Effects of Solids-Loading on Moisture Permeability Coefficients of Free Films

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Abstract □ The effects on the water vapor transmission properties of free polymer films by the incorporation of dispersed solid filler materials (solids-loading) were studied. Two mineral talcs and titanium dioxide were separately incorporated, in a range of concentrations, in a standard plasticized cellulosic film comprised of hydroxypropyl methylcellulose and ethylcellulose (3:1). The nature of the additive dispersed solid filler material and its general surface chemistry, particle size, particle-size distribution, and concentration were found to influence the water permeation properties of the free films. Film thickness did not provide a standard variable of analysis for films containing various concentrations of dispersed solid or the same concentration of different solids. The mass of polymer in any standard cross section of film did provide a meaningful method of analyzing solids-loading effects. Over the solids-loading range studied, the rate of water vapor transmission decreased as solids-loading increased for both talc systems. The titanium dioxide films had a minimum water vapor transmission rate at an intermediate solids-loading value. A linear increase in the permeability coefficient was observed as the amount of polymer in the film cross section increased.

Keyphrases □ Solids-loading, two mineral talcs and titanium dioxide—effect on moisture permeability coefficients of cellulose free films □ Films, hydroxypropyl methylcellulose-ethylcellulose—effect of incorporating dispersed solid fillers (talcs and titanium dioxide) on moisture permeability coefficient □ Permeation (moisture) of cellulose films—effect of incorporating dispersed solid fillers (talcs and titanium dioxide) □ Conspergents—effects on moisture permeability of cellulose films

To expedite the coating of particles or tablets, water-insoluble or slowly soluble materials are often added in suspension in the polymer film-forming solution to increase solids-loading, to accelerate correspondingly the build-up of the film coat structure, and to reduce coating time and costs. Such filler coating materials may, however, greatly change the properties of the resultant films and their subsequent applications and uses.

The development and pharmaceutical applications of synthetic polymers as film structures have been recognized only in the last 15–20 years, resulting in film coating of pharmaceutical dosage forms for product protection or controlled drug release. Virtually nothing has been published that quantitatively indicates the effects of conspergents (dispersed nonpolymeric nonfilm-forming additives) upon the

properties of pharmaceutical polymer films. Only very recently have pharmaceutical scientists begun to examine the structural, mechanical, and physiochemical properties of films related to film application, performance, and use (1, 2).

EXPERIMENTAL

Materials—A hydroxypropyl methylcellulose[1] and a low molecular weight ethylcellulose[2] were the two polymers used. A 3% (w/v) concentration of hydroxypropyl methylcellulose-ethylcellulose (3:1) was used to cast free films from a solvent system of methylene chloride-methanol-isopropanol (4:3:3). A surfactant, polysorbate 20[3], 14.3%, and a plasticizer, propylene glycol, 34.1%, on a w/w basis calculated from the nonvolatile percent, were also included in each formulation. The water-insoluble additive agents (conspergents) selected for dispersion in the previously described polymer system are shown in Table I.

Preparation of Conspergent Suspension in Polymer Organosol—The conspergent was blended with all of the solvent including the propylene glycol and surfactant in a single-speed blender[4] for 5 min. This produced complete dispersion of the insoluble additive at low viscosity. The suspension was then transferred to a magnetic stirrer[5], and the polymer was added slowly with stirring. Then the suspension was covered and allowed to solvate for 24 hr with continued stirring at a speed setting of 4. The suspension was again placed in the blender for 3 min, after which the films were immediately cast. Although slight aeration resulted from redispersion in the blender in this step, the cast films were observed to be devoid of air bubbles.

Preparation of Free Films—Several methods were evaluated for casting free films. A glass substrate (polished side of a pill tile) was selected as yielding the smoothest, most uniform films. The glass substrate was coated by hand using disposable wipers with a 2% (v/v) silicone release agent[6] in xylene, which was then baked on at 250° for 2 hr. Plexiglas strips, 12.7 × 0.93 × 1.27 cm (5 × 0.37 × 0.5 in.), were used to partition the substrate into cells so that different volumes could be cast, yielding several film thicknesses for each formulation. The film casting was done in an airtight glove box, which served as a casting chamber to house the films during drying and to facilitate control of temperature and relative humidity. The temperature inside the chamber was controlled by circulating water at the required temperature through a radiator inside the chamber. The relative humidity inside the chamber was in the range of 40–50% as checked by the wet-dry bulb technique (3), and the temperature was controlled at 30 ± 2°. The films were allowed to dry for 24 hr in the chamber; they were then removed and stored in an oven in a desiccator with anhydrous calcium sulfate desiccant[7] at approximately 0% relative humidity and 30 ± 1° for 1 week prior to evaluation and testing.

Density Determination of Free Films—An indirect method of determining the film density was used employing film thickness and the relation $D = m/V$, where D = density of free film, m = weight of film sample in grams, and V = volume of film sample (cm^3) or (standard area) × (measured average thickness). *The thickness of each film disk was measured in the center and*

Table I—Additives Selected for Evaluation

Additive	Chemical Composition	Median Particle Size, μm[a]
Italian talc[b]	Hydrous magnesium silicate	20.5
Talc USP	Hydrous magnesium silicate	12.5
—	Titanium dioxide	2.7

[a] Coulter counter determination. [b] Lot 3MEA 064, Mead Johnson Co., Evansville, Ind.

[1] Methocel 50 cps, 60 HG, Dow Chemical Co., Midland, Mich.
[2] Ethocel 50 cps standard ethoxy, Dow Chemical Co., Midland, Mich.
[3] Polyoxyethylene sorbitan monolaurate (Tween 20), Atlas Chemical Industries, Wilmington, Del.
[4] Model F.C.1 14, Waring Corp., New York, N.Y.
[5] La Pine Scientific Co., Chicago, Ill.
[6] 200 Fluid, Dow Chemical Co., Midland, Mich.
[7] Drierite, W. A. Hammond Drierite Co., Xenia, Ohio.

Table II—Italian Talc Water Vapor Transmission Data for Films

Film Density, g/cm³	Additive[a], %	Weight of Exposed Film, mg	Polymer, %	Weight of Polymer Exposed, mg	Film Thickness mils	Film Thickness cm × 10⁻³	Rate of Moisture Transport, mg/hr[b]	R_{wvt}, × 10⁻⁵ᶜ	Permeability Coefficient, × 10⁻⁷
1.176	0	13.75	59.45	8.17	2.79	7.08	6.37	13.3	9.43
		15.83		9.41	3.21	8.15	6.00	12.6	10.2
		18.06		10.74	3.66	9.30	5.66	11.8	11.0
		20.43		12.15	4.14	10.52	5.27	11.0	11.6
		22.56		13.41	4.58	11.62	5.22	10.9	12.7
1.190	10	14.52	56.12	8.15	2.91	7.39	5.79	12.1	8.95
		16.43		9.22	3.29	8.36	5.65	11.8	9.88
		16.43		10.84	3.87	8.36	5.26	11.0	10.8
		10.31		11.96	4.27	10.85	5.09	10.7	11.6
		21.32		12.66	4.52	11.48	4.90	10.3	11.8
1.204	20	22.50	53.13	11.95	4.46	11.32	4.73	9.89	11.2
		25.31		13.45	5.01	12.73	4.72	9.87	12.6
		29.58		15.72	5.86	14.88	4.40	9.21	13.7
		40.22		21.37	7.97	20.23	4.12	8.62	17.5
1.232	40	21.17	48.03	10.17	4.10	10.41	4.96	10.4	10.8
		23.27		11.18	4.51	11.44	4.65	9.73	11.1
		34.88		16.75	6.75	17.15	4.13	8.65	14.8
		36.73		17.64	7.11	18.06	4.07	8.52	15.4
1.260	60	21.13	43.82	9.26	4.00	10.16	4.61	9.65	9.80
		24.56		10.76	4.65	11.81	4.38	9.17	10.8
		26.89		11.78	5.09	12.93	4.32	9.04	11.7
		29.24		12.81	5.54	14.06	4.19	8.76	12.3
		37.44		16.41	7.09	19.00	3.74	7.83	14.1
		41.06		17.99	7.77	19.74	3.71	7.76	15.3
		44.05		19.30	8.34	21.18	3.60	7.53	16.0
1.288	80	26.51	40.29	10.68	4.91	12.47	4.32	9.05	11.3
		28.60		11.52	5.30	13.45	4.27	8.92	12.1
		41.37		16.67	7.66	19.46	4.17	8.73	17.0
		44.92		18.10	8.32	21.13	4.07	8.51	18.0
		50.90		20.51	9.43	23.94	4.04	8.44	20.2
1.316	100	22.96	37.28	8.56	4.16	10.57	4.17	8.72	9.21
		25.65		9.56	4.65	11.81	4.19	8.77	10.4
		27.70		10.33	5.02	12.75	4.18	8.74	11.2
		38.90		14.50	7.05	17.91	3.59	7.51	13.5
		46.88		17.48	8.50	21.58	3.34	6.98	15.1

[a] Percent (w/w) of polymer. [b] Rate of moisture transport = slope of the line in milligrams per hour. ᶜ Water vapor transmission rate = grams per (hour × square centimeters area × millimeters mercury). Table values are multiplied by 10⁻⁵ to produce experimental values.

around the periphery with a micrometer[8], reading to 1 × 10⁻⁵ in., and the weighings were carried out on an analytical balance. All thickness and weight measurements were made after residual solvent had been removed from the samples by storing the films as previously described for 1 week.

Water Vapor Transmission Study—Water vapor transmission rates were determined for all film formulations studied. The design of the transmission cell was very similar to the permeation cell used by Patel et al. (4) and Gore (5). It consisted of a 7-dram, screw-capped, cylindrical glass bottle with a circular hole, 1.5 cm in diameter, in the screw cap. A circular piece of film was placed between two rubber gaskets, which were then fixed inside the screw cap. Each rubber gasket also had a circular opening of 1.45 cm diameter. The area of the exposed film was 1.65 cm². The bottle contained approximately 5 ml of supersaturated sodium tartrate solution, which gave an internal relative humidity of 91% at 30°, equivalent to a vapor pressure of 28.96 mm Hg (6). The bottles were filled with the solution so that the distance from the film to the liquid surface was 4.75 cm.

The bottles were tightly sealed with the screw caps and placed in a desiccator over anhydrous calcium sulfate. The desiccator was placed in an oven at 30° and the bottles were allowed to equilibrate for 12 hr, at which time each cell was weighed on an analytical balance. These weights were labeled time-zero. Subsequent weighings were made in the same manner at 12-hr intervals for 72 hr. The amount of moisture transmitted through the film at any time is given by the loss of weight of the transmission cell at that time. Ten samples of four or more different film thick-

nesses were used for transmission measurements for each formulation.

An extensive review of the mathematical derivation and theory for calculating rates of moisture permeation was covered by several workers (4, 7–9). In this work, the water vapor transmission properties of the formulations studied were evaluated as functions of time, film thickness, weight of polymer exposed, and conspergent concentrations. The temperature, area of the film exposed, and vapor pressure gradient across the film were held constant.

The amount of moisture transmission due to the diffusion across the film membrane was expressed by Fick's law (10). Since one primary objective was to observe the effect of film thickness upon the water vapor transmission, this rate was calculated using the equation (7) modified by excluding the film thickness. Thus:

$$R_{wvt} = W/(A \, \Delta p) \qquad (Eq. 1)$$

where:

R_{wvt} = rate of water vapor transmission
W = amount of moisture transmitted per unit time in grams per hour
A = area of film exposed in square centimeters
Δp = vapor pressure gradient across film (28.96 mm Hg)

The water vapor transmission rate, R_{wvt}, is defined as the amount of moisture transmitted per unit time through a film of unit area when the film is subjected to a vapor pressure gradient of unity. R_{wvt} was expressed in the following dimensions: grams of moisture per (hours × square centimeters of film × millimeters mercury) at 30°. The value of W was calculated as the slope of the line resulting from a plot of moisture transmitted versus time. The variables A and Δp were maintained constant.

The permeability constant for each formulation was also deter-

Table III—Water Vapor Transmission Data for Talc USP Films

Film Density, g/cm³	Additive[a], %	Weight of Exposed Film, mg	Polymer, %	Weight of Polymer Exposed, mg	Film Thickness		Rate of Moisture Transport, mg/hr[b]	R_{wvt}, × 10⁻⁵ᶜ	Permeability Coefficient, × 10⁻⁷
					mils	cm × 10⁻³			
1.165	0	13.62	59.45	8.10	2.79	7.08	6.37	13.3	9.44
		15.68		9.32	3.21	8.15	6.00	12.6	10.2
		17.89		18.64	3.66	9.30	5.66	11.8	11.0
		20.24		12.03	4.14	10.52	5.27	11.0	11.6
		22.35		13.29	4.58	11.62	5.22	10.9	12.7
1.184	10	11.22	56.12	6.30	2.26	5.74	7.11	14.9	8.54
		12.06		6.77	2.43	6.17	6.43	13.5	8.30
		24.26		13.61	4.89	12.41	4.82	10.1	12.5
		33.68		18.90	6.78	17.23	4.65	9.74	16.8
		44.32		24.87	8.93	22.67	4.26	8.93	20.2
1.203	20	17.50	53.13	9.30	3.47	8.81	5.20	10.9	9.59
		19.37		10.29	3.84	9.75	5.06	10.6	10.3
		24.91		13.23	4.94	12.54	4.75	9.94	12.5
		26.60		14.13	5.27	13.39	4.26	8.92	11.9
		27.85		14.80	5.52	14.02	4.31	9.03	12.7
1.241	40	17.99	48.03	8.64	3.46	8.70	5.01	10.5	9.20
		19.67		9.45	3.78	9.60	4.91	10.3	9.86
		25.33		12.17	4.87	12.36	4.38	9.17	11.3
		35.53		17.07	6.83	17.34	3.92	9.21	14.2
		36.90		17.72	7.09	18.01	3.80	7.95	14.3
1.280	60	22.15	43.82	9.71	4.13	10.48	3.81	7.99	8.37
		30.50		13.37	5.68	14.43	3.43	7.18	10.4
		36.67		16.07	6.83	17.35	3.30	6.91	12.0
		38.38		16.82	7.15	18.16	3.23	6.77	12.3
1.318	80	24.35	40.29	9.81	4.41	11.19	3.67	7.69	8.60
		32.62		13.14	5.90	14.99	3.44	7.21	10.8
		35.21		14.19	6.37	16.18	3.28	6.88	11.1
		45.96		18.52	8.32	21.12	3.03	6.34	13.4
		48.97		19.73	8.86	22.50	2.92	6.11	13.8
1.356	100	25.28	37.38	9.42	4.45	11.29	3.47	7.26	8.19
		35.71		13.31	6.28	15.95	3.12	6.54	10.4
		40.73		15.18	7.16	18.19	3.11	6.52	11.9
		43.10		16.07	7.58	19.25	3.08	6.45	12.4
		46.24		17.24	8.13	20.65	2.95	6.17	12.7
		48.05		17.91	8.45	21.46	2.85	5.97	12.8
		51.21		19.09	9.01	22.87	2.79	5.85	13.4

[a] Percent (w/w) of polymer. [b] Rate of moisture transport = slope of the line in milligrams per hour. ᶜ Water vapor transmission rate = grams per (hour × square centimeters area × millimeters mercury). Table values are multiplied by 10⁻⁵ to produce experimental values.

mined and may be given by (7):

$$P_{erm} = R_{wvt}t \qquad \text{(Eq. 2)}$$

where P is the permeability constant, and R_{wvt} and t are as previously defined. The units for the permeability constant are (grams × centimeters) per (square centimeters × hours × millimeters mercury). The permeability constant should be independent of thickness in films that exhibit Fickian diffusion.

Determination of Percent Polymer Free Films—Knowledge of the weight content of each component in each film formulation permitted calculation of the percent polymer by weight contained in each formulation:

hydroxypropyl methylcellulose	4.500
ethylcellulose	1.500
propylene glycol	3.108 (3.0 ml)
surfactant	0.984 (0.9 ml)
	10.092

$$\text{percent polymer} = \frac{6.000}{10.092 + \text{additive}} \times 100 \qquad \text{(Eq. 3)}$$

Determination of Weight of Polymer Exposed for Water Vapor Transmission Studies—As previously described, the densities of the films were determined. By using the density–volume relationship and knowing the density, area, and thickness of each film formulation, it was possible to calculate the weight of each film disk subjected to water vapor determination. By knowing the weight of this film disk and the percent by weight of polymer it

contained, it was thus possible to calculate the weight of polymer exposed to water vapor transmission in the film disk volume.

RESULTS AND DISCUSSION

Evaluation and Selection of Film Formulations and Film-Casting Techniques—The selection of a film-forming technique for uniform films is of paramount importance in research where film thickness must be accurately determined and controlled. The importance of this aspect of the research is compounded when the film is not homogeneous in nature but is actually a suspension of insoluble additives in the film-forming agent, such as the conspergents in Table I suspended in the cellulose combination studied.

The water-insoluble additive must be uniformly dispersed throughout the dried film to prevent concentrated areas of unequal strength or weakness and to provide a film specimen that will yield reproducible results over a given area. The method of film casting considered most acceptable for this work was to disperse the conspergent (Table I) in the solvent system. This produced complete dispersion of the conspergent unhampered by high viscosity which resulted after the suspending cellulosic suspending agents were added.

Several methods were evaluated for the production of free films, and the results indicated that a glass substrate previously coated with a releasing agent produced the most suitable films for this research. The release agent enhanced the smoothness of the glass substrate in addition to facilitating removal of the dried films from the substrate with minimal stress imparted to the films. The release agent was applied in such a diluted concentration, 2%, that negligible quantities of the agent were deposited on

Table IV—Water Vapor Transmission Data for Titanium Dioxide Films

Film Density, g/cm³	Additive[a], %	Weight of Exposed Film, mg	Polymer, %	Weight of Polymer Exposed, mg	Film Thickness mils	Film Thickness cm × 10⁻³	Rate of Moisture Transport, mg/hr[b]	R_{wvt}, × 10⁻⁵c	Permeability Coefficient, × 10⁻⁷
1.166	0	13.63	59.45	8.10	2.79	7.08	6.37	13.3	9.44
		15.69		9.33	3.20	8.15	6.00	12.6	10.2
		17.91		10.65	3.66	9.30	5.66	11.8	11.0
		20.26		12.04	4.14	10.52	5.27	11.0	11.6
		22.38		13.30	4.58	11.62	5.22	10.9	12.7
1.211	10	18.69	56.12	10.49	3.68	9.35	5.58	11.7	10.9
		21.55		12.09	4.25	10.78	5.16	10.8	11.6
		25.65		14.39	5.05	12.83	5.13	10.7	13.8
		33.84		18.99	6.67	16.93	4.78	10.0	17.0
1.255	20	18.05	53.13	9.59	3.43	8.71	4.83	10.1	8.81
		21.74		11.55	4.13	10.49	4.63	9.69	10.2
		23.38		12.42	4.44	11.28	4.58	9.60	10.8
		33.26		17.67	6.32	16.05	4.06	8.49	13.6
		36.53		19.41	6.94	17.63	3.74	7.84	13.8
1.433	60	23.00	43.82	10.08	3.83	9.72	5.47	11.5	11.1
		26.80		11.74	4.46	11.33	5.29	10.9	12.4
		47.29		20.72	7.87	19.99	4.62	9.67	19.3
		49.45		21.67	8.23	20.90	4.60	9.63	20.1
1.521	80	31.38	40.29	12.64	4.92	12.49	5.63	11.8	14.7
		49.51		19.95	7.76	19.71	5.23	11.0	21.6
		65.81		22.08	8.59	21.82	5.01	10.5	22.9
		64.64		26.04	10.13	25.73	4.99	10.4	26.9
		67.12		27.04	10.52	26.72	4.82	10.1	26.9
1.610	100	27.39	37.28	10.21	3.95	10.03	5.87	12.3	12.3
		41.13		15.33	6.09	15.47	5.33	11.2	17.3
		42.54		15.86	6.30	16.00	5.11	10.7	17.1
		50.04		15.65	7.41	18.82	5.12	10.7	20.2
		67.77		25.26	10.04	25.49	4.47	9.36	23.8

[a] Percent (w/w) of polymer. [b] Rate of moisture transport = slope of the line in milligrams per hour. [c] Water vapor transmission rate = grams per (hour × square centimeters area × millimeters mercury). Table values are multiplied by 10⁻⁵ to produce experimental values.

the film surface. Furthermore, since the release agent was baked onto the surface of the substrate at 250° for 2 hr, the probability of its transference was reduced.

In contrast with the technique of peeling the dried film from an aluminum substrate or uncoated glass substrate (7, 11), the dried films were lifted from the silicone-coated glass substrate virtually free of adhesion. This low order of adhesion and ease of film removal from the substrate were of great importance relative to maintaining the integrity of the film and preventing prestressing or distortion.

Determination of Free Film Densities—The densities of the films were determined for all film formulations (Tables II–IV). Figure 1 illustrates the linear relationship observed between film density and percent additive for the 0, 20, 60, and 100% additive formulations, and Table V shows the statistical constants determined for the relationship between film density and percent additive (w/w) with respect to polymer weight. The film densities for
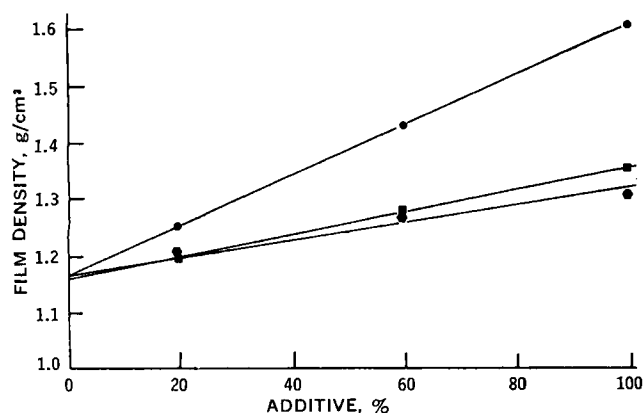
the 40 and 80% additive formulations were calculated from the established relationship between film density and percent additive for each additive material as described in the *Experimental* section. An average of five or more thickness determinations of each film specimen was made for each experimental density determined ±0.00001 in.

As seen in Fig. 2, the order of particle size decreases from Italian talc to talc USP to titanium dioxide. The median particle size for these additives was given in Table I. Figure 1 shows a linear increase in film density with decreasing additive particle size for all three insoluble film additives studied. This effect would be ex-
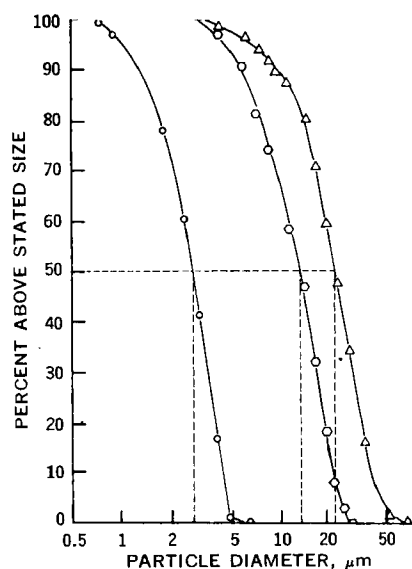

Figure 1—*Density of free films as a function of percent additive (w/w) with respect to polymer. Key: ●, titanium dioxide; ■, talc USP; and ◐, Italian talc.*

Figure 2—*Coulter counter particle-size analysis. Key: ○, titanium dioxide; △, Italian talc; and ⊘, talc USP.*

Table V—Statistical Constants for the Relationship between Film Density and Percent Additive (w/w) with Respect to Polymer

Additive	Correlation Coefficient, r	Slope of the Line, $m \times 10^{-3}$	Y Intercept
Italian talc	0.96	1.395	1.176
Talc USP	0.98	1.912	1.165
Titanium dioxide	0.99	4.440	1.166

Figure 4—*Relationship between rate of moisture transport and film thickness for 10% Italian talc free films.*

pected based on the closer packing of the particles as the particle size decreases. However, it is also noted that the film density difference between the two talcs was not great. Although the median particle-size difference was substantial, the talc particle distributions overlapped each other. On the other hand, the film density of the titanium dioxide films was substantially greater than either of the talc films at any solids-loading value. The change in density with a change in solids-loading was greatest with the titanium dioxide films.

The amount of the moisture transmitted through all of the films was found to be directly proportional with time over 72 hr and was also related to the film thickness and composition. Figure 3 shows the relationship between time and milligrams of water vapor transmitted for free films containing 10% Italian talc (w/w) with respect to polymer. A similar relationship was observed for all film formulations that contained conspergents found in Table I.

It was determined (Fig. 4) that the rate of water vapor transmission across the film membranes for the solids-loaded films, in milligrams per hour, was directly related to film thickness in the thickness range studied. Statistical analysis showed the correlation coefficients for standard films (no conspergent) and conspergent films to be 0.98 or better, with two formulations showing a correlation coefficient of 0.92 and 0.93.

As seen in Tables II–IV, the rate of water vapor transmission, in grams per (hours × square centimeters × millimeters mercury), hereafter referred to as R_{wvt}, was determined for each formulation studied. Figures 5–7 show the relationship between this R_{wvt} and the weight (milligrams) of polymer exposed in the film disk (see *Experimental*). Since the films studied were two-component systems of homogeneous polymer–plasticizer dispersed with varying concentrations of heterogeneous conspergent additive, film thickness did not necessarily reflect the amount of polymer in the cross section of a standard area film disk.

As seen in Fig. 4, the rate of moisture transport decreased with increasing film thickness. Figure 5 illustrates the decrease in the R_{wvt}, which was consistently observed as the weight of polymer exposed in the Italian talc films increased (film thickness was increased and/or conspergent concentration was decreased). Figure 5 also demonstrates that the change in rate of moisture transport
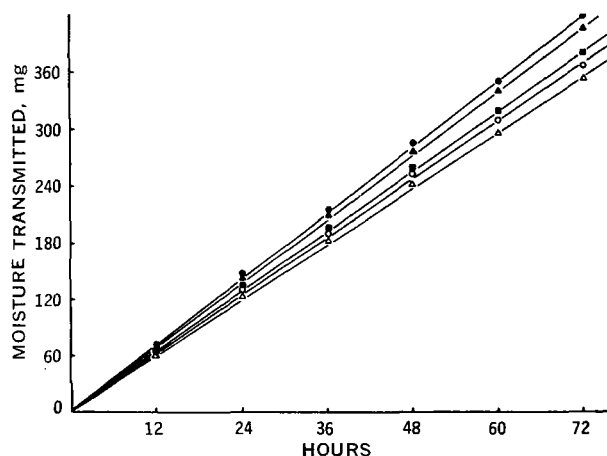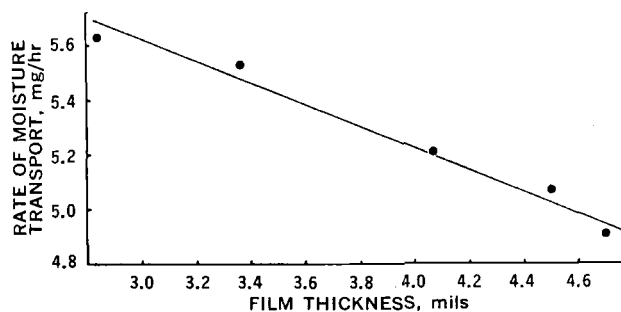
can indeed be meaningfully expressed as a function of the amount of polymer in the film.

A consistent decrease in the R_{wvt} as a function of increasing Italian talc additive concentration was observed, at any mass of polymer exposed (Fig. 5), with the exception of the 80% formulation. The 0 and 10% additive formulations showed a much more marked decrease in R_{wvt} with an increase in weight of polymer exposed in comparison to the 20, 40, 60, and 100% additive formulations, which approached a plateau in rate of change of decreasing R_{wvt} with an increase in weight of polymer exposed. The 20, 40, 60, and 100% additive curves were displaced to lower values (Fig. 5), an indication of a decreasing transmission level with an increase in additive concentration at any weight of polymer in the film cross section.

Thus, the films containing 0 and 10% Italian talc additive with increasing film thickness or increasing polymer weight in the cross section produced substantial decreases in rate of water vapor transmission, whereas increasing film thickness or mass of polymer in the cross section of the films containing 20% and more additive did not produce an equally substantial decrease in R_{wvt}. Increasing dispersed additive concentration in the film structure rather consistently reduced the water vapor transmission rate, due probably to the increased hydrophobicity of the film. However, possibly due to the reduced integrity of the films containing 20% or more additive, increasing film thickness did not substantially increase protection to water vapor transmission.

In a similar manner, Fig. 6 shows a consistent decrease in R_{wvt} as a function of increasing talc USP additive concentration and as a function of increasing weight of polymer in the film disk exposed to moisture transport. A plateau in rate of change of decreasing R_{wvt} was reached at the 60, 80, and 100% additive formulations (Fig. 6).

Figure 7 illustrates the rate of change of R_{wvt} with increasing amounts of polymer exposed for titanium dioxide films. A different phenomenon is observed here. As with the two mineral talcs, the R_{wvt} decreased with increasing weight of polymer exposed, but the relationship between decrease in rate of R_{wvt} and percent additive was different. The R_{wvt} decreased as it did in the talc formulations until it reached the 20% additive formulation, at which concentration the decrease of R_{wvt} appeared to have reached its maximum. The 60% additive formulation showed a rate of decrease of R_{wvt} similar to that of the 10% additive formu-

Figure 3—*Water vapor transmission as a function of time for 10% Italian talc free films. Key [film thickness (mils)]: ●, 2.91; ▲, 3.29; ■, 3.87; ○, 4.27; and △, 4.52.*
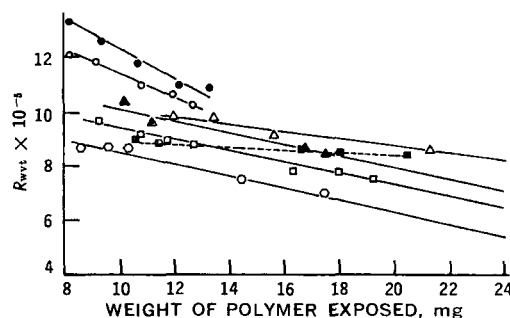

Figure 5—*Rate of water vapor transmission as a function of weight of polymer exposed for Italian talc free films. Key (percent additive): ●, 0; ○, 10; △, 20; ▲, 40; □, 60; ■, 80; and ○, 100.*
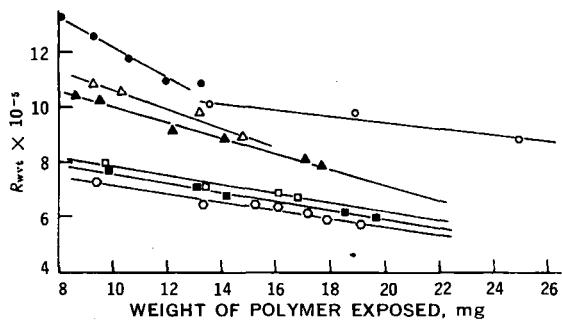
Figure 6—*Rate of water vapor transmission as a function of weight of polymer exposed for talc USP free films. Key (percent additive):* ●, 0; ○, 10; △, 20; ▲, 40; □, 60; ■, 80; and ⊘, 100.

Figure 8—*Permeability coefficient as a function of weight of polymer exposed for Italian talc free films. Key (percent additive):* ●, 0; ○, 10; ⊘, 20; ■, 40; □, 60; △, 80; and ▲, 100.

lation, and the 80 and 100% additive formulations showed an even greater R_{wvt} than the lower titanium dioxide concentrations in the thickness range studied.

The difference in change of R_{wvt} and percent additive between pigment films containing titanium dioxide and additive films such as those containing mineral talcs in film formulations may be due to the striking difference in the conspergent surface characteristics, the surface of the talc particles being more complex and having a variation of chemical groups in its molecules (12). The elemental contents of talcs vary greatly among themselves according to their sources and, therefore, give rise to a more varied and complex surface than that shown by titanium dioxide. The surface differences, in addition to particle-size effects, could affect the cohesive forces within the film, film structure, and the influence imparted by an additive to the permeability properties of films.

Obviously, numerous factors affect the water permeability through conspergent loaded films, such as particle packing, particle distribution, film microstructure, and overall film hydrophilicity/hydrophobicity. Interaction between these variables could also be expected. Accordingly, it is not possible to predict the effect of solids-loading on the permeability properties of films comprised of different conspergent materials.

Figures 8–10 show the relationship between the permeability coefficient and weight of polymer exposed for the three conspergent systems. Figure 8 shows a linear increase in the permeability coefficient as the amount of polymer in the film cross section exposed to moisture transport increases and suggests that the permeability coefficient is independent of percent additive in the formulations for Italian talc and predominantly dependent on the weight of polymer exposed, with the coarsest additive's 80% formulation again being the only exception.

Figure 9 also shows a linear increase with a positive slope for this relationship, but the permeability coefficient also appears to be a function of the additive concentration for talc USP film formulations. No systematic relationship between solids-loading and permeability was noted for the titanium dioxide films (Fig. 10). An apparent permeability minimum was reached at 20% loading, after which permeability increased. This finding could be explained by the Chatfield (13) theory, which states that pigmenta-
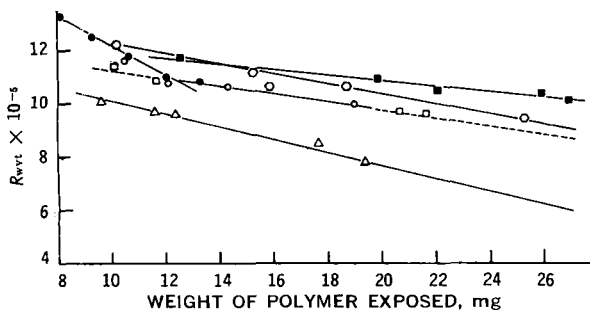
tion decreases the moisture permeability of films until the critical pigment volume is reached. In Fig. 10, this critical pigment volume appears to be approximately 20%, above which concentration permeability increases. The presence of pigment particles in the film lengthens the path through which the moisture passes and is equivalent to a thicker unpigmented film. Above the critical pigment volume concentration, there is insufficient film-producing medium in the film structure to bind the pigment particles together so there are pores in the film through which the moisture passes.

In this study, the relationship between permeability and film thickness for the three conspergents studied clearly indicated a linear correlation existed between these properties. No statistically significant differences were found between the mineral talcs, but the titanium dioxide containing films showed a trend away from Fickian behavior at higher solids-loading. This again supports Chatfield's (13) theory in that pigment particles in the film above the critical pigment concentration give rise to pores in the film due to insufficient binding.

SUMMARY AND CONCLUSIONS

The nature of the dispersed film additive, its particle size, its surface characteristics, and the concentration of insoluble additives must be considered in evaluating the water vapor transmission properties of free polymeric films containing dispersed solids.

When analyzing the moisture permeation properties of free films containing dispersed solids, it was noted that film thickness was not a standard variable, since films of the same thickness containing the same volumes of different dispersed solids or different percentages of the same dispersed solid vary in the percentage or weight of polymer in any standard cross section of free

Figure 7—*Rate of water vapor transmission as a function of weight of polymer exposed for titanium dioxide free films. Key (percent additive):* ●, 0; ○, 10; △, 20; □, 60; ■, 80, and ⊘, 100.
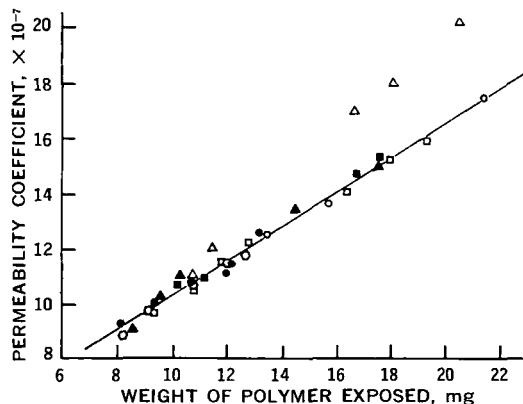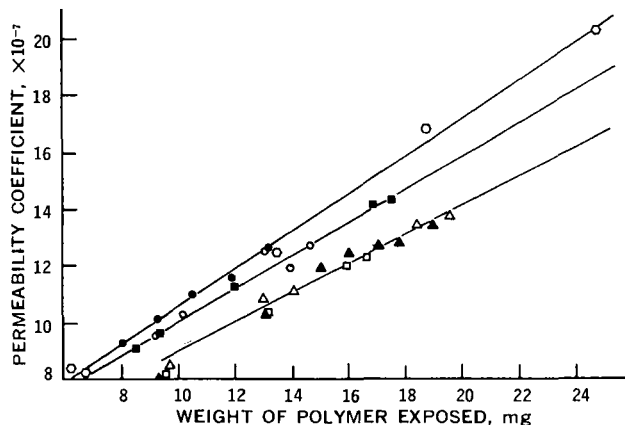

Figure 9—*Permeability coefficient as a function of weight of polymer exposed for talc USP free films. Key (percent additive):* ●, 0; ○, 10; ⊘, 20; ■, 40; □, 60; △, 80; and ▲, 100.
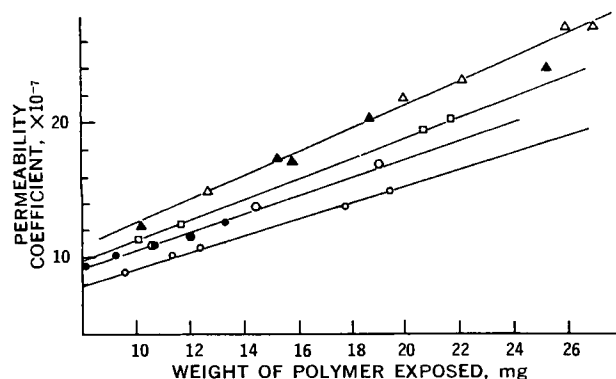
Figure 10—*Permeability coefficient as a function of titanium dioxide content (w/w with respect to polymer) in free films. Key (percent additive):* ●, *0;* ○, *10;* ○, *20;* □, *60;* △, *80; and* ▲, *100.*

film. A meaningful way of analyzing moisture permeation of free films containing dispersed solids has been suggested in which the permeability coefficient, which incorporates film thickness, is related to the mass of polymer in the film cross section analyzed. This type of analysis permits the comparison of permeability and water vapor transmission behavior of films containing different dispersed solids. In one talc-containing film system, no significant change in permeability was observed with a change in weight of polymer contained in the cross-sectional area of the films at different solids-loading stages; in another talc system, there was an effect on the permeability coefficient with a change in this variable. Titanium dioxide film systems appeared to exert a different effect on permeability properties, as predicted by Chatfield's (13) theory.

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