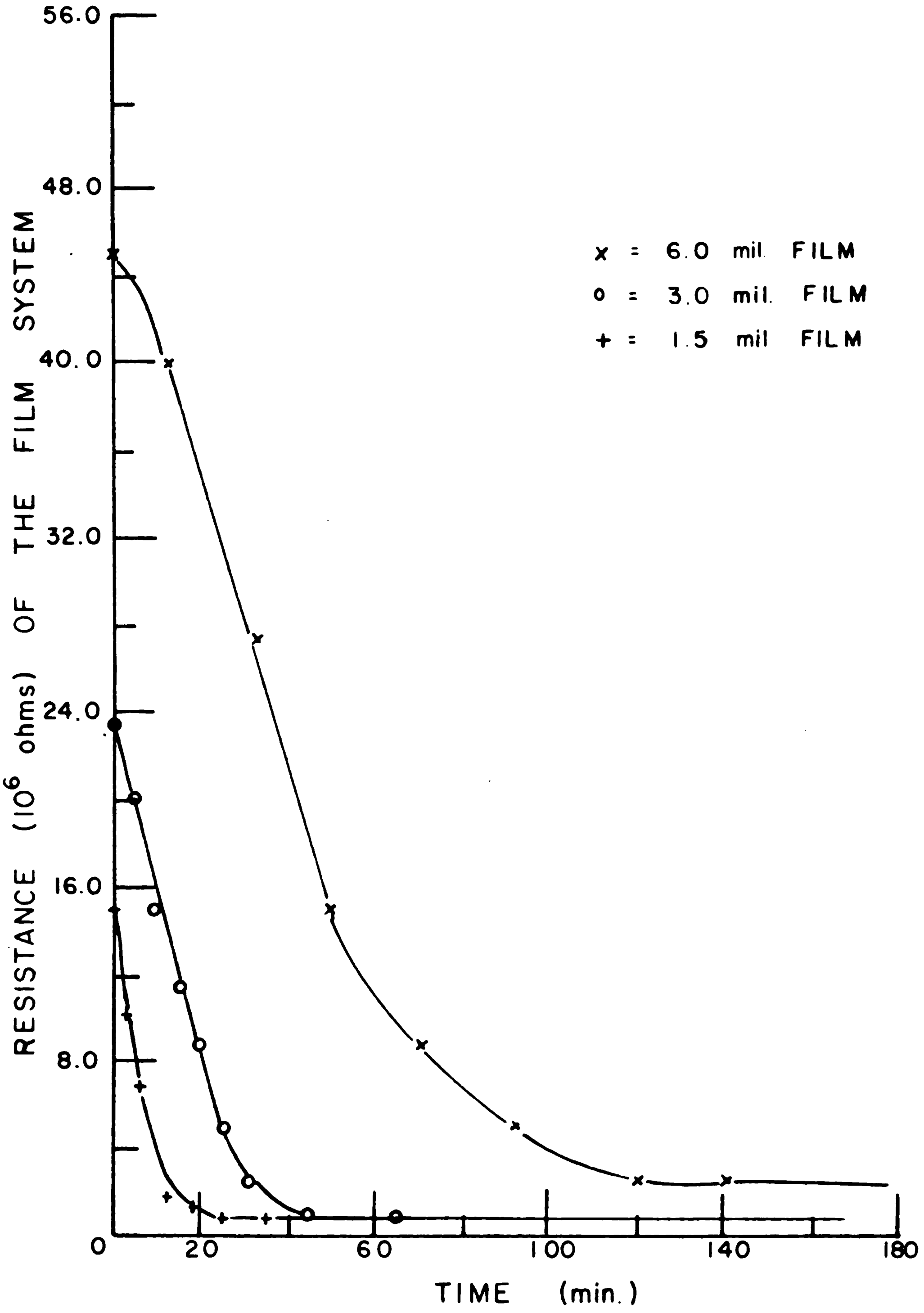

56.0
48.0
40.0
32.0
24.0
16.0
8.0
0
20
60
100
140
180
RESISTANCE (10^6 ohms) OF THE FILM SYSTEM
TIME (min.)
x = 6.0 mil FILM
o = 3.0 mil. FILM
+ = 1.5 mil FILM

Fig. 18 -- The total liquid water permeation through three different thicknesses of the long oil linseed pure alkyd paint (paint no. 2) indicated by the resistance decrease was plotted versus the elapsed time.

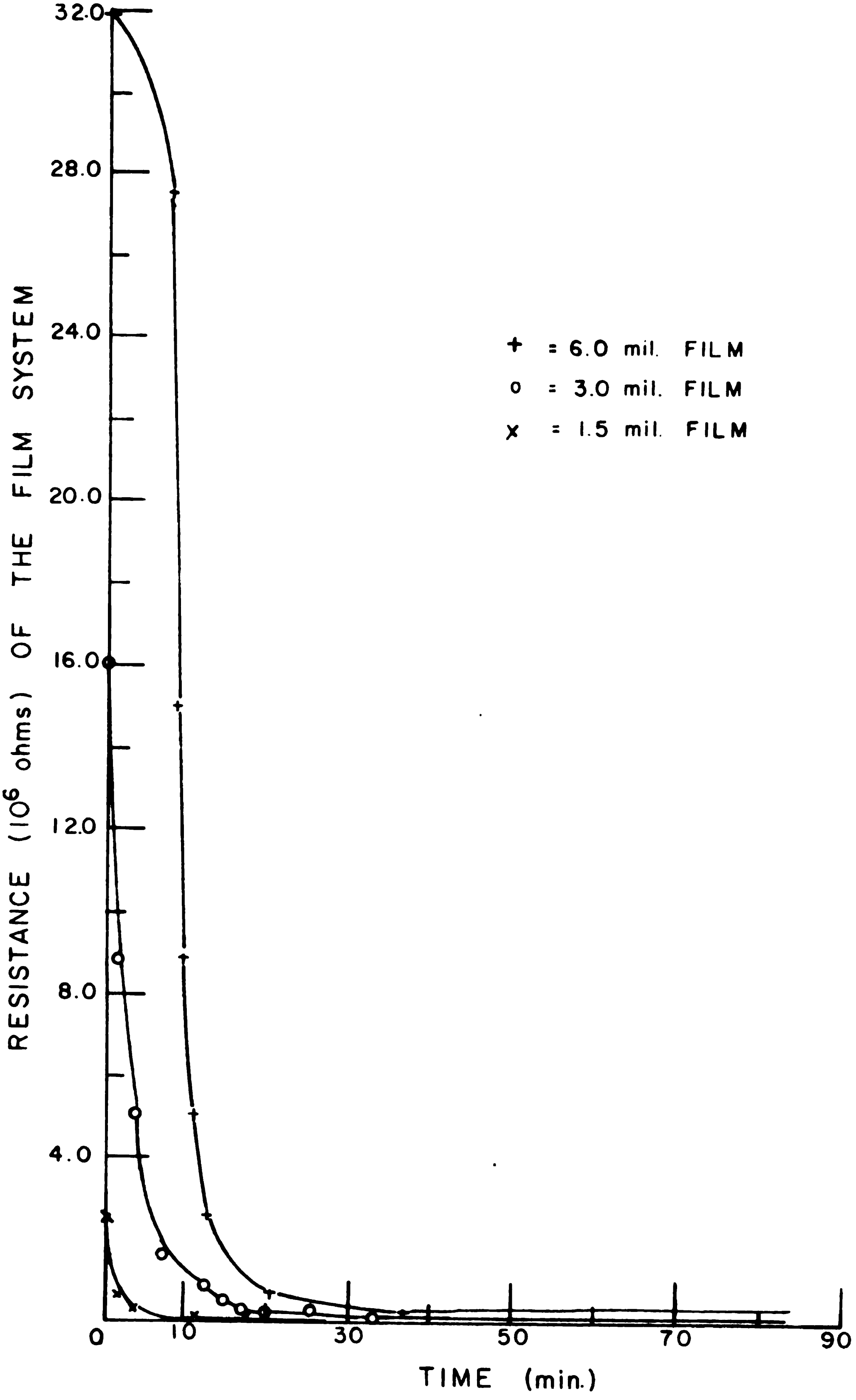

32.0
28.0
24.0
20.0
16.0
12.0
8.0
4.0
RESISTANCE (10^6 ohms) OF THE FILM SYSTEM
+ = 6.0 mil. FILM
o = 3.0 mil. FILM
x = 1.5 mil. FILM
0
10
30
50
70
90
TIME (min.)

Fig. 19 -- The total liquid water permeation through three different free film thicknesses of the one coat latex (paint no. 3) indicated by the resistance decrease was plotted versus the elapsed time.

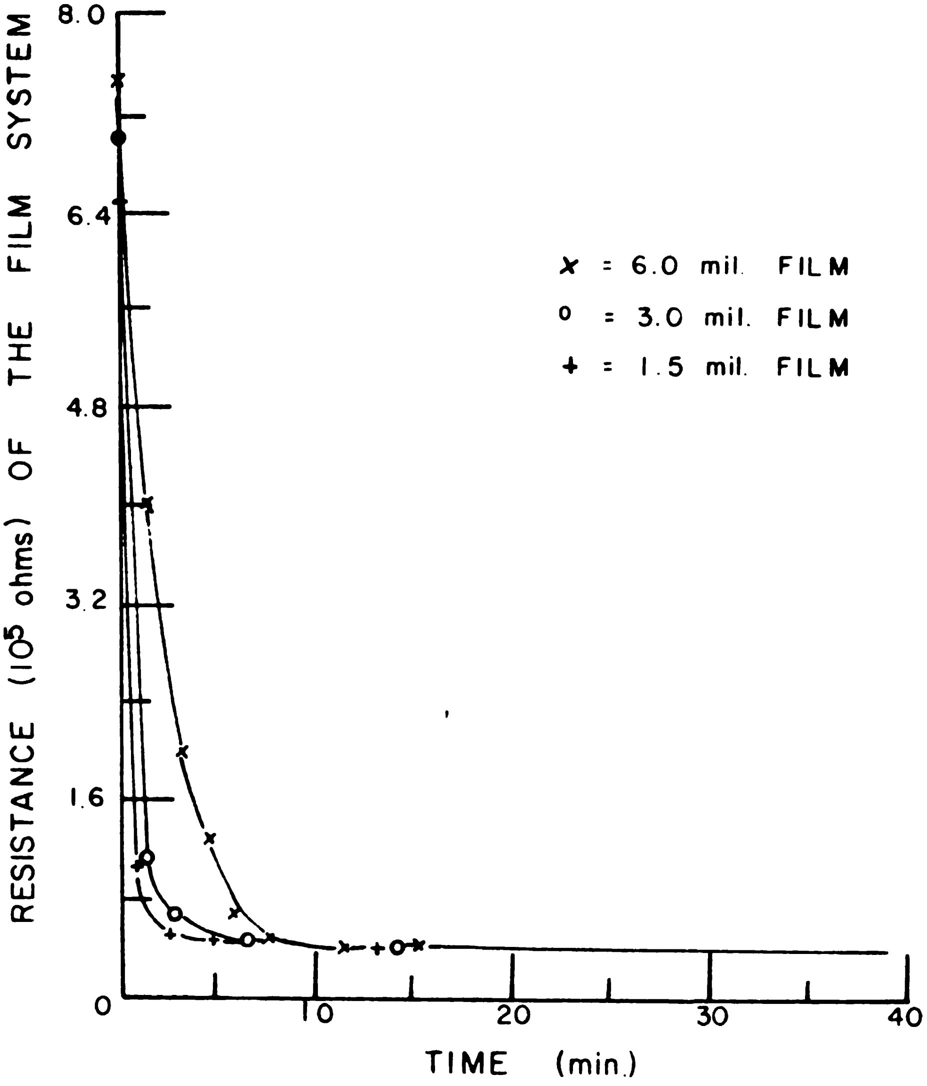

RESISTANCE (10^5 ohms) OF THE FILM SYSTEM
8.0
6.4
4.8
3.2
1.6
0
10
20
30
40
TIME (min.)
x = 6.0 mil. FILM
o = 3.0 mil. FILM
+ = 1.5 mil. FILM

Fig. 20 -- The total liquid water permeation through 3.0 mil. free films of the acrylic emulsion paints (paints nos. 4 and 5) indicated by the resistance decrease was plotted versus the elapsed time.

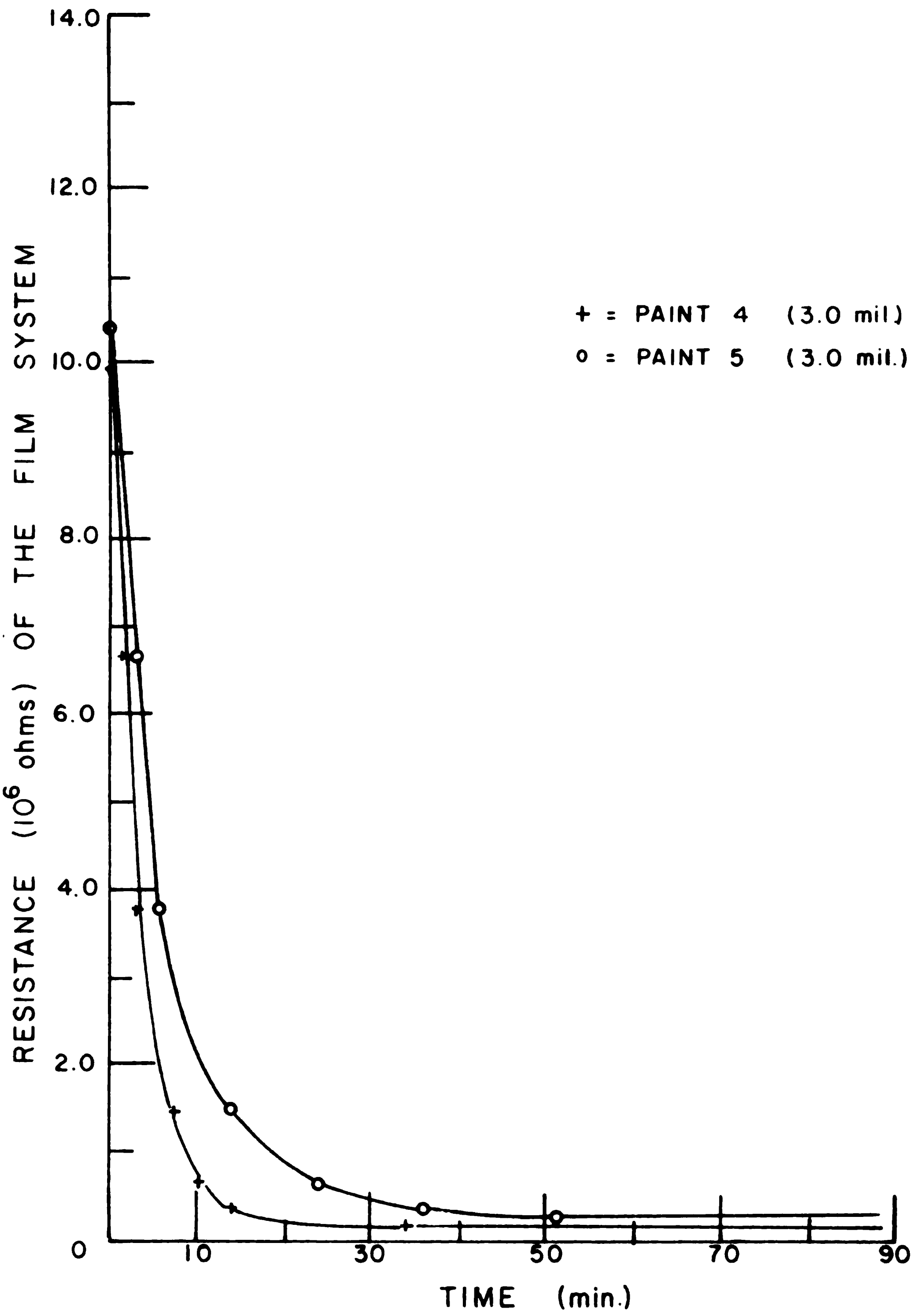

14.0
12.0
10.0
8.0
6.0
4.0
2.0
0
RESISTANCE (10⁶ ohms) OF THE FILM SYSTEM
+ = PAINT 4 (3.0 mil)
o = PAINT 5 (3.0 mil.)
10
30
50
70
90
TIME (min.)

Fig. 21 -- The total liquid water permeation through two different thicknesses of the one coat latex paint (paint no. 3) on the standard redwood substrate was indicated by the resistance decrease plotted versus the elapsed time.

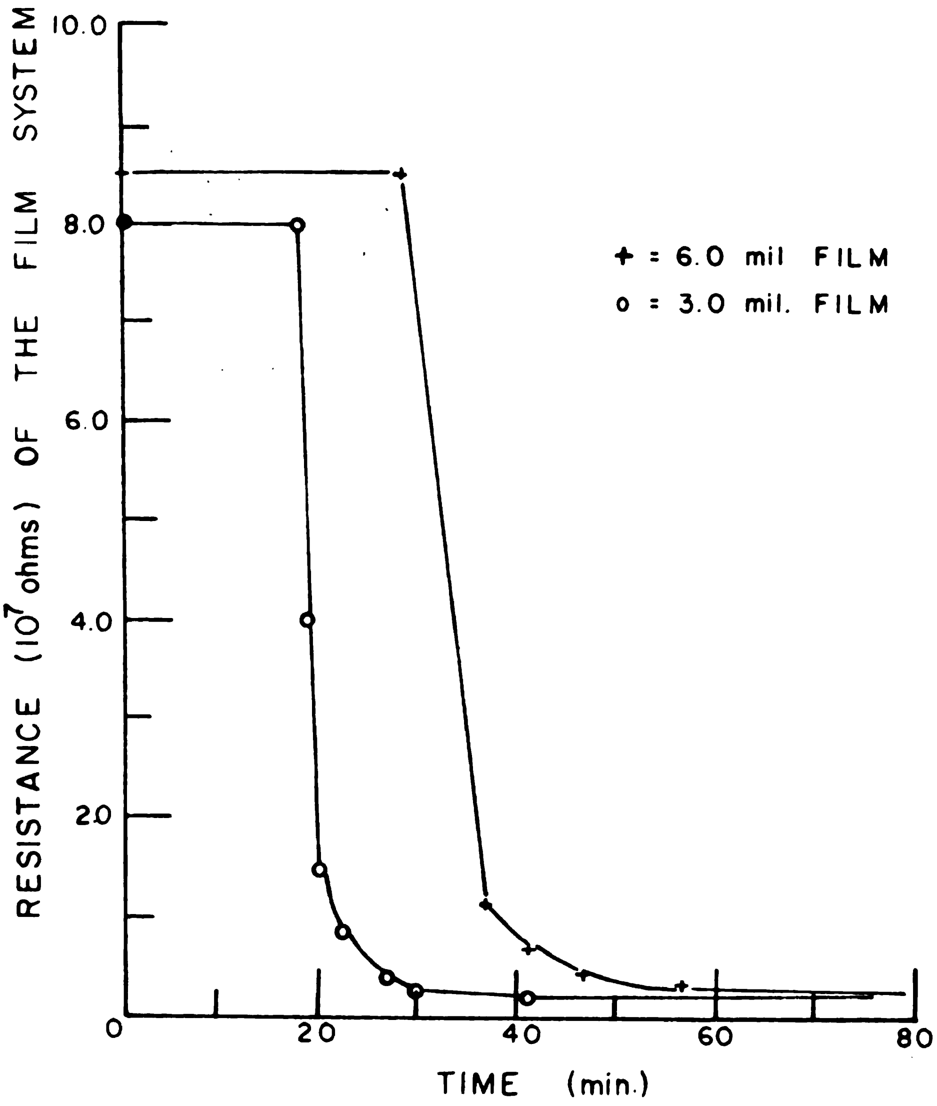

RESISTANCE (10^7 ohms) OF THE FILM SYSTEM
10.0
8.0
6.0
4.0
2.0
0
20
40
60
80
TIME (min.)
+ = 6.0 mil FILM
o = 3.0 mil. FILM

Fig. 22 -- The total liquid water permeation through 3.0 mil. films of the one coat latex paint (paint no. 3) on flat grain, fast and slow growth samples was indicated by the resistance decrease plotted versus time. The permeation through the standard system was plotted for comparison.

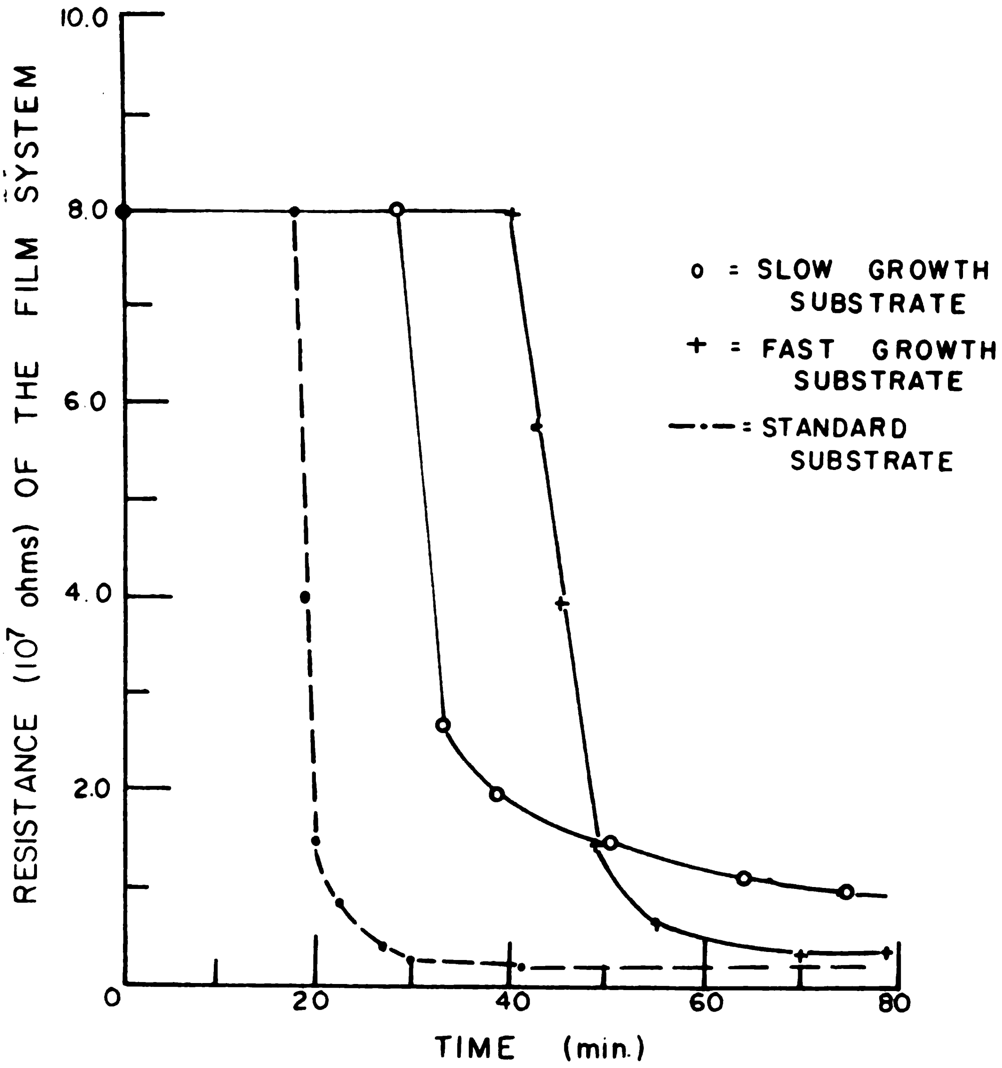
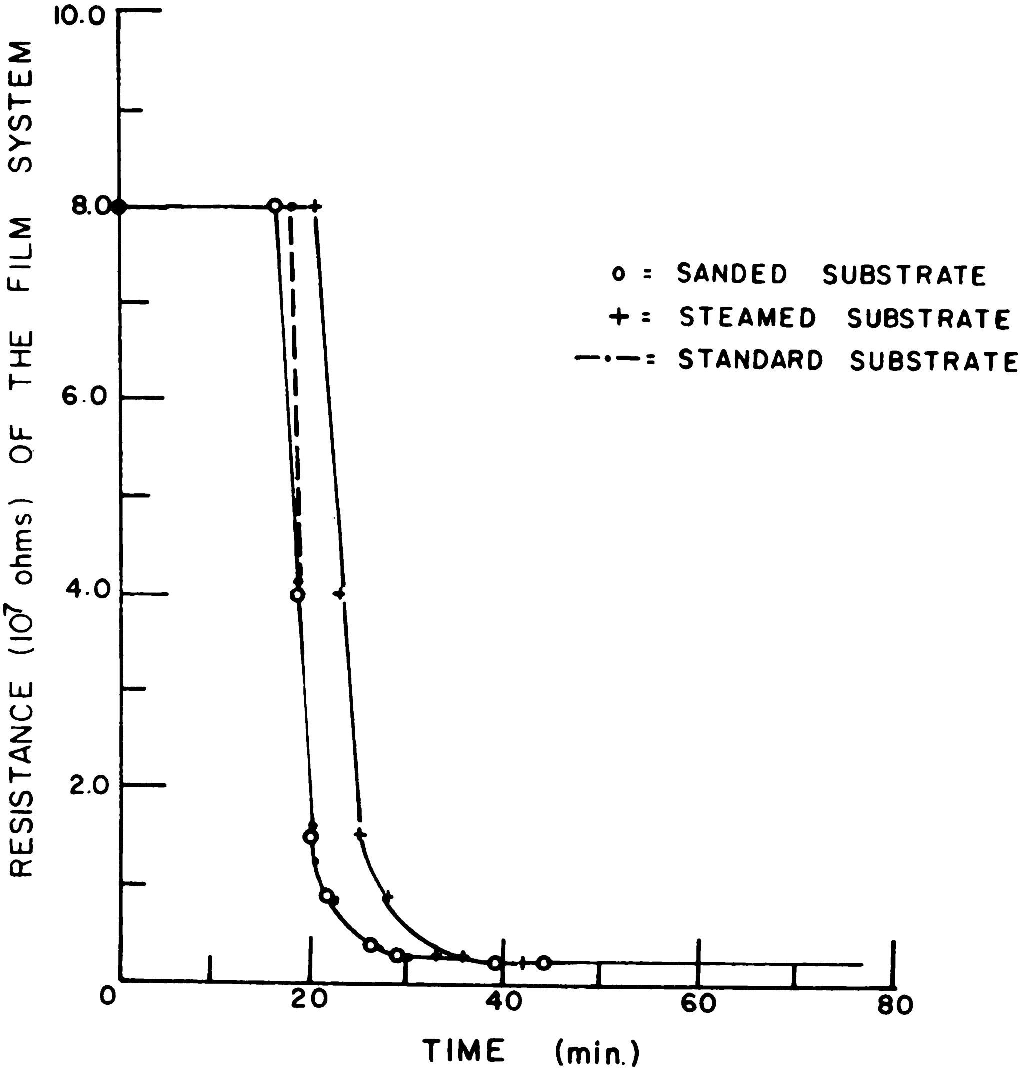

10.0
8.0
6.0
4.0
2.0
0
20
40
60
80
TIME (min.)
RESISTANCE (10^7 ohms) OF THE FILM SYSTEM
o = SLOW GROWTH SUBSTRATE
+ = FAST GROWTH SUBSTRATE
—·— = STANDARD SUBSTRATE

Fig. 23 -- The total liquid water permeation through 3.0 mil. films of the one coat latex paint (paint no. 3) on sanded and steamed substrates was indicated by the resistance decrease plotted versus the elapsed time. The permeation through the standard system was plotted for comparison.


10.0
8.0
6.0
4.0
2.0
0
20
40
60
80
RESISTANCE (10^7 ohms) OF THE FILM SYSTEM
TIME (min.)
o = SANDED SUBSTRATE
+ = STEAMED SUBSTRATE
—•—= STANDARD SUBSTRATE

DISCUSSION OF RESULTS

Water Vapor Studies

Free Films

Free films of oil and water base paints were tested for permeability to water vapor and some of the expected results were confirmed. The oil base paints due to their chemical and physical composition were less permeable than the latex water base paints, which form a film by a different principle.

The water base paints are emulsions, where the polymerized particles are dispersed in the water phase. Surface active agents (emulsifying agents), either ionic or non-ionic, form a protective layer around the latex particle so that flocculation does not occur and a suitable viscosity is obtained. The water evaporates from the latex emulsion causing the polymer particles to pack in random fashion due to cohesive forces. The latex particles strongly adhere to one another but do not fuse together forming a continuous film. Therefore, appreciable microscopic voids are present and a hydrophilic capillary network in some cases is formed due to the emulsifying agents on the surface of the latex particles.

Oil base films polymerize on the substrate by an oxidative mechanism at the sites of unsaturation in the fatty acid segments. If the paint has adequate wetting and flow properties, a large number of microscopic voids are not present so water must diffuse by a random diffusion method dependent upon segmental motion of the polymer. Also, there is a greater degree of pigment dispersion in oil films, thus reducing agglomeration present in latex paints that further opens up the film. However, oil films are hydrophilic to varying degrees because of oxidative decomposition products, some of which are water soluble, and all are highly polar with an affinity for water. But these are minor effects compared to the void and capillary structures present in latex films.

Comparison of the permeabilities of the two oil base paints, No. 1 and 2, illustrates a significant difference in the results of the 6.0 mil. and 1.5 mil. films. Paint No. 1, a processed linseed oil formulation with a smaller amount of bodied linseed oil and tung oil, had a lower permeability than paint No. 2. The bodied linseed oil would be less sensitive to water than unbodied linseed oil since it was polymerized by heat in the absence of oxygen. However, tung oil has a greater degree of unsaturation causing a faster drying rate with more oxidative decomposition products. Paint No. 2 was a long oil linseed pure alkyd with 25 percent phthalic anhydride, and 65 percent linseed oil on a solids basis. The phthalic anhydride would incorporate almost twice as many ester linkages into the film as compared to the linseed oil paint. The ester linkage is not hydrolyzed under normal in-use conditions but the bond is sensitive to water and may be a contributing factor in increased permeability.

The pigments used in the paints also affected the properties of the film, specifically, permeability. Paint No. 1 contained white lead and titanium dioxide, probably the rutile form, in approximately equal amounts. Paint No. 2 contained almost twice as much of the non-reactive pigment, titanium dioxide, as paint No. 1 and according to Browne (5 & 6), titanium dioxide has four times the water absorptive properties as white lead. Possibly due to scission reactions in the film structure, non-volatile fatty acids have been found during the film formation process. These acids react with white lead to form lead soaps which are very water repellent, thus decreasing the osmotic force caused by the water soluble decomposition products present in the film. The silicate extenders which have greater water absorptive properties than titanium dioxide were not a factor in this comparison since they were used in approximately equal amounts.

The free film permeability curves in Figures 3 and 4 illustrate that there was a marked difference in the initial permeation of the two oil base free films. Paint No. 1 had a higher initial permeation possibly due to surface conditions caused by a greater pigment content than paint No. 2. However, this effect decreased as the paint continued to swell. The 1.5 mil. films were permeated rapidly, especially those of Paint No. 1 which reached steady state conditions immediately.

There was a significant decrease in the permeability coefficients of the water base free films as compared to the oil base films. Paint No. 3, a copolymer of poly (vinyl acetate) and a high molecular weight acrylic, showed an extremely high permeability to water vapor, while paints No. 4 and 5, acrylic emulsion formulations, were not as permeable. In formulation No. 3, the copolymer particles were significantly larger than the acrylic particles, thus forming a less cohesive film. Also, the polymer was amorphous due to its bulky acetate groups and its atactic stereoregularity. Due to the acetate group, the polymer is water sensitive and some authors believe that water breaks the acetate bond allowing a greater permeability.

The acrylic polymer is probably polymerized by an anionic addition mechanism. If no impurities were present it is possible to get an extremely narrow molecular weight distribution thus, increasing the homogeneity of the film. Also, if the emulsifying agent was ionic or non-ionic affects the film's permeability by the agent's attraction for the polar water molecule.

The acrylic emulsion paints No's 4 and 5, had essentially the same formulation except for 10.8 percent of basic lead silicate in paint No. 5. This pigment reacts with organic colorants leached from the wood to form insoluble substances that are not transmitted to the topcoats. The addition of this pigment increased the permeability to water vapor of paint No. 5 as compared to paint No. 4. The permeation curves were the same except in magnitude so that the relationship for paint No. 5 Figure _6_ was included and that for paint No. 4 was omitted.

The graphs in Figures _5_ and _6_ are misleading, because a linear relationship described the final permeation through the oil base films in contrast to the final curvilinear relationship for the water base film. The oil base films had an initial net absorption of water while the film was coming to equilibrium with the surrounding conditions. This caused a swelling of the film and an initial curvilinear relationship between the weight loss and time. The final linear steady state portion of the graph indicates a steady state permeation. The water base films reached the steady state almost immediately. However, the high permeability of the water base films caused a rapid loss of water. This resulted in a curvilinear, final portion of the graph due to a lack of water in the cups. The steady state conditions were reached immediately so that the permeability coefficient was able to be calculated from the inital data.

Film thickness was inversely related to vapor transmission except with paint No. 3. However, the permeability coefficients were not consistently reduced because the weight loss was not in an exact inverse proportion to the film thickness. With the oil base films, no definite conclusions were drawn concerning the thickness effect on the permeability coefficient. However, in most cases the percentage reduction in weight loss due to increased thickness was greater than with water base films.

The permeation rates were essentially the same for the two free film thickness of paint No. 3. This was possibly due to film defects present in the thicker film or the water transport was not affected by the thickness due to the capillary structure. Dry film thickness of 6.0 mils. were not obtained with water base films applied in one coat. This was due to the lack of ability to compensate for the thickness reduction caused by the water evaporation.

Coatings Applied to Substrates

The second part of the vapor study was concerned with the effect of redwood substrates on the permeability of the five films tested in the first part. A definite coating-substrate interaction was noted with four of the five films, but only with paint No. 1 on the redwood substrate, was there a decrease in the permeability as compared to the total resistance to permeation of the uncoated redwood substrate and the free film. This was termed a positive interaction. The other films, with the exception of paint No. 3, had negative reactions, i.e., an increase in the permeability of the coated substrate as compared to the permeability of the substrate and free film combined. The results concerning paint No. 3 were not considered significant due to the large permeability and the slight interaction effect noted.

Paint No. 1, a linseed oil based undercoat, was specifically formulated to contact the wood substrate. Extenders and pigments were formulated to increase the flow and wetting of the paint on the wood so that intimate contact was made creating an adhesive bond. The mechanism of the paint-wood intereaction is not known, thus limiting knowledge of the degree of mechanical and specific adhesion. It is believed that specific adhesion dominates since paints are not made to penetrate further than the excised cells. Assuming the coating wetted the wood surface, a chemical union through hydrogen bonds was possible. The electronegative end of the bonds could have been the reactive hydroxyl groups of the cellulose and the ester linkages in the polymerized oils. This would have reduced the internal attraction for water thus reducing the permeability of the combined system and would account for the increased resistance to permeation of the 3.0 and 1.5 mil. film of paint No. 1. The decrease in resistance of the 6.0 mil. film could have been due to film defects. To allow for penetration into the coarse textured redwood, two coats of the paints were applied with sufficient time for drying between coats. Stresses due to drying and other imperfections present in the thicker film may have caused a decrease in permeability.

When working with wood it must be remembered that surface irregularities due to the nature of the wood and due to machining are always present.

It is possible that some of the extractives present in redwood reacted with the coating. This was suggested by a result in part III of the vapor studies where the standard substrate was steam treated to reduce the soluble extractive content. This pre-treatment increased permeability when coated, as compared to the free film of paint No. 3 and the uncoated substrate. However, this could have been due to grain raising or an increased roughness even though the substrates were conditioned after steaming. Considering the extractive effect, redwood contains from 15 to 30 percent by weight of extractives composed mainly of tannins, other polyphenolic compounds and cyclitols, polysaccharides and simple sugars. These compounds could form hydrogen bonds with the finishes if contact were made with the reactive substituents groups present in the extractive material.

Considering the permeation results obtained with paint No. 2 on the standard redwood substrate, it is difficult to determine why the permeation rates increased to such a great extent. Figure 8 illustrates that the initial curvilinear relationship is still in evidence but at a higher rate. The viscosity of paint No. 2 was greater than paint No. 1 but not to such a degree that flow was impaired. A possible explanation, since the tests were conducted on different samples and uniform results were obtained, is that the substrate hindered the coating either physically or chemically altering its permeability to water vapor.

The acrylic emulsion finishes on the redwood substrate also showed a negative interaction. The decrease in resistance to permeation could have been caused by failure of the water base films to sufficiently wet the wood due to the hydrophobic constituents in the wood. Also the water dispersant of the paint may have swelled the crushed surface fibers causing them to protrude into the film. This would have resulted in a wicking action allowing water to penetrate at a greater rate. If the water was absorbed to a large extent by the surface of the wood, possibly film formation may have been hampered by lack of mobility of the latex particles.

The results as seen in Figure 10 are essentially the same as those for the free films except for the decrease in the permeation rate. The straight line results of the free films indicated that there was a definite pathway through the film with no initial resistance. The only limitation was the amount of water that could pass through per unit of time. The effect of the wood substrate seems to be an increase in free volume present and a decrease in the cohesive strength of the film, thus keeping the same shape relationship but with a different rate.

Direct comparisons of the interaction effect between oil base paints on the redwood substrate and water base paints on the substrate were not too meaningful. All of the components of an oil base paint can penetrate into the excised cells of the substrate while polymer fragments dispersed in the water of a latex paint are too large to penetrate. Therefore, since two coatings were applied to allow for penetration into the substrate, more paint material was present with the oil base paints than with the water base paints.

Paint No. 1 Applied to Various Substrates

The third part of this project was concerned with the effect of various redwood substrates on the permeability of a 3.0 mil. film of paint No. 1. Substrate variations were due to machining processes, chemical and physical variations, and grain directions. This work supported the result of part II concerning the positive interaction of paint No. 1 on the standard substrate in all but two of the substrate variables. These two cases were exceptional substrate modifications which accounted for the deviation. Therefore it is assumed that paint No. 1 interacts with the redwood substrate to decrease the permeability as compared to the sum of the free film and uncoated substrate results.

The machined substrate variables supported the above statement except for the negative interaction of the sliced substrate variable. As seen in Figure 13, this variable caused a curvilinear relationship indicating an initial low permeability increasing to the highest permeability of the substrate systems tested. This was probably because of the initial resistance of the film to water penetration, but once inside the film a wicking action due to the surface fibers protruding into the film, transported the water. Also, the coating didn't wet the rough, sliced surface as well as a smooth planed surface reducing the adhesion at the coating-substrate interface.

The permeation results of the sanded substrate variable were not significantly different from the standard substrate which was planed. This was to be expected since the roughness factors were similar resulting in wetting of the same degree. Also the densities of the two substrates were the same so that a greater degree of interaction with the excised cell wall material was not present.

A system, where the coated redwood standard was inverted so that the uncoated side of the system was in contact with the saturated water vapor, was used to determine the effect of wood swelling on the permeability. The moisture content of the wood was approximately doubled so that cell wall dimensions were increased, especially in the tangential direction. The polymer coating adhering to the excised cell walls had to undergo even greater dimensional changes than on a whole fiber since the restrictive wrapping of the outer two layers of the cell wall were not effective on the excised cell walls. This caused an increase in the limited swelling of redwood resulting in stress on the films. On this assumption, the films were further opened up, thus increasing the permeability to water vapor.

Paint No. 1 was not as elastic as paints No. 4 and 5, but its elasticity allowed for linear expansion and only a permeability increase of 22 percent was present. The inverted substrate had the same linear relationship between weight loss and time as the standard substrate Figure 14, except the degree of permeation was greater.

Considering the substrates that were chemically and physically different from the standard, only the steamed substrate had a negative interaction with paint No. 3. The substrate was rendered more permeable after 7 hours of steaming at atmospheric pressure, probably due to removal of pit incrustations and opening of blocked pit apertures. During this time, 20 percent of the alcohol soluble extractives and 15 percent of the water soluble extractives were converted into soluble material and deposited at or near the veneer surface. A minor effect of steaming could have been the migration of fatty extractives, located in longitudinal and ray parenchyma, to the veneer surface. Since the ethyl ether-soluble extractives, designated "fats", comprise only one percent of the extractive content of redwood the effect, if present, would have been minor. With these occurrences the surface properties of the redwood substrate were definitely altered. The wettability of the surface was probably greatly reduced and any interaction between the wood and paint was limited by the presence of extractives. The initial relationship, Figure 12, is slightly convex upward similar to the standard coated system. However, the steamed redwood substrate system doesn't reach steady state condition until 36 hours after the standard, illustrating that the substrate conditions had been altered.

The remaining redwood substrates used were not obtained from the same cant but from different boards resulting in substrates with different physical properties. The permeability, surface properties and density of these substrates were variable. The density and permeability of these samples are listed in Table 3, but the surface properties are not known. Since the previous histories concerning the moisture content prior to drying, the drying conditions, and the location of the boards in the tree were variable, the extractive content and extractive location varied from substrate to substrate. This factor was minor in analyzing the permeability results but it must be considered.

The redwood sapwood substrate was the same as the heartwood standard substrate except for its lack of extractives. There were no restrictions to vapor passage due to pit encrustations, blocked pit apertures or blocked tracheids so that permeation of the uncoated substrate was the highest tested. The permeability coefficient of the coated sapwood was 22 percent larger than that of the redwood standard substrate. This was mostly due to the greater permeability of the substrate but also the lower interaction between the paint and substrate had an effect. The positive interaction value indicates that there was a substrate coating interaction reducing permeability. However, the interaction value was 43 percent less than the standard value. The lower interaction may have been caused by an increased swelling due to lack of extractives or the lack of extractive-coating interaction. However, paint has superior wetting properties when extractives are absent.

A surface similar to the standard redwood substrate but aged for over 1.5 years was coated and tested for permeability. The permeability coefficient of the coated aged substrate was larger than the standard's coefficient, possibly due to the slightly greater permeability of the former. The major cause was a 40 percent decrease in the interaction between the substrate and the paint. The interaction was lessened because the exposed cellulose of the excised cell walls lost its reactive hydroxyl groups and collected physiological debris. The relationship between weight loss and time, Figure 11, is linear nearly corresponding to that of the standard indicating similar permeation mechanisms.

Hemlock, a denser, finer textured wood having a lower extractive content than redwood, was used as a substrate variable. The permeability coefficient of hemlock was 43 percent larger than that of the coated redwood standard partly due to the greater permeability of the uncoated hemlock substrate. There was only a small degree of positive coating-substrate interaction which is difficult to explain. The hemlock substrate was denser, therefore it had more wood to contact the paint. It was also finer textured than redwood and had a gradual transition between springwood and summerwood. All of these factors should have increased the positive interaction but it is known that hemlock does not take and hold paint as well as redwood. The logical explanation is that there was an extractive-paint interaction with the redwood. This would account for part of the interaction since the redwood sapwood, essentially void of extractives, had one half of the interaction of the standard substrate. It is difficult to consider the results of the steamed redwood substrate since the extractives were still present but some were insoluble and the surface was modified. Therefore, it seems that the extractive-coating interaction was a major factor for redwood's better painting properties than those of hemlock.

The final three variables were concerned with the effect of grain direction and growth rate on the permeability of the applied coating. However, the past history of the samples was not known so that the extractive content and location, as well as density, were variable, thus reducing the significance of the results.

The density was 20 percent lower in the edge grain, fast growth redwood samples because of the greater amount of springwood present. This caused a 10 percent increase in the permeability coefficient of the coated substrate. Part of the permeability increase was due to the greater porosity of the uncoated redwood substrate, but there was also a 20 percent decrease in the interaction. This was expected because of the decrease in the amount of excised cell wall material on which the paint is adsorbed. The excised cell walls have been found to be 30 times more reactive than the lumen walls so there was a definite reason for the interaction decrease. The different extractive content due to different veneers and the greater amount of springwood was a minor factor in this instance.

The flat grain substrates, both slow and fast growth, had greater densities than the standard substrate. The slow growth sample was 14 percent denser and was approximately three times less permeable than the fast growth sample. Both of the uncoated redwood samples deviated approximately 47 percent from the permeability of the standard uncoated substrate. The slow growth sample was less permeable and the fast growth sample was more permeable than the standard redwood substrate. However the permeability of the coated flat grain substrates were both lower than that of the standard. The interactions were both approximately 63 percent larger than those of the standard, partially accounting for the permeability decrease.

The 63 percent interaction increase was largely due to the greater density which is mostly accounted for by the substrate cut. On the surface of each flat grain substrate there was predominance of denser summerwood, which is not as permeable as the springwood but the summerwoods pits are usually in the aspirated state. All of the paint ingredients are able to penetrate into the excised cells but only the oil can pass through the pits and penetrate further. This greater penetration decreases the hygroscopicity of the substrate itself and permits more paint material to be applied. The greater amount of paint material, along with the greater interaction due to more excised walls present, accounts for the lower permeability of the coated flat grain redwood samples. Therefore it seems that grain direction was not the major substrate variable, rather the greater density and increase in summerwood increased the interaction, thus decreasing the permeability of the coated substrate.

Liquid Water Permeability Studies

Free Films

The results presented in Table 4 and Figures 17-23 do not indicate the difficulty of obtaining reproducible data. It is believed that the results illustrated by the graphs are an indication of the permeability of the film. However, in Figures 17-20, the lower leveling portion of the graph has little meaning since it is dominated by the filling-up process, where the films become saturated on the metal substrates. The method of least squares was not used to draw the graphs because of the inherent limitation of the testing accuracy.

The basis of measurement of the permeation rate was the time to reach equilibrium of the film system and the initial slope of the resistance relationship. The initial induction period, indicated in Figures 21-23, may have been due to a limitation of the VTVM. Small changes in resistance were impossible to record when the voltmeter was at its highest calibration and the reading was at the high end of the logarithmic scale. Only when the resistance decreased significantly could any results be recorded.

Free films of the paints indicated that the thickness of the film was directly related to the intial electrical resistance of the measured circuit. This was due to greater amount of material separating the electrodes. Paint No. 1 had a larger resistance than paint No. 2 possibly because of the greater integrity of film 1 or the increased ester linkages of paint No. 2. The slope of the resistance decreased, indicating the permeation rate decreased with increasing film thickness for paint No. 1, Figure 17. However, the slopes of paint No. 2 were directly related to film thickness Figure 18. This seems to indicate that paint No. 1 formed a more uniform film, with a higher cohesive energy and less internal stresses, so that as the film thickness increased the integrity of the film remained the same. The increased slope of the graph of paint No. 2 indicates a greater resistance decrease caused by greater permeation. The time required to reach equilibrium, however, decreased as the film thickness decreased indicating that thicker films required a greater period of time to reach the saturated state than the thinner films. This is not a valid indication of permeation rate, since it is affected by the thickness factor, which is not considered in the calculation. The equilibrium time is a valid comparison when films of the same thickness are tested.

Various author believe that liquid water permeation is similar to water vapor permeation at 100 percent relative humidity, except that the vapor molecules have a greater energy due to greater entropy and a higher kinetic component. Reflecting back to the vapor studies, the 6.0 mil. free film of paint No. 2 had a larger permeability coefficient than the 3.0 mil. film but a lower transport rate measured by the weight loss per 24 hours. These results are respectively related to the greater permeation rate and the longer time needed to reach equilibrium in the liquid studies. It is meant that the 6.0 mil. film retards the passage of water greater than the 3.0 mil. film of paint No. 2 but not in proportion to the increase in thickness. The 1.5 mil. film of paint No. 2 and paint No. 1 had larger weight losses per 24 hours than the corresponding 3.0 mil. films in the vapor study and also a shorter equilibrium time in the liquid study. This indicates a limited resistance to liquid and water vapor permeation. Therefore the 3.0 mil. film in the oil base paints was the optimum thickness.

The permeability coefficients of the various thicknesses of paint No. 1 in the vapor studies were all similar. However, the vapor permeability was inversely related to the film thickness. The permeability coefficient of the vapor studies cannot be compared to the measurements of the liquid studies because it considers film thickness in the calculation. The liquid results test the variable thickness but do not account for it. However the liquid penetration results, based on the time needed to reach equilibrium, were similar to the vapor studies based on weight loss per 24 hours. The thicker film was less permeable to water.

Free films of paint No. 3 behaved similar to paint No. 1; that is, the penetration rate was inversely related to the film thickness except with the 1.5 mil. free film. The permeation rates to liquid water were essentially the same for the 1.5 mil. and the 3.0 mil. free film, causing paint No. 3 to differ from paint No. 1. However, the time to reach equilibrium for the 1.5 mil. film was 50 percent of the time needed for the 3.0 mil. free film. This indicates a direct relation between time to reach equilibrium and thickness but no relation between penetration rate and thickness for paint No. 3.

The resistances recorded for paint No. 3 were significantly lower than those for the other four films. Possibly the acetate groups or the capillary structure caused the reduced electrical resistance of the film. Paints No. 4 and 5, although both were also water base films, had electrical resistances of similar magnitude to the oil base films. The permeation rates of these acrylic emulsion paints were higher than those of the oil base films by an average factor of 10. This indicates the presence of voids and the possibility of a capillary structure, though not as great nor hydrophilic as that postulated for paint No. 3.

Free films of paint No. 4, the acrylic undercoat for non-staining woods were less permeable than paint No. 5, agreeing with the vapor permeation results. The only major difference in formulation was the addition of 10.8 percent of basic lead silicate to paint No. 5. Although the silicate pigments are more water absorptive than the other pigments used, it seems unlikely that it would cause a permeation difference of 50 percent. A possible reason for the greater permeability may have been due to the difficulty of paint application. Foaming was prevalent with both paints but more so with paint No. 5. Equal amounts of distilled water were added to improve the paint properties but defects may have still occurred, accounting for the greater permeability of paint No. 5 as compared to paint No. 4.

Coatings Applied to Various Redwood Substrates

Part II of the liquid permeability study was concerned with the effect of various wood substrates on the permeability of a standard film. The resistances caused by paints 1, 2, 4 and 5 on the redwood substrate were too high to measure because of the resistant nature of the films and the limited permeation rates not great enough to substantially reduce the electrical resistance. The lower initial resistance and the greater permeability of paint No. 3 enabled the use of it as the standard coating for the various redwood substrates. However, the validity of a direct comparison of the substrate effect between the vapor and liquid studies was limited because of the use of two different coatings. Some comparisons were made since both films acted similar but differed in magnitude.

Two thicknesses of paint No. 3, 3.0 mil. and 6.0 mil, were applied to the standard substrate. The initial resistance increased as the thickness increased and the slope indicating the permeation rate increased as the thickness decreased. Both of the results were the same as those found using free films, but were different from the vapor study results with the paint. The thicker films of paint No. 3 were as permeable as the thinner films to water vapor possibly because of the greater energy of the vapor molecules. The thicker films would have provided a more effective barrier against liquid water due to its lower energy. It was stated concerning the vapor studies that the capillary structure and the hydrophilic components in the film controlled the permeation so that thickness was not a dominant factor. However, in the liquid studies, thickness was an important factor.

The interaction effect could not be measured, due to the different methods of testing used for the free films and the applied films.

Similar permeation results were found using liquid water as with water vapor when the grain direction was varied. For the flat grain samples, the permeation of liquid water rates were reduced approximately 50 percent as compared to the coated standard. The times needed to reach equilibrium were also greater for the flat grain samples supporting the results found with the slopes. The permeation differences between the fast and slow growth samples were not as pronounced as in the vapor studies because the measured permeation was not through the entire substrate. The measurement was taken .5 mils under the surface so that the difference in the substrate permeabilities was not a direct factor influencing the permeation rate. Therefore, considering that both substrates had similar magnitudes of interaction with the coating in the vapor studies and had similar permeabilities in the liquid studies, it seems that the flat grain redwood substrates affected the coating's permeability the same with liquid water as with water vapor. This conclusion along with the free film results where the thickness was inversely proportional to the transport rate demonstrate the equivalence between liquid water and water vapor permeation.

The sanded redwood substrate was slightly less permeable to liquid water than the standard substrate, while the differences in the water vapor results, although opposite, were also exceedingly small. These slight differences found in the two studies indicate a possible equivalence between the two penetrants.

The steamed redwood substrate variable reduced the permeability of the coating as compared to the standard results. This was unlike the vapor results where the steamed substrate caused an interaction decrease as compared to the standard redwood substrate. However, the steamed substrate variable does not afford a valid basis for the evaluation of the equivalence of liquid water and water vapor pentrants. The limited comparison is due to the fact that two different coatings were used and the specific results of each cannot be compared. If the steamed substrates were coated with paint No. 3 and tested for vapor permeability then a comparison could have been made.

The graphs of the coated substrates in Figure 21-23 all follow the same pattern with the high initial electrical resistance and the subsequent sharp decrease of the resistance. This was because of the electrical resistance properties of wood in relation to its moisture content. The dielectric constant of dry air is 1 and for oven dry wood it is 4.2. The constant increases with increasing density and increasing temperature, but the major factor is the moisture content of the wood when above its fsp. The dielectric constant for water is 81 so that the wood constant increases greatly as the moisture content increases. To illustrate this, the resistance across 1.25 in. of redwood at 7 percent moisture content is 22.4×10^3 megohms but at 8 percent it is 4.68×10^3 megohms. This property of wood accounts for the constant initial resistance and the sharp decrease in resistance. For as soon as the moisture penetrates through the film, the moisture content of the wood increases, thus sharply reducing the resistance of the circuit.

The leveling off portion of the graph indicates a point of equilibrium where the moisture was permeating through the film at a constant rate.

The equivalence of permeation effects of liquid water versus water vapor has been generally indicated but not proven. A more concentrated study with fewer variables and the same standard paint is needed to determine the experimental equivalence.

CONCLUSION

1. The substrate caused a definite effect on the permeability of the organic coatings tested. The permeability of only the linseed oil paint (paint No. 1) applied on the redwood substrate was less than the permeability of the substrate and free film combined.
2. As the amount of excised cell wall material of redwood in contact with the applied coating increased, the applied film's permeability decreased. As the age of the excised surface increased, the permeability of the applied coating increased.
3. Swelling of the redwood substrate increased the permeability of the applied oil base film. This was indicated by the standard coated system which was inverted so that the wood substrate was in contact with the saturated water vapor.
4. The permeability of paint No. 1 applied to redwood increased as the surface roughness factor increased.
5. The presence of extractives in redwood decreased the permeability of the applied film; steam conversion of the extractives in the substrates tested increased the permeability of the applied films.
6. The linseed oil paint was more permeable on the hemlock substrate than on the redwood substrate.
7. The necessity of testing the permeability of paints when applied to the actual substrate rather than in the free film form has been illustrated.

8. The test procedure for determinatioon of liquid water permeation of applied coatings had a limited application.

9. Similar permeation trends were obtained for liquid water and water vapor penetrants passing through free films and applied films of the paints tested. The only exception was the films of paint No. 3 because of its high permeability and low electrical resistance.

APPENDIX I

Specific Formulations of the Paints Tested

The Oil Base Films

Paint no. 1 -- Sherwin Williams 450 Undercoat

Pigment by weight		56%	
Titanium dioxide			21%
Basic lead carbonate			24%
Silicates			41%
Calcium carbonate			14%
Vehicle by weight		44%	
Processed linseed oil			42%
High polymer oil			15%
Bodied linseed	60%		
Tung oil	40%		
Driers			
Litharge			
Lead isodeconate			
Manganese isodeconate			

Paint no. 2 -- Rockcote 850, Low Lustre White House Paint

Pigment by weight		44%	
Titanium dioxide			46%
Silica and silicates			54%
Vehicle by weight		56%	
Long oil linseed pure alkyd			27%
Phthalic anhydried	25%		
Linseed oil	65%		
Raw linseed oil			10%

Mineral spirits and driers		62%
Manganese tallate	.015%	
Lead tallate	.6%	
Fungicide (Phenyl mercury oleate)		1.0%

Water Base Films

Paint no. 3 -- Muralo 350 One Coat Latex

Vehicle	72.4%	
Copolymer of polyvinyl acetate and a high molecular weight acrylic		32.9%
Esters and glycols		6.2%
Water non-volatile		60.9%
*Pigment	27.6%	

Chromium oxide
Titanium dioxide
Calcium carbonate
Silica and silicates

Paint no. 4 -- Rhoplex AC-34 303 (Acrylic Emulsion)

Material	Percent by Weight	Gallons
Tamol 731 (25%)	0.62	0.76
Triton X-102	0.18	0.22
Ant. foamer	0.09	0.13
Ethylene glycol	2.22	2.67
Pine oil	0.27	0.33
Hydroxyethyl cellulose (2.5%)	6.87	9.41
Preservative	0.16	0.11
Rutile titanium dioxide	13.35	4.29
Calcium carbonate	13.64	6.79
Crystalline silica	4.45	2.27
Letdown		
Rhoplex AC-34 (46%)	57.86	73.01
Antifoamer	0.09	0.13
Ammonium hydroxide (28%)	0.18	0.27

Material	Percent by weight	Gallons
Pigment volume content	29.8%	
Solids weight	58.2%	
volume	44.7%	
pH	9.4-9.7	
Viscosity range	73-79 Krebs	

Paint no. 5 -- Rhoplex AC-34 347 (Acrylic Emulsion)

Water	2.17	3.02
Tamol 850	0.39	0.45
Nopco NXZ	0.086	0.13
Pine oil	0.26	0.33
Ethylene Glycol	2.16	2.69
Methasol 57	.15	0.11
Hydroxyethyl cellulose (2%)	14.0	19.70
Basic lead silicate:EP-202	10.8	2.35
Ti-pure R-610 (TiOi)	12.9	4.37
Snowflake (CaCO$_2$)	9.32	4.77

Letdown

Rhoplex AC-34 (46%)	47.65	62.10
Nopco NXZ	.086	0.13

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