

Adsorption of Water Vapor by Unsupported Organic Films

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INTRODUCTION

In order to develop more fully a proposed theory of corrosion at the metal organic film interface already reported,¹ a more adequate analysis of the structure and sorptive properties of the organic film is obviated. The present report concerning the sorptive properties of eight unsupported organic films constitutes the first phase of the current study, while a later report will deal with the correlation of these properties of the films with their behavior as protective coatings of iron under conditions favorable to the formation of underfilm corrosion.

Workers have found that among the factors that control the rates of film interaction with the environment are diffusion, permeability, and sorption. Permeability has been shown by Waack et al.² to be diffusion-controlled but independent of film thickness for several typical synthetic polymer films. Thomas³ in studies of the permeability, diffusion, and sorption of both synthetic polymer and linseed oil films, found that sorption is dependent upon relative humidity but is independent of temperature. Liepina⁴ observed that the electrokinetic properties are by no means the only controlling factors in permeability of films. Rates of sorption of water vapor by varnish films reported by Thomas and Gent⁵ are similar to those found in the present study. Finally, Browne⁶ concludes that permeability and water vapor adsorption bear little or no relation to each other, and that permeability is not governed by pores through which air can pass.

In the present study, the structural properties of eight organic films were examined on the basis of observed adsorption isotherms, from which were calculated the BET areas, relative vapor pressure required to produce a monolayer, number of active sites for adsorption of water vapor, and the effect of

variations in the preparations of the films upon their adsorption behavior.

MATERIALS AND EXPERIMENTAL METHODS

The films were prepared as coatings on steel plate and tin plate carefully selected from production stock commonly used for making cans. Coatings were applied by means of a roller applicator at controlled thicknesses in the range of 0.0001 in. on a dry basis. Coating weights, along with their descriptive compositions are listed in Table I. All films were baked at 180°C. and were subsequently stored at low relative humidity in a dry box.

TABLE I
Specifications of Films Examined

Type	Applied weight, mg./4 in. ²	Free film thickness, × 10 ⁴ , in.
Oleoresinous	22	3.1
Phenolic	17	3.5
Vinyl (heavy)	26	4.0
Vinyl (light)	13	2.2
Alkyd	22	3.1
Epoxy	17	2.8
Hydrocarbon A	18	3.4
Hydrocarbon B	20	3.5

Removal of the films was achieved by two methods. In the electrolysis method, films were removed from both the steel and tin plates by an electrolysis technique in which the panel was made the cathode in a 1% sodium carbonate solution, and with the use of a platinum gauze anode. At a potential of 12 v., the vinyl films came off within seconds, while the epoxy and hydrocarbon films required several hours. Presoaking of the panels in

the electrolyte prior to electrolysis enhanced the removal of the films, although there is some question concerning the alteration of certain structural properties of the films as a result of the intimate contact of the film with an aqueous solution.

In the second method, the films were removed from tin plate by placing the edge of the coated panel in a shallow pool of mercury. In a few minutes, the resulting tin amalgam at the film-metal interface destroyed the adhesion of the film and it was readily lifted from the panel. All films were stored in closed jars at room conditions until examined.

Adsorption isotherms were obtained by an eight-place gravimetric apparatus in which all eight films, supported by quartz helical springs (sensitivity in the range of 1 mg./mm.) were simultaneously exposed to controlled amounts of water vapor whose pressure was measured by an oil manometer containing Apiezon B oil. The extension of the quartz springs, which were housed in a constant temperature air bath, was observed by projecting an image of a point selected midway on the supporting fiber between the sample and the spring onto a screen. This provided a magnification of the vertical movement to approximately thirteen times the actual movement. Readings of the change of weight of a 400-mg. sample of film could be made with accuracy to within ± 0.015 mg. Both the air chamber which housed the springs and the water bath in which the samples were immersed were thermostatically controlled to constant temperature within $\pm 0.1^\circ\text{C}$. The all-glass vacuum system was constructed with precision, high-vacuum stopcocks lubricated with Apiezon N grease and conventional auxiliary components, including a McLeod gauge and mercury manometer. The water vapor was derived from a sample of distilled water that was alternately frozen and thawed three times with moderate outgassing within the vacuum system.

RESULTS AND DISCUSSION

Rates of Adsorption

Film samples were permitted to equilibrate with ambient vapor pressure at each observation for a period of at least 90 minutes. The rates of water vapor adsorption, given in Figures 1, 2, and 3, show that the vinyl films, for example, reached equilibrium with a 0.80 relative vapor pressure after only 15 min., while the phenolic, hydrocarbon, and alkyd films show a slight tendency to increase their adsorption, even after 75 min.

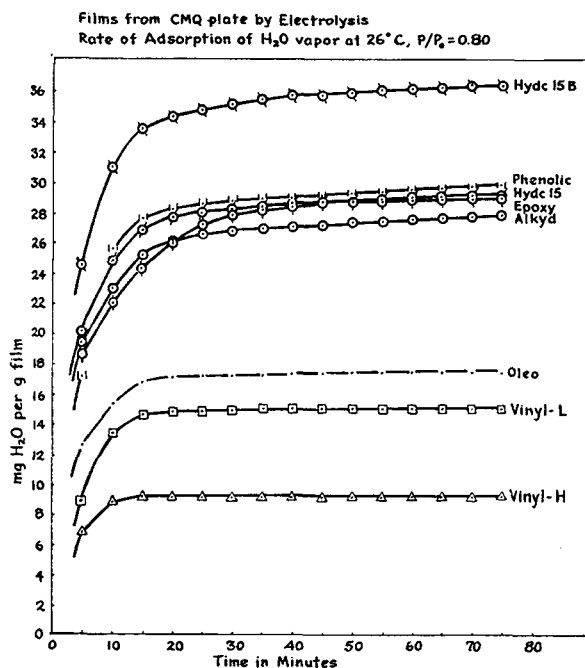


Fig. 1. Rates of adsorption of water vapor at 26° by films obtained from CMQ plate by electrolysis.

The data on rates of adsorption clearly shows that the method of removing the films from their metal substrates affects their structure. For example, the relative positions of the rate curves for the various films in Figures 1, 2, and 3 shows considerable variation, depending upon the source of the films. The vinyls, oleoresinous, and alkyd films are among those consistently adsorbing the least moisture, but the behavior of the hydrocarbons and epoxy films is erratic. Further, the films obtained from the steel plate by electrolysis adsorb consider-

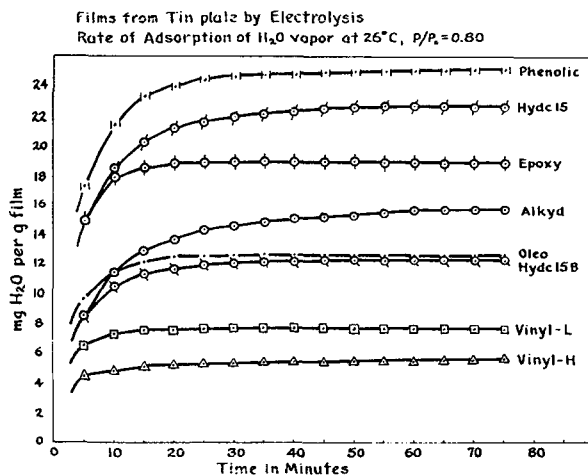


Fig. 2. Rates of adsorption of water vapor at 26° by films obtained from tin plate by electrolysis.

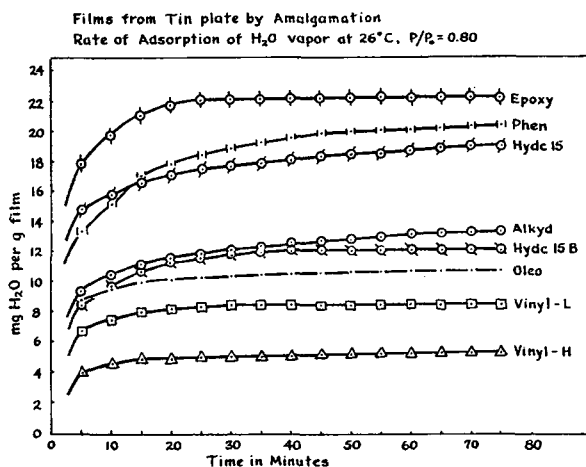


Fig. 3. Rates of adsorption of water vapor at 26° by films obtained from tin plate by amalgamation.

ably greater quantities of water vapor than films obtained from tin plate. This difference in degree of adsorption may be attributed to a difference in structure of the films at the metal-film interface, but it is more likely the result of the more vigorous treatment needed to remove the films from the steel. Consequently, the films obtained from tin plate by the amalgamation technique are considered to be least distorted in structure, although the behavior of all films was studied with equal interest.

Adsorption Isotherms

Adsorption isotherms for the eight films were obtained in a conventional manner at 15, 26, and 44°C. Figure 4 gives the raw isotherms for the adsorption of water vapor by the vinyl film (which showed the least adsorption) and by the phenolic film (which was among those that showed the great-

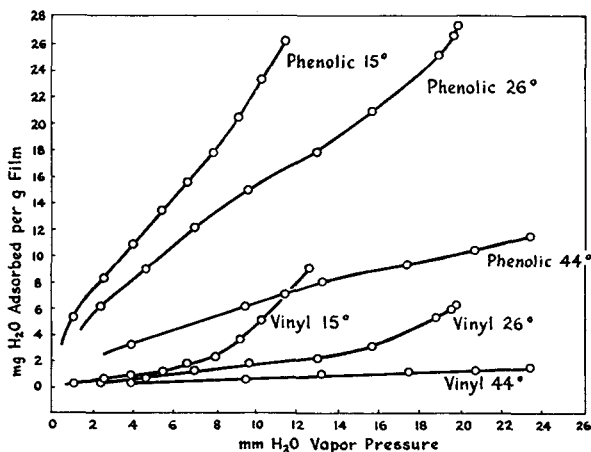


Fig. 4. Adsorption isotherms for vinyl and phenolic films at three temperatures.

est amount of adsorption). Reproducible curves were obtained with all films. The films out-gassed in 24 hours at 10⁻⁴ mm. Hg to their original weights, showing that neither perceptible hydrolysis nor volatilization of the film components was produced by the adsorption of the water vapor.

The adsorption curves for all films were generally smooth, not showing any decided breaks that might indicate phase changes in the adsorption process. Most of the curves were of the typical S-shaped, Type II isotherms, although they were considerably more shallow than curves shown by many high surface area adsorbates. With certain films, such as the oleoresinous, phenolic, and vinyls, however, there was an abnormal increase in the amount of water vapor adsorption at approximately 0.6 relative pressure and particularly at 26°C. That is, most of the films adsorbed water vapor in quite smoothly increasing amounts over the pressure range from 0.01 to 0.85 relative pressures, excepting those indicated above.

BET Results

A conventional analysis by means of the BET equation of the isotherm data obtained at the three temperatures showed that all films exhibited linear plots in the range of 0.05 to 0.4 relative pressures, several films giving linear plots up to 0.5 relative pressures. Three examples of these plots, representative of those produced by the data collected in this study, are shown in Figure 5. From these data were collected the parameters of vapor pressure required to form a monolayer, the BET areas (an area of 10.6 A.² per water molecule⁴ being assumed), and the *c* values. In Table II these data are summarized for the films removed from tin plate by the

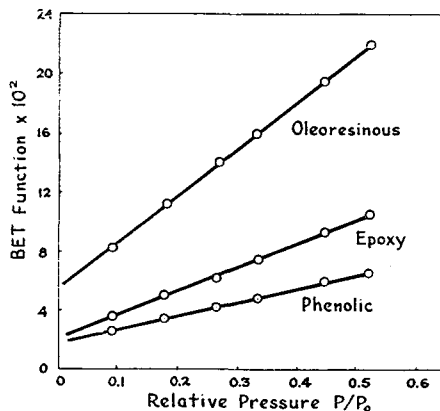


Fig. 5. BET plots of data derived from the adsorption isotherms for oleoresinous, epoxy, and phenolic films.

TABLE II
BET Data Derived from Water Vapor Adsorption Isotherms
of Films Removed from Tin Plate by Electrolysis

Film	Temp., °C.	P/P_0 at θ = 1	W_m , mg./g.	No. of active sites/g. \times 10^{-20}	c
Oleoresinous	15	0.31	3.06	10.2	5.3
	26	0.32	3.76	12.5	3.3
	44	0.30	3.09	10.3	3.7
Phenolic	15	0.25	8.70	29.0	8.1
	26	0.26	9.07	30.3	12.0
	44	0.24	8.34	27.8	11.0
Vinyl (heavy)	15	0.36	0.89	3.0	3.8
	26	0.32	1.16	3.9	6.4
	44	0.35	0.65	2.2	7.0
Vinyl (light)	15	0.36	1.02	3.4	3.8
	26	0.37	1.41	4.7	5.5
	44	0.28	0.90	3.0	6.7
Alkyd	15	0.34	3.89	13.0	2.9
	26	0.34	5.29	17.8	3.3
	44	0.32	4.95	16.4	3.2
Epoxy	15	0.20	5.65	18.8	14.0
	26	0.25	6.02	20.1	15.0
	44	0.20	5.02	16.7	15.0
Hydrocarbon	15	0.27	7.36	24.6	5.5
	26	0.33	7.95	26.5	3.9
	44	0.30	6.45	21.6	5.5
Hydrocarbon B	15	0.32	2.66	8.9	5.9
	26	0.35	3.36	11.2	5.1
	44	0.29	2.92	9.7	6.6

electrolysis method. The relative vapor pressure required to form a monolayer is notably consistent, varying between 0.20 and 0.37, the values for phenolic and epoxy films being lower values than those for most of the other films. Even though the data are not sufficient to permit a definite conclusion, there is reasonable evidence that the temperature has little or no effect on the amount of water vapor adsorption, a conclusion reached by Thomas³ for vinyl, methacrylate, cellulose acetate, and linseed films.

From Table II it is further indicated that the vinyl films are the least porous of the lot, as indicated by the W_m values, the amount of water vapor required to form a monolayer. In place of reporting BET areas, the number of active sites are listed as a means of comparing the degree of hydrophilicity of the films. The number of adsorption sites is calculated from W_m as follows:

$$n = \frac{\text{BET area}}{10.6 \times 10^{-20}}$$

where the factor in the denominator is the projected area of a water molecule in square meters.

In contrast to Thomas' results,³ the present study shows values for c in the BET equation considerably greater than unity. This indicates that there is considerable energy (above that involved in the heat of liquefaction) associated with the adsorption process. This is particularly true for the epoxy and phenolic films.

In order to avoid excessive detail, the data derived from the films removed from tin plate by amalgamation and from iron by electrolysis are not listed here. These were, however, regularly similar to those in Table II. Chief exceptions were the areas shown by the films removed by amalgamation. Apparently, the removal of the films by electrolysis results in an increase in surface that is reactive toward water vapor. Film removed by amalgamation generally showed 20 to 30% fewer active sites than those films removed by electrolysis. The electrolysis process, no doubt, creates new active sites that ordinarily do not exist in the virgin film. It is suggested that the crystallinity of the film, a characteristic that greatly influences the sorptive capacity of a polymer,⁸ is decreased in the process of removal of the films by electrolysis. As a result, the films obtained by amalgamation are more nearly identical to the original film structures than are those obtained by electrolysis.

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Synopsis

Eight organic coating films were removed from their metal substrates by two very different methods and were examined by means of water vapor adsorption isotherms. The data obtained in this study reveal the rates of adsorption, the relative pressure required to form a monolayer, the number of active sites for water vapor adsorption, and the parameters in the classical BET isotherm equation. Removal of the films by electrolysis in an alkaline bath and by amalgamation of the tin plate produced films of considerably different structure. Since the electrolysis procedure subjects the film to mechanical and possibly chemical alterations, it is proposed that the increase in water vapor adsorption by the former type of films is the result of decreased crystallinity. Consequently, the films removed by amal-

gamation are considered to be more similar in total structure to the original films.

Résumé

Huit films de recouvrement organiques enlevés de leurs substrats métalliques par deux méthodes très différentes, ont été examinés au moyen des isothermes d'adsorption de la vapeur d'eau. Les résultats obtenus dans cette étude fournissent les vitesses d'adsorption, la pression relative nécessaire à former une couche monomoléculaire, le nombre de sites actifs pour l'adsorption de vapeur d'eau, et les paramètres dans l'équation classique des isothermes BET. L'enlèvement des films par électrolyse dans un bain alcalin et par amalgamation de la plaque d'étain produit des films de structures très différentes. Vu que le procédé électrolytique soumet le film à des altérations mécaniques et éventuellement chimiques, on propose que la quantité plus grande de vapeur d'eau adsorbée par le premier type de films résulte d'une cristallinité plus faible que l'autre type. En conséquence les films enlevés par amalgamation sont plus semblables par leur structure globale aux films originaux.

Zusammenfassung

Acht organische Filmüberzüge, die von ihrem Metallsubstrat durch sehr verschiedenartige Methoden abgehoben worden waren, wurden in bezug auf ihre Wasserdampf-Adsorptionsisotherme untersucht. Die bei dieser Untersuchung erhaltenen Ergebnisse liefern die Adsorptionsgeschwindigkeiten, den zur Bildung einer monomolekularen Schichte erforderlichen Druck, die Anzahl der aktiven Zentren für die Wasserdampfadsorption und die Parameter für die klassische BET-Isotherme. Die Entfernung der Filme einerseits durch Elektrolyse in einem alkalischen Bad und andererseits durch Amalgamierung der Zinnplatte lieferte Filme mit beträchtlichen Strukturunterschieden. Da der Elektrolysevorgang begreiflicherweise den Film mechanischen und wahrscheinlich auch chemischen Änderungen unterwirft, wird die Annahme vorgeschlagen, dass das grössere Ausmass der Wasserdampfadsorption beim ersteren Filmtyp das Ergebnis einer im Vergleich zum letzteren Typ verringerten Kristallinität ist. Es werden daher die durch Amalgamierung abgehobenen Filme als in der Gesamtstruktur den ursprünglichen Filmen ähnlicher betrachtet.

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