Swelling of Paint Films in Water
X. Rate of Penetration of Water, Permeability to Water Vapor, and Penetrability to Air in Relation to Water Absorption

F. L. BROWNE

Chemist, Forest Products Laboratory,[1] Forest Service, U. S. Department of Agriculture

Differing theories exist on resistance of house paints to blistering. Tests were made to measure the permeability to water and water vapor and the ability to breathe of some paints for which water absorption and swelling had already been determined. Factors are discussed which apparently affect the speed of penetration into various coatings.

PREVIOUS ARTICLES in this series (5)[2] reported the extent to which free and bound films of various paints and paint vehicles absorb water and swell when soaked in water. The data suggest strongly that the absorption and swelling of paints in water may be closely related to their tendency to blister and peel under practical conditions of service on houses. Those house paints that are known from actual experience to blister easily are also high in absorption and swelling, whereas those paints similarly known to be relatively resistant to blistering and peeling are also low in absorption and swelling.

Other workers have observed a relation between water absorption and blistering of coatings (30, 35), both on wood (8, 19) and on metal (1, 17, 20, 23, 27, 28). To compare water absorption with tendency to blister, there is need for more quantitative data on blistering pressure (18) or other direct measure of blistering.

American technologists often emphasize another property of coatings, their permeability to water vapor, as a measure of sensitiveness to moisture blistering. As far back as 1934, Gardner (12) suggested that readily permeable paints would resist blistering, and proposed to make permeable paints by incorporating porous pigments such as diatomaceous silica. It was thought that such paints "breathe" sufficiently to let water escape from the painted surface of wood faster than it can penetrate through boards from behind (4, 8, 15, 31). So-called "breather-type" paints have been sold commercially, but examination of some of them has failed to confirm that they have greater permeability than do ordinary paints. They did prove more resistant to blistering and lower in absorption and swelling than most ordinary paints, however, but paints may be highly resistant to blistering and yet low in permeability (34). It remains to be determined whether extremely high permeability affords reliable protection against blistering.

The differing theories on resistance to blistering made it desirable to measure the permeability and ability to breathe of some of the paints for which the absorption of water and swelling had already been determined. It was of interest to learn: 1) how long it takes for water in contact with the exposed surface of high- and low-swelling coatings to penetrate to the interface with the substrate, 2) the relative permeability of free films to water vapor, and 3) the penetrability of free films by dry air under a moderate difference in pressure.

The composition of the paints used in these tests was reported in papers VI and VII of the series (5).

Time Required for Water to Penetrate

Glass microscope slides 1½ by 3 inches in size were marked with crossed stripes of an aqueous solution of cobalt chloride containing a very small proportion of methyl cellulose. The markings, ⅜ inch wide, were blue in color when dry, and turned pink when exposed for a few minutes to air with a relative humidity of 65 per cent or more. They returned promptly to the original blue color when brought back to air with a relative humidity of 30 per cent or less. The weight of the markings was determined by weighing the slides before and after the solution was applied. To determine the density of the marking material, dried coatings on glass were scraped off with a razor blade and measured by the pycnometric method in kerosene. The thickness of the markings, calculated from the weight, area, and density, was 0.11 to 0.17 mil.

The marked slides were coated with paint at the desired thickness with doctor blade, suction plate, and suitable shims. Five single-pigment, raw linseed oil paints of pigment volume 0.30, pigmented with basic carbonate white lead, antimony oxide, titanium dioxide, zinc oxide, and magnesium silicate, respectively, were tested. The first two pigments make low-swelling paints, the fourth makes high-swelling paint, and the others make paints of intermediate swelling. For each paint, slides were prepared with coatings that were approximately 2 mils, 4 mils, and 6 mils thick when dry.

One complete set of specimens was tested for water penetration when the paint coatings were 8 days old. A second complete set was exposed for 15 days to ultraviolet light in a weatherometer, but without spraying with water. (It was found that water turned the cobalt chloride markings pink within one to two days, and the coatings became blistered over the markings soon afterward.)

To observe the rate of penetration of water, the test specimens were placed with the painted face down on glass rods that rested on the bottom of a shallow dish, and the dish was filled with water until about ½ inch of water covered the specimens. The blue markings were then readily visible through the water and glass against the white background of the paints. The lapse of time was observed between submergence and the first appearance of change from blue to pink color, between submergence and complete change from blue to pink, and between submergence and blistering of the coatings. Blistering could be detected without lifting the specimens out of the water because formation of a blister allowed the dissolved cobalt chloride to gather in a rounded droplet of solution that was easily recognized

[1] Maintained at Madison, Wis., in cooperation with the University of Wisconsin.
[2] Numbers in parentheses refer to Literature Cited.

The Author: F. L. Browne received B. Chem. degree from Cornell U., Ph. D. in colloid chemistry from U. of Wisconsin. He joined the Forest Products Lab staff in 1918, helped develop casein glues for wood airplanes of World War I. In 1921–22 he was a National Research Fellow at Wisconsin. Since 1929 Dr. Browne has edited the General and Physical Chemistry Section of Chemical Abstracts.

Table 1.—TIME REQUIRED FOR WATER TO PENETRATE COATINGS OF LINSEED OIL PAINTS ON GLASS WHEN IMMERSED IN WATER

Composition of paint (pigment in linseed oil at pigment volume 0.30)	Coatings not weathered					Coatings weathered in artificial sunlight				
	Thickness of coating	Time required for first penetration	Time required for complete penetration	Time required for blistering	Water absorbed by free film in 3 days[1]	Thickness of coating	Time required for first penetration	Time required for complete penetration	Time required for blistering	Water absorbed by free film in 3 days[1]
	Mils	Hr.	Hr.	Hr.	Percent by volume	Mils	Hr.	Hr.	Hr.	Percent by volume
Basic carbonate white lead	2.3	11	29	32	8.9	1.3	7	24	24	9.9
	3.8	13	29	29		3.8	7	35	29	
	6.9	13	48	37		6.6	7	35	35	
Antimony oxide	2.1	7	24	13	5.3	1.3	2	3	2	2.5
	3.6	10	24	13		3.1	2	12	5	
	7.3	13	31	24		6.4	3	24	18	
Rutile titanium dioxide	1.9	2	9	6	26.5	1.3	1/8	3	2	8.3
	3.5	7	13	11		2.9	2	8	5	
	6.9	11	24	13		6.4	3	24	18	
Zinc oxide	1.6	3	9	7	83.3	1.4	2	12	5	28.2
	4.1	3	24	24		3.7	2	24	24	
	7.0	3	24	24		6.1	3	12	35	
Magnesium silicate	1.6	2	9	6	56.2	1.4	2	3	3	9.9
	3.8	7	24	24		3.3	2	5	12	
	6.4	10	24	24		6.3	3	12	24	

[1] Data from Browne, paper VI (5)

by the variation in intensity of color fom center to edge of the droplet.

Results of the tests of time of penetration are reported in Table 1.

Water penetrated some portions of a paint coating much more rapidly than others. For example, with the unweathered coating of titanium dioxide paint 1.9 mils thick, pink spots strongly contrasting wth the rest of the blue stripes could be seen within two hours. The spots slowly increased in size and number. After six hours, about half the total area of the stripes were pink, the other half still blue. Nine hours elapsed before the last of the blue color changed to pink. All other coatings exhibited a similar course of events, although differing in time scale, with an initial appearance of pink in spots that grew slowly in size and number until all blue changed to pink. Essentially the same behavior has recently been reported by Pragst (26), who allowed an aqueous solution of methylene blue to diffuse through coatings of paint on glass.

Although more time was required for water to penetrate the thicker coatings of paint, the time was not always proportional to thickness. Thus with the unweathered coating of white lead paint 2.3 mils thick, first penetration was observed in 11 hours, and the coating 3 times as thick, 6.9 mils, was penetrated in 13 hours. Unweathered coatings of zinc oxide paint 1.8, 4.1, and 7.0 mils thick were all penetrated first in three hours. On the other hand, first penetration of coatings of antimony oxide, titanium dioxide, and magnesium silicate paints was always delayed by increased thickness at least as much as proportionality would indicate. With weathered coatings of all paints, first penetration usually occurred sooner than with corresponding unweathered coatings, and increased thickness delayed first penetration relatively little.

The relatively short time sometimes required for first penetration, and the lapse of time between first penetration and complete penetration, together with the variable relation between coating thickness and time of penetration, suggest that paint coatings have an exceedingly heterogeneous internal structure that is more readily penetrated in some places than in others (21, 29). Bell's (2) discussion of the structure of paint films, particularly his photographs of the formation of Benard cells and electron photomicrograph of a cross section of a paint film, furnish adequate explanation of the observed irregularity of penetration.

James (16) measured the time required for water to penetrate coatings of red iron oxide paints and the clear vehicles with which they were made by an electrical method. Most of his coatings were 1.6 mils thick, thinner than any of the unweathered coatings reported in this paper. Coatings of linseed-tung oil vehicle with or without pigments apparently were penetrated almost immediately, but their water content continued to increase for several days. Coatings of clear and of pigmented phenolic-resin varnish, linseed-rosin-epoxide resin, and linseed-pentaerythritol alkyd vehicle were penetrated in 15 to 90 minutes, but continued to gain water for several days.

As reported in Table 1, unweathered coatings of white lead and of antimony oxide paints, which are low in water absorption, always required a longer time for first penetration and nearly always took longer for complete penetration than coatings of similar thickness of the high-absorbing titanium dioxide, zinc oxide, and magnesium silicate paints. Among the weathered coatings, white lead paint remained slowest to permit either first or complete penetration, but antimony oxide paint, despite its low absorption, was penetrated about as rapidly as any of the other paints. For unweathered coatings, high absorption seems to hasten penetration, although the two are by no means exactly parallel. For weathered coatings, other factors appear to be more important than water absorption in determining speed of penetration.

Blisters usually appeared in the coatings over the stripes of cobalt chloride either somewhat before or at least soon after penetration was complete. It was difficult to tell when blistering began in the thicker weathered coatings of zinc oxide and magnesium silicate paints, because the coatings were too hard to yield readily in blisters, and the blisters, when they became observable, were relatively large and only gently curved. There was seldom any observable blistering where no stripes of water-soluble material were interposed between coating and glass. The pressure responsible for blistering arose therefore from osmosis (17). Adhesion may have been as badly impaired by penetration of water around as over the water-soluble stripes, but sufficient pressure to overcome the mechanical resistance of the film to flexing may have been lacking where there was no soluble material to give rise to osmosis.

Permeability to Water Vapor

The permeability of free paint films to water vapor was measured by the Payne cup method (22, 25). Distilled water was placed in the cup, and the paint film to be observed was clamped in position. The cup was then placed in a desiccator over calcium chloride in a room held constantly at 70° F., and the cup was weighed daily to

determine the loss of water through the paint film. Steady state conditions were reached within one day. The rate of loss during the second and third days, which was nearly constant, was taken as a measure of the permeability of the film. The permeability is expressed as the number of milligrams of moisture vapor lost per square centimeter of film area per day for a film 1 millimeter thick, which is known as the specific permeability, P_s. The relation is

$$P_s = \frac{ml}{qt}$$

in which m is the weight of water lost in milligrams, q is the area of film exposed in square centimeters, l is the thickness of the film in millimeters, and t is the time in days. The calculation assumes that permeability is inversely proportional to film thickness. The assumption is not always correct (7, 29), but the error is not serious for the comparatively small variation in thickness of the films used for the study.

Each film was weighed immediately before and again immediately after the permeability test. The film was then dried in a desiccator over calcium chloride and weighed once more. The difference between the second and third weighings was recorded as the moisture held by the film at the end of the test period. The difference between the first and third weighings was recorded as the change in weight (usually negative) of the moisture-free film during test.

The results with oil and oleoresinous films are recorded in Table 2, in which the films are arranged in order of decreasing absorption of water by the unweathered films when soaked for three days, as reported in prior papers (5). The films are separated into four groups according to the absorption of water by the unweathered films. These groups are: above 49, between 20 and 49, between 10 and 20, or below 10 per cent of water by volume. Results with latex films are similarly recorded in Table 3.

The results show that the permeability of paint films to water vapor is not primarily related to their water absorption. Among the unweathered pigmented oil and oleoresinous films, there was 100-fold variation in water absorption (0.8 to 86.4), but only 9-fold variation in specific permeability (0.06 to 0.54). For the group with absorption greater than 49 per cent (average 73.9), the permeability ranged from 0.15 to 0.30, and averaged 0.23. For the group with absorption less than 10 per cent, the permeability ranged from 0.06 to 0.33, and averaged 0.16. The next to the lowest permeability, 0.07, and the highest permeability, 0.54, occurred in the same group.

Although weathering usually decreased both water absorption and per-

Table 2.—SPECIFIC PERMEABILITY TO WATER VAPOR (AT 70° F.) OF FREE FILMS OF OIL AND OLEORESINOUS PAINTS, TABULATED IN ORDER OF DECREASING ABSORPTION OF WATER DURING 3-DAY SOAKING

Unweathered films						Composition of film		Weathered films				
Water absorbed on soaking for 3 days A/V_0	Prior paper of this series from which data for A/V_0 were taken (5)	Specific permeability: P_s	Moisture absorbed during test	Change in weight of dry film during test	Thickness of film	Pigment	Vehicle	Water absorbed: on soaking for 3 days A/V_0	Specific permeability: P_s	Moisture absorbed during test	Change in weight of dry film during test	Thickness of film
Percent by volume		Mg. per sq. cm. per day	Gm. per 100 cc.	Gm. per 100 cc.	Mil			Percent by volume	Mg. per sq. cm. per day	Gm. per 100 cc.	Gm. per 100 cc.	Mil
GROUP WITH A/V_0 MORE THAN 49 PERCENT												
86.4	VI	0.17	2.9	-0.3	3.3	Titanium-zinc, Ti_{85}	alkyd	20.2	0.11	1.3	-0.5	3.0
85.3	II	.30	7.3	-1.4	6.1	Zinc oxide	H_2O (36° F.)	28.0	.24	1.7	-.7	3.6
83.3	VI	.35	6.0	-.2	3.8	Zinc oxide	H_2O	28.2	.31	2.2	+.1	3.7
73.5	VI	.15	3.6	-.5	2.9	Lead-zinc, Pb_{85}	alkyd	20.3	.08	1.3	-.7	3.0
69.2	VI	.27	1.0	-.1	4.3	Antimony-zinc, Sb_{25}	alkyd	20.2	.12	1.1	-1.0	2.8
62.5	VIII	.25	6.8	-1.5	4.1	Titanium-zinc, Ti_{75}	H_2O					
61.8	VI	.19	1.8	-.4	2.9	Zinc oxide	alkyd	17.8	.10	.7	-.1	2.9
[1](56.2)	VI					Magnesium silicate	H_2O	9.9	.34	.9	0	3.1
Average 73.9		.23	4.2	-.6	3.7			20.7	.19	1.3	-.4	3.2
GROUP WITH A/V_0 BETWEEN 20 AND 49 PERCENT												
40.3	VI	.23	1.1	-.6	3.0	Magnesium silicate	alkyd	12.1	.20	1.5	-.6	2.8
31.8	VI	.16	1.4	-1.9	4.2	Zinc oxide	H_2O	14.2	.16	.8	-.3	3.9
29.8	VIII	.17	10.6	-1.9	3.9	Lead-zinc, Pb_{85}	H_2O					
28.5	II	.34	1.1	-.2	4.1	Titanium dioxide	H_2O (36° F.)	5.3	.27	1.6	-.2	3.3
28.0	VI	.29	1.6	-.3	5.2	Magnesium silicate	H_2O	14.9	.33	1.3	-.7	4.5
26.5	II	.45	1.4	-1.2	3.9	Titanium dioxide	H_2O	8.3	.26	1.6	-.7	3.0
25.3	VI	.19	1.5	-1.2	4.8	Titanium-zinc, Ti_{85}	H_2O	16.2	.16	.9	-.7	4.5
23.2	II	.07	1.1	-1.5	2.8	Commercial "Breather-Type"	[3]					
22.8	VI	.18	.9	-.8	2.7	Titanium-antimony, Ti_{25}	alkyd	5.8	.16	1.1	-.3	3.0
[2](21.8)	VI	[2](1.39)	[2](1.8)	[2](-1.3)	[2](7.5)	No pigment	H_2O					
Average 26.2		.25	2.3	-1.0	3.8			10.8	.22	1.2	-.5	3.6
GROUP WITH A/V_0 BETWEEN 10 AND 20 PERCENT												
18.0	VI	.11	2.1	-.3	5.0	Antimony-zinc, Sb_{25}	H_2O	14.7	.15	.6	-.4	4.8
16.6	VI	.25	1.0	-.6	3.9	Titanium dioxide	alkyd	3.4	.11	.6	-.3	3.2
16.3	VI	.15	2.6	-.8	4.6	Lead-zinc, Pb_{85}	H_2O	15.7	.11	1.3	-.4	4.4
16.3[4]	(4)	.09	1.3	-.2	4.2	Commercial "Flatter-Resistant"	[5]	8.6	.15	1.2	0	4.1
15.3	VI	.21	.7	-.2	5.2	Magnesium silicate	Phen.	8.9	.15	.8	-.3	4.9
10.5	II	.14	.5	-.5	4.8	White lead	H_2O (36° F.)	5.4	.09	.8	-.4	3.6
10.3	II	.19	2.0	-3.8	3.8	Zinc oxide	H_2O (160° F.)	10.2	.15	1.1	-2.3	3.5
Average 14.8		.16	1.5	-.9	4.4			9.6	.13	.9	-.6	4.1
GROUP WITH A/V_0 LESS THAN 10 PERCENT												
9.8	VI	.14	.4	-.2	4.8	Zinc oxide	Phen.	5.3	.11	.4	+.3	4.2
9.7	VI	.10	.6	-.8	3.1	White lead	alkyd	4.2	.06	.8	-.6	3.0
[2](9.0)	VI	[2](.32)	[2](.5)	[2](0)	[2](4.4)	No pigment	H_2O					
8.9	VI	.14	.5	-.3	3.8	White lead	H_2O	9.9	.10	.7	+.3	3.8
[2](7.7)	VI	[2](.27)	[2](.7)	[2](-.6)	[2](3.9)	No pigment	alkyd	[2](5.8)	[2](.19)	[2](.6)	[2](-.4)	[2](4.9)
7.3	VI	.11	.5	-.1	4.8	Antimony-zinc, Sb_{25}	Phen.	4.2	.12	.7	-.6	4.5
6.8	VI	.86	1.2	-.9	5.4	Titanium dioxide	H_2O	3.9	.25	.7	+.1	4.3
6.4	VI	.16	.7	-.1	4.9	Titanium-zinc, Ti_{85}	Phen.	4.3	.13	.7	-.3	4.5
[2](5.3)	VI					Antimony oxide	H_2O	2.5	.24	1.0	+.4	2.5
4.5	VI	.11	.5	-.3	4.8	Lead-zinc, Pb_{85}	Phen.	5.4	.08	.5	-.3	4.6
3.4	II	.11	1.0	-.9	3.7	White lead	H_2O (160° F.)	5.3	.07	.9	-.3	3.5
3.1	II	.33	1.0	+.5	3.9	Titanium dioxide	H_2O (160° F.)	4.4	.34	1.5	0	3.6
3.1	VI	.10	.7	-.6	4.2	White lead	H_2O	4.8	.11	.8	-.3	3.9
2.5	VI	.16	.5	-.1	5.4	Titanium dioxide	Phen.	1.9	.12	.4	-.1	4.9
2.2	VI	.20	.7	-.3	3.8	Antimony oxide	alkyd	2.4	.12	1.0	+.6	2.8
1.8	VI	.06	.2	0	4.7	White lead	Phen.	1.5	.05	.5	-.1	4.4
[2](1.5)	VI	[2](.25)	[2](.6)	[2](-.3)	[2](4.0)	No pigment	Phen.	[2](1.5)	[2](.16)	[2](.8)	[2](-.2)	[2](3.4)
.9	VI	.12	.4	-.2	4.9	Antimony oxide	Phen.	.9	.11	.4	-.7	4.7
.8	VI	.27	.2	0	6.0	Antimony oxide	H_2O	1.5	.25	.4	-.2	4.7
Average 4.7		.16	.6	-.3	4.5			3.9	.14	.7	-.3	4.0

[1] "H_2O" means raw linseed oil; "H_2O" means bodied linseed oil; "alkyd" means long-oil alkyd-resin varnish; "phen." means phenolic-resin varnish. The pigment volume was 0.30 except in the commercial "breather-type" paint. All films were formed (dried) at approximately 75° F. except those marked "(36° F.)" or "(160° F.)".

[2] Values in parentheses were not included in computation of the average values for the group.

[3] A trade-brand paint made with titanium dioxide, mica, and magnesium silicate in a vehicle of tung-oil varnish and bodied linseed oil; pigment volume 0.39.

[4] Not previously reported.

[5] A trade-brand paint made with titanium dioxide and magnesium silicate in a "copolymer" vehicle; pigment volume 0.30.

meability, water absorption generally was decreased proportionately much more than permeability. Thus for the most absorptive group, weathering lessened the average absorption from 73.9 to 20.7 per cent, whereas it only lessened the average permeability from 0.23 to 0.19. Among the unweathered pigmented latex films in Table 3, water absorption ranged from 7.0 to 75.9 per cent, well within the range for oil and oleoresinous paints, but permeability ranged from 1.44 to 6.45, far above the range of 0.06 to 0.54 for oil and oleoresinous paints. Weathering usually decreased the permeability of latex films proportionately much more than it did that of oil and oleoresinous films, but weathering was less effective in decreasing the absorption of latex than of oil or oleoresinous films. In fact, weathered latex films often absorbed more water after they were weathered than before. With some latex films, weathering increased water absorption while it decreased permeability.

All films absorbed moisture during the permeability test. The moisture absorption varied from 0.1 to 10.6 grams per 100 cubic centimeters of film. In general, those films that were high in water absorption in the soaking test were also relatively high in moisture absorption during the permeability test, although the parallelism between water absorption and moisture absorption was imperfect. Measurement of moisture absorption was purely incidental to the measurement of permeability. As a quantitative measure of moisture absorption, the method was crude and subject to much uncertainty because the films were exposed to damp air on one face and to dry air on the other face. Also, there was often a small but variable amount of condensed water on the damp face. More reliable measurements of the hygroscopicity of films of some oil paints were reported in paper II (5), from which it can be seen that the moisture absorbed during the permeability test was only a fraction of the absorption by similar films when both faces were exposed for three days to air at 97 per cent relative humidity. Thus a film of zinc oxide in linseed oil absorbed 15.8 grams of moisture per 100 cubic centimeters from air of 97 per cent relative humidity, but only 6.0 grams during the permeability test.

There was nearly always a slight change in the weight of the dry films during the permeability test. Among the unweathered films, 57 lost from 0.1 to 5.3 (only 4 of them over 1.9) grams per 100 cubic centimeters, 4 remained unchanged, and 1 gained 0.5 gram per 100 cubic centimeters. Among the weathered films, 43 lost from 0.1 to 2.3 grams per 100 cubic centimeters, 3 remained unchanged, and 11 gained from 0.1 to 0.6 gram per 100 cubic centimeters. Paint films, of course, generally lose weight steadily after they have passed the point of maximum weight soon after they have been formed. The small number of positive changes in weight observed may indicate that the downward course in weight may sometimes be interrupted by temporary additions of oxygen or combined moisture.

To study the characteristic effects of different pigments and of different vehicles on the specific permeability of films, parts of the data of Tables 2 and 3 were regrouped, certain aver-

Table 3.—SPECIFIC PERMEABILITY TO WATER VAPOR (AT 70° F.) OF FREE FILMS OF LATEX PAINTS, TABULATED IN ORDER OF DECREASING ABSORPTION OF WATER DURING 3-DAY SOAKING AS REPORTED IN PAPER VII OF THIS SERIES (5)

Unweathered films					Composition of film		Weathered films				
Water absorbed on soaking for 3 days: A/V_o	Specific permeability: P_s	Moisture absorbed during permeability test	Change in weight of dry film during test	Thickness of film	Pigment	Latex vehicle[1]	Water absorbed on soaking for 3 days: A/V_o	Specific permeability: P_s	Moisture absorbed during permeability test	Change in weight of dry film during test	Thickness of film
Percent by volume	Mg. mm. per cm.^{2} per day	Gm. per 100 cc.	Gm. per 100 cc.	Mil			Percent by volume	Mg. mm. per cm.^{2} per day	Gm. per 100 cc.	Gm. per 100 cc.	Mil
GROUP WITH A/V_o MORE THAN 49 PERCENT											
75.9	5.96	1.6	+0.8	3.4	Commercial, TiO_2, silicates	PVA[2]	12.5	1.34	0.8	-0.5	3.1
	3(1.49)	3(.6)	3(-.5)	3(3.1)	Commercial, TiO_2, silicates	PVA[2]					
3(57.9)	3(1.33)	3(1.2)	3(-.4)	3(3.9)	No pigment	acrylic	3(68.7)	3(1.34)	3(.4)	3(+.2)	3(3.4)
51.5	3.15	4.2	-.6	3.9	White lead	sty.-but. MC	15.0	1.12	2.9	-.9	3.6
50.5	6.03	.1	0	3.4	Zinc oxide	acrylic	42.5	5.40	.1	-1.5	2.5
49.7	5.49	.2	-.2	2.7	Zinc oxide	PVA	61.7	6.60	.3	-2.1	2.5
Average 56.9	5.16	1.5	-.4	3.3			32.9	3.61	1.0	-1.2	2.9
GROUP WITH A/V_o BETWEEN 20 AND 49 PERCENT											
30.2	2.42	1.1	-.1	4.8	Magnesium silicate	acrylic	119	.62	.4	+.1	4.3
27.7	3.05	2.8	-.4	4.4	Zinc oxide	sty.-but. MC	23.7	.94	.7	-.7	3.7
23.0	3.29	.7	-.9	4.8	Titanium dioxide	PVA	15.0	1.84	.2	+.2	4.2
22.7	1.44	1.8	-.4	4.9	White lead	acrylic	47.2	.53	1.5	-.1	4.6
20.6	3.80	1.7	-.2	3.8	Magnesium silicate	sty.-but. MC	8.1	.42	.6	+.4	3.5
20.4	4.57	1.2	-.1	5.2	Zinc oxide	sty.-but.	18.7	.25	3.6	-.9	4.8
Average 24.1	3.09	1.5	-.3	4.6			38.6	.77	1.2	-.2	4.2
GROUP WITH A/V_o BETWEEN 10 AND 20 PERCENT											
15.3	3.92	1.2	-.6	3.7	Titanium dioxide	sty.-but. MC	5.9	.13	1.9	-.7	3.6
13.3	6.45	.7	-1.5	5.8	Magnesium silicate	sty.-but.	10.6	.21	.9	+.2	4.2
11.9	6.08	2.0	-.2	7.3	White lead	sty.-but.	16.7	.05	5.4	-1.1	5.0
10.9	5.23	1.1	-.2	5.0	Titanium dioxide	sty.-but.	15.2	1.03	1.4	-.3	5.0
Average 12.8	5.42	1.2	-.6	5.4			12.1	.35	2.4	-.5	4.4
GROUP WITH A/V_o LESS THAN 10 PERCENT											
8.9	2.39	2.5	-2.5	4.4	Magnesium silicate	PVA	18.2	1.10	.4	+.4	4.0
3(8.7)	3(6.77)	3(6.9)	3(-5.3)	3(5.4)	No pigment	sty.-but	Styrene-butadiene films were destroyed by cracking during weathering				
3(8.2)	3(2.34)	3(1.0)	3(-2.1)	3(4.0)	No pigment	PVA	3(48.9)	3(1.33)	3(.7)	3(+.6)	3(3.5)
7.0	3.87	.7	-.2	4.7	Titanium dioxide	acrylic	6.5	1.61	.3	+.1	5.0
Average 7.9	3.13	1.6	-1.3	4.5			12.3	1.35	.3	+.2	4.5

[1] Trade brand latexes were used. "Acrylic" means a polyacrylic latex; "PVA" polyvinyl acetate; "sty.-but." a styrene-butadiene; "sty.-but. MC" a styrene-butadiene latex with addition of methyl cellulose.

[2] A trade-brand PVA latex paint.

[3] Values in parentheses were not included in computation of the average values for the group.

[4] The same trade-brand paint the unweathered film of which was leached in water and redried before testing. The absorption of water by the leached film was not measured quantitatively but was observed qualitatively to be much less than that of the unleached film.

age values computed, and the results recorded in Table 4. Thus in the first line of Table 4 are reported the average permeability and average water absorption of the four unweathered films and the four weathered films of the white lead paints made with the raw linseed oil, bodied linseed oil, alkyd-resin varnish, and phenolic-resin varnish vehicles. In the eighth line of Table 4 are reported the average permeability and average water absorption of five unweathered and five weathered films with phenolic-resin varnish pigmented with white lead, titanium dioxide, zinc oxide, lead-zinc, and titanium zinc.

In oil and oleoresinous vehicles, white lead and zinc oxide made films of lower specific permeability than corresponding films with antimony oxide, magnesium silicate, or titanium dioxide. White lead and zinc oxide are chemically basic and capable of reaction with free fatty acids or acid decomposition products in paint films, whereas the other pigments are unreactive in this sense. White lead made less permeable films than zinc oxide. The pigments had very different effects on water absorption. Thus white lead caused low absorption as well as low permeability, but zinc oxide caused highest absorption despite relatively low permeability. Antimony oxide, which produced lowest absorption, stood high in permeability.

In latex vehicles, pigments had relatively less effect on permeability than they did in oil and oleoresinous vehicles. White lead, magnesium silicate, and titanium dioxide stood in the same relative order, but zinc oxide was out of line in that it gave higher permeability than any other pigment in latex vehicles. In water absorption by latex films, white lead failed to take the low relative position it did among oil and oleoresinous films.

Among oil and oleoresinous vehicles, phenolic-resin varnish made the least permeable and raw linseed oil the most permeable paint films. Bodied linseed oil and alkyd-resin varnish made films of intermediate and about equal permeability. Phenolic-resin films were also lowest in water absorption, whereas bodied linseed oil was intermediate, and alkyd resin and raw linseed oil were relatively high. The unpigmented oil and oleoresinous vehicles (recorded in Table 2 but not in Table 4) made clear films that were more permeable than the pigmented films with the same vehicles, but in water absorption the clear films were intermediate among the pigmented films with the same vehicles.

Among latex vehicles, styrene-butadiene made pigmented films that, before weathering, were on the average more permeable but less absorptive of water than the pigmented films of the other latexes. The unweathered pigmented films with the other latexes did not differ significantly in either permeability or water absorption. Pigmented films of styrene-butadiene and of styrene-butadiene with methyl cellulose became much less permeable after they were weathered, so much so that they were little higher in permeability than some oil paints. On the other hand, weathering decreased the permeability of pigmented polyacrylate and polyvinyl acetate films only moderately, and they remained far more permeable than any oil paints. Weathering tended to increase the water absorption of the latex films except those made of styrene-butadiene with methyl cellulose, for which the absorption decreased after weathering.

Unpigmented films of polyacrylate and polyvinyl acetate were less permeable before weathering than any of the pigmented films of the same latex, and after weathering were less permeable than corresponding films pigmented with titanium dioxide or zinc oxide. Such behavior stands in strong contrast with that of the clear and pigmented films with oil and oleoresinous vehicles. The unpigmented film of styrene-butadiene was somewhat more permeable than any of its pigmented films, but the unpigmented film could not be tested after weathering because

Table 4.—SPECIFIC PERMEABILITY AND WATER ABSORPTION AS AFFECTED BY PIGMENT AND VEHICLE INGREDIENTS OF FILMS

Pigment or vehicle ingredient considered	Kind and number of vehicle or pigment ingredients averaged	Specific permeability, P_s		Water absorption, A/V_o	
		Unweathered films	Weathered films	Unweathered films	Weathered films
		Mg. mm. per cm^2 per day		Percent by volume	
Pigments:					
White lead, L	oil and oleoresinous (4)	0.10	0.08	5.9	5.1
Lead-zinc, LZ_{25}	oil and oleoresinous (4)	.14	.09	31.0	13.8
Zinc oxide, Z	oil and oleoresinous (4)	.18	.17	46.7	16.4
Titanium-zinc, TZ_{25}	oil and oleoresinous (4)	.19	.13	44.6	13.5
Antimony oxide, A	oil and oleoresinous (4)	.20	.18	2.3	1.8
Magnesium silicate, X	oil and oleoresinous (4)	.24	.25	34.9	11.4
Titanium dioxide, T	oil and oleoresinous (4)	.28	.18	13.1	4.4
Oil and oleoresinous vehicles					
Phenolic-resin varnish	L, T, Z, LZ_{25}, TZ_{25} (5)	.13	.10	5.0	3.7
Bodied linseed oil	L, T, Z, LZ_{25}, TZ_{25} (5)	.17	.16	16.3	10.9
Alkyd-resin varnish	L, T, Z, LZ_{25}, TZ_{25} (5)	.17	.12	49.6	13.2
Raw linseed oil	L, T, Z, LZ_{25}, TZ_{25} (5)	.25	.22	42.2	15.5
Pigments:					
White lead, L	latex vehicles (3)	3.56	.57	28.7	26.3
Magnesium silicate, X	latex vehicles (4)	3.76	.59	18.2	39.0
Titanium dioxide, T	latex vehicles (4)	4.08	1.15	14.0	10.6
Zinc oxide, Z	latex vehicles (4)	4.78	3.30	37.1	36.6
Latex vehicles:					
Polyacrylic resin	L, T, Z, X (4)	3.44	2.04	27.6	53.8
Styrene-butadiene and methyl cellulose	L, T, Z, X (4)	3.48	.65	28.8	13.2
Polyvinyl acetate	T, Z, X (3)	3.72	3.18	27.2	31.6
Styrene-butadiene	L, T, Z, X (4)	5.58	.39	14.1	15.3

it failed to remain intact. The high permeability of the latex vehicles when compared with oil and oleoresinous vehicles, together with the differences in relative permeability of unpigmented and pigmented films and the generally low swelling efficiency of latex paints, even before weathering, that was pointed out in paper VII (5), all suggest that the permeability of latex depends largely on a condition of porosity caused by failure of the droplets of emulsified polymers to coalesce to form a continuous matrix (9). This condition is absent in oil and oleoresinous films. It should be noted, however, that latex paints of low permeability comparable with oil paints are said to be obtainable by special formulation with suitable pigments (14).

Variation of Permeability with Temperature

Further information about the nature of the permeability of paint films was obtained by studying the effect of temperature on the permeability of films of 12 paints. The equation given previously for specific permeability, P_s, as customarily used by paint technologists applies at only one temperature, at which the vapor pressures on the two faces of the film differ always by the same amount. A more general relation for a permeability constant, P, is

$$P = \frac{ml}{qtp}$$

in which m is the mass of water vapor in grams that passes through a film of thickness l in centimeters and area q in square centimeters during time t in hours under a difference in vapor pressure of p in centimeters of mercury (6, 7, 11, 13, 24, 29, 32, 33). (Choice of units of measurement varies among the workers.) If the vapor pressure over calcium chloride is considered zero, p may be taken as the vapor pressure of water at the temperature of measurement, and then:

at 38° F., $P = 72.3 \times 10^{-7} P_s$
at 70° F., $P = 22.3 \times 10^{-7} P_s$
at 156° F., $P = 1.88 \times 10^{-7} P_s$

If the permeability constant is inversely proportional to the thickness of film and directly proportional to the difference in vapor pressure, the relation between permeability constant and temperature is

$$P = P_o e^{-E/RT}$$

in which P_o is the permeability constant independent of temperature, E is an activation energy, R is the gas constant, T is the absolute temperature, and e is the base of natural logarithms. The logarithm of P should then be proportional to $1/T$ (6, 7, 11, 24, 32).

Films of 12 paints and clear vehicles reported in Tables 2 and 3 were selected for measurement of permeability at different temperatures. The permeability of each film was determined first at 38° F., then at 70° F., and finally at 156° F. Specific permeability was converted to a permeability constant by the equations cited. The results appear in Fig. 1, in which P is plotted on a logarithmic scale against $1/T$.

The logarithm of the permeability constant was linearly related to $1/T$ for all films tested. The constant was much larger for latex films than for oil and oleoresinous films, although at 156° F. ($1/T = 2.9 \times 10^{-3}$) the largest constant for an oil film was nearly as large as the smallest constant for a latex film. The 12 constants spread over a much wider range at 38° F. ($1/T = 3.6 \times 10^{-3}$) than at 156° F.

For six of the eight oil or oleoresinous films, the slope of the line relating *log P* to $1/T$ was negative, which indicates that the activation energy was greater at high than at low temperature. Such negative slope has generally been reported in the literature on permeability of films of plastics and paints to water vapor and gases. But for two oil or oleoresinous paints, white lead in alkyd resin and weathered white lead in raw linseed oil (lines 6 and 8 in Fig. 1), and for all four latex films studied, the slope of *log P* versus $1/T$ was positive. It therefore appears possible for the activation energy to be greater at low than at high temperature. Positive slope is not peculiar to white lead, raw linseed oil, the alkyd resin, or weathered films, because negative slopes were observed for unweathered white lead in raw linseed oil and for weathered lead-zinc in alkyd resin. Positive slope, however, may be characteristic of latex films.

The permeability constant is further related to the diffusion constant, D, and the solubility of water vapor in the film, S, by the relation $P = DS$. The activation energy is the sum of the activation energy for diffusion and the heat of solution of water vapor in the film. Since a decrease in diffusion with increase in temperature is highly improbable, the positive slope of *log P* versus $1/T$ for latex and some oil films suggests that the solubility of water vapor in such films decreases with rising temperature. Experimental data to test the suggestion are not yet available.

It should be pointed out that water vapor passed through all films more rapidly at 156° F. than at 38° F., whether the permeability constant increased or decreased. Thus for the film of titanium dioxide in polyacrylic latex (line 12 in Fig. 1), for which *log P* fell off most rapidly with rising temperature, the Payne specific permeability, P_s, was 29.1 at 156° F. and only 2.16 at 38° F.

The Payne-cup method was chosen for the measurements of permeability because much of the published data for paint films has been obtained by that method. The method is attractive for its convenience, but it is open to possible objections, especially for determinations at other than room temperature. Once the cup has been closed with a film that is impenetrable by air under a pressure gradient, there can be no movement of air in or out of the cup to offset the change in volume of enclosed air when the temperature is altered or when moisture vapor escapes through the film. Flexible films are then stretched, and their exposed area is increased by the difference between the internal and external pressures. On the other hand, if the film is penetrable by air under a pressure gradient, there may also be loss of moisture vapor by penetration in addition to the loss by permeation. Moreover, poor circulation of air inside and outside the cup may result in pressure of moisture vapor somewhat below saturation at the film interface within the cup and greater than zero at the film interface outside the cup. Thus it is desirable to test further the relations between the temperature coefficient of the permeability constant and the absolute temperature by some method that is less open to objection than the Payne cup.

More recent tests have shown that the logarithm of the permeability constant may not always be related linearly to the reciprocal of the absolute temperature. Chips of paint from the Washington Mansion at Mount Vernon, Virginia, gave permeability constants of 8.8×10^{-7} at 36° F., 29.0×10^{-7} at 70° F., and 36.1×10^{-7} at 156° F. The constant at 36° was much too low to comply with a linear relation. The chips were 73 to 110 mils thick, and were made up of white paint containing sand to produce a rough surface. The paint was applied in about 20 paintings from 1775 to 1956.

Penetration by Air under Pressure Difference

The term breathing properly applies to a movement of air into or out of a discretely porous or cellular body such as the lungs under a difference of pressure. Gardner (12) apparently so intended, when he introduced the term, to distinguish some paint films

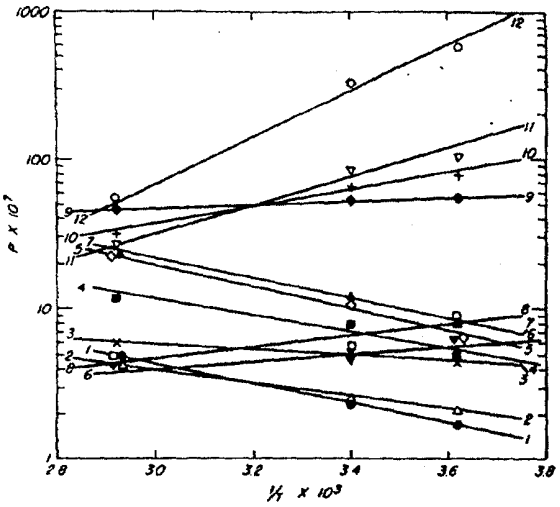

Fig. 1.—Permeability constant, P, plotted on a logarithmic scale as a function of the reciprocal of the absolute temperature for films numbered as follows: 1. Lead-zinc in alkyd resin, weathered; 2. White lead in bodied linseed oil; 3. White lead in raw linseed oil; 4. Zinc oxide in raw linseed oil; 5. Bodied linseed oil without pigment; 6. White lead in alkyd resin; 7. Titanium dioxide in raw linseed oil; 8. White lead in raw linseed oil, weathered; 9. Polyvinyl acetate latex without pigment; 10. Titanium dioxide in styrene-butadiene latex; 11. White lead in styrene-butadiene latex; 12. Titanium dioxide in acrylic latex.

Table 5.—PENETRATION OF FILMS OF OIL PAINTS BY AIR UNDER A PRESSURE GRADIENT

Composition of oil-containing film	Pigment volume of film	Rate of passage of air under 0.38 atmosphere difference of pressure through 3.14 square centimeters of: Unweathered film Cc. per min.	Weathered film Cc. per min.
Commercial "breather-type" paint	0.39	0	0.6
Commercial "blister-resistant" paint	.30	0	----
Raw linseed oil paints pigmented with:			
Basic carbonate white lead	.60	0	0
Basic carbonate white lead	.30	0	0
Zinc oxide	.60	5.3	----
Zinc oxide	.55	.6	----
Zinc oxide	.30	0	.25
Titanium dioxide	.60	21.9	----
Titanium dioxide	.55	18.8	----
Titanium dioxide	.50	0	8.7
Titanium dioxide	.45	----	11.8
Titanium dioxide	.30	0	0
Magnesium silicate	.30	0	0

Table 6.—PENETRATION OF FILMS OF LATEX PAINTS BY AIR UNDER A PRESSURE GRADIENT

Composition of latex-containing film	Rate of passage of air under 0.38 atmosphere difference of pressure through 3.14 square centimeters of: Unweathered film Cc. per min.	Weathered film Cc. per min.
Commercial polyvinyl acetate paint	0	0
Polyvinyl acetate latex with:		
No pigment	0	0
Zinc oxide	1800 F*	2000 F
Titanium dioxide	0 F	0 F
Magnesium silicate	0 F	0 F
Polyacrylate latex with:		
No pigment	0	64 F
White lead	0 F	78 F
Zinc oxide	1500 F	1900 F
Titanium dioxide	0	1
Magnesium silicate	0	0
Styrene-butadiene latex with:		
No pigment	0	----
White lead	0	230
Zinc oxide	0	0
Titanium dioxide	46 F	1600 F
Magnesium silicate	0	1
Styrene-butadiene latex with methyl cellulose and:		
White lead	0 F	920 F
Zinc oxide	1	65
Titanium dioxide	0 F	0
Magnesium silicate	0	0

*The symbol F indicates films that could be seen to contain small vacuoles caused by retention of foam after the wet film hardened.

from others. All breathing paint films should therefore be readily penetrated by air, but not all films should breathe, even though all paint films tested so far are permeable to water vapor in at least some degree. It was therefore of interest to learn whether ordinary paint films let air pass through under a pressure gradient, and if not, whether there are paint films that do.

A suitable device for the purpose was made with an Asbeck–Van Loo critical pigment volume cell (1). The cell consists of two bell-shaped parts of glass, the wide portions of which fit together in a ground-glass joint. The bottom part, which forms the male piece of the joint, is closed by a fritted glass disk set flush with the glass rim. The narrow portion of each part ends in an outlet tube. The outlet of the male part was inserted through a rubber stopper in the mouth of a 1-liter filter flask, the side arm of which was connected through a stopcock to a water aspirator for suction. An open-arm mercury manometer was provided to measure the pressure of air in the filter flask. There was also a bleeder tube with stopcock to admit air for precise adjustment of suction at the beginning of a test, prompt release of suction after a test, and admission of air when calibrating the apparatus. The total volume of air at atmospheric pressure contained within the apparatus between the surface of the fritted glass disk and the aspirator stopcock was 1290 cubic centimeters.

A circular sample of paint film to be tested was cut exactly to the diameter of the fritted glass disk. A ring made of a short piece of copper tubing 2 centimeters in diameter inside was centered over the film. A rim of molten paraffin was then formed between the outer surface of the copper ring and the glass rim of the cell and allowed to harden. Thus only the portion of the paint film enclosed within the copper ring was exposed for possible penetration by air. The female part of the cell was then placed in position over the sample, and its outlet tube was closed by a short piece of rubber tubing and pinchcock.

Air was evacuated from the apparatus and the suction was adjusted through the bleeder tube until the manometer registered —28.9 centimeters of mercury, a pressure difference of approximately 0.38 atmosphere. A constant level in the manometer for five minutes indicated that the apparatus was free from leaks. The pinchcock at the outlet of the female part of the cell was then removed, and a stop-watch was set in motion at the same time. If the paint film permitted air to pass, the manometer reading was recorded when exactly five minutes had elapsed. Impenetrable films, of course, permitted no change in manometer reading. If a film was so porous that the pressure rose to —7.9 centimeters of mercury within five minutes, the time required for pressure to rise from —28.9 to —7.9 was recorded, and several successive tests of the film were made.

To permit computation of the rate of passage of air through the films, the apparatus was calibrated as follows: The fritted glass disk was sealed with a disk of paper entirely covered by a layer of paraffin. The system was evacuated to a manometer reading of —28.9 centimeters of mercury. Successive volumes of approximately 50 cubic centimeters, accurately measured in a gas burette, were admitted through the bleeder tube, and the manometer reading was recorded after each admission until the manometer reached —7.9 centimeters of mercury. A cali-

bration curve was then drawn to relate manometer readings to volume of air at atmospheric pressure.

When the fritted glas disk was left open, air passed through it at the rate of 3320 cubic centimeters a minute. When an impenetrable paint film was perforated five times with the point of a common pin and then tested, it allowed 321 cubic centimeters of air to pass a minute.

Table 5 reports the results obtained with some oil paints. A commercial "breather-type" paint, said to resist blistering because it is porous enough to breathe, allowed no air to pass through its unweathered film and only 0.6 cubic centimeters a minute through its weathered film. Its specific permeability to water vapor (Table 2) was also very low. Such paint cannot properly be said to breathe, although it may well be reasonably resistant to moisture blistering. Another commercial paint said to resist blistering but not claimed to breathe allowed no air to pass and was also very low in specific permeability to water vapor (Table 2).

Single-pigment paints made with raw linseed oil and white lead, zinc oxide, titanium dioxide, or magnesium silicate at 0.30 pigment volume, which is within the range of pigment volume customary for house paints, allowed no air to pass through their unweathered films. The weathered films were also impenetrable or, in the case of the weathered zinc oxide film, very nearly so. Unweathered films porous enough to pass air, however, were made with zinc oxide and with titanium dioxide by raising the pigment volume to a point far above that practicable for house paints. Thus the zinc oxide paint film at 0.55 pigment volume passed 0.6 cubic centimeters of air a minute, and at 0.60 pigment volume it passed 5.3 cubic centimeters a minute. The titanium dioxide paint film at 0.55 pigment volume passed 13.3 and at 0.60 pigment volume 21.9 cubic centimeters a minute. Films of white lead paint, weathered or unweathered, were impenetrable even at 0.60 pigment volume. The critical pigment volume, the point above which there is no longer enough linseed oil to fill all the spaces between particles of pigment in the dried films (1, 3, 10, 27), was shown in paper IV (5) to lie between 0.55 and 0.60 for white lead paint, 0.45 and 0.50 for zinc oxide paint, and 0.40 and 0.45 for titanium dioxide paint. It may be concluded, therefore, that films of oil paints breathe in the sense of becoming penetrable by air under a pressure gradient when the paints are made at a pigment volume somewhat above the critical. The data of Table 5 suggest further that weathering tends to develop penetrability to air in some films that before weathering were impenetrable. Sufficient weathering to cause paint films to crack renders them readily penetrable to air, of course.

Results with films of latex paints are reported in Table 6. Most of the unweathered films and 8 of the 18 weathered films allowed no air to pass. Four unweathered and 10 weathered films were penetrated by air. Two unweathered and four weathered films were porous enough to let through 920 to 2000 cubic centimeters a minute. Penetrable weathered films always passed more air than their unweathered counterparts. Neither the composition of the latex nor the kind of pigment seems to govern penetrability, because both penetrable and impenetrable films were obtained with each kind of latex and with each pigment.

The behavior of latex paints in tests of permeability to water vapor and their low swelling efficiency when soaked in water were attributed to porosity caused by failure of droplets of emulsion to coalesce completely when the films harden. Such porosity evidently need not render the films penetrable by air if the pores are not connected with one another. Penetrability by air may require larger pores that join together to afford continuous passageway.

Clearly, water vapor permeates most paint films by some mechanism other than passage through interconnected pores, because penetration by air under a pressure gradient and permeability to water vapor are not at all parallel. Fifteen unweathered latex films that were impenetrable by air ranged in specific permeability to water vapor from 1.33 to 6.77 (Table 3), compared with a range of 0.07 to 0.45 (raw linseed oil without pigment 1.39) for films of oil paint (Table 2). Latex films through which air passed at 1500 or 1800 cubic centimeters a minute were lower in specific permeability to water vapor than some of the latex films through which no air passed. Weathering rendered penetrable some latex films that were impenetrable to air before weathering, and increased the penetrability of those latex films that were previously penetrable. Weathering often had the opposite effect on specific permeability to water vapor, however. Thus, for example, when films of titanium dioxide in styrene-butadiene latex were weathered, penetrability increased 46 to 1600 cubic centimeters of air a minute, but specific permeability to water vapor decreased from 5.23 to 1.03.

Latex paints have a notable tendency to retain foam unless they are made with effective anti-foaming agents. Such agents were not used in the latex paints made in the laboratory. The latex films that were tested for penetration by air were therefore examined by transmitted light under a microscope. Some of the films (indicated in Table 6) contained easily observable vacuoles that presumably were left by foam in the wet paint after the film hardened. Some vacuoles clearly afforded passage from one side of the film to the other. Others apparently were completely enclosed within the film. Most of the penetrability of latex films to air may therefore be attributed to open pores left by foamy paint. There were some films with vacuoles that were impenetrable, however, and some apparently free from vacuoles that were penetrable, especially the weathered film of white lead in styrene-butadiene latex that passed 230 cubic centimeters of air a minute. But permeability of the films to water vapor apparently was unrelated to the presence of vacuoles, because the eight unweathered latex films with observable vacuoles ranged in specific permeability from 1.44 to 6.03 (average 3.87), whereas the 11 films without observable vacuoles ranged from 1.33 to 6.77 (average 4.24).

Most films that were penetrable to air could be tested repeatedly with concordant results, which indicates that the films were unaltered by the pressure gradient of 0.38 atmosphere during test. Four weathered films of latex paints, three with and one without observable vacuoles, were exceptions. With the film of white lead in polyacrylic latex, five successive tests of air penetrability gave rates of 78, 96, 118, 123, and 145 cubic centimeters a minute, respectively. Such increasing penetrability might be attributed to repeated fracturing of the walls of vacuoles under stress exerted by the pressure gradient on a film rigid enough to resist compression. But the other three exceptional films exhibited a reverse behavior, a decrease in penetrability with each successive test. The weathered film of unpigmented polyacrylic latex gave successive rates of penetration of 64, 45, and 36 cubic centimeters of air a minute, the weathered film of zinc oxide in styrene-butadiene latex containing methyl cellulose gave successive rates of 65, 56, 54, 52, and 51 cubic centimeters a minute, and the weathered film of white lead in styrene-butadiene latex, which contained no observable vacuoles, gave successive rates of 230 and 90 cubic centimeters a minute. Decrease in penetrability in successive tests may indicate that the film becomes permanently compressed, and the effective cross section of its pores

becomes diminished by application of pressure.

Conclusions

1. The penetration of water through coatings of oil paints can be observed by application of the coatings over a thin layer of blue cobalt chloride in methyl cellulose on clean glass. The coatings may then be weathered before testing by exposure to artificial sunlight (without spraying with water). Tests are made by immersing the coated specimens in water and observing the time required for the cobalt chloride to change from blue to pink and for the coating to become blistered.

2. Penetration of water occurs earlier in some portions of a given coating than in others. First penetration through unweathered coatings was observed in 2 to 13 hours, but penetration was completed only after 9 to 48 hours. The "wet line" advancing through a coating evidently is of very irregular depth, which suggests a heterogeneous film structure. Although longer time is required in general for water to penetrate thick than thin coatings of a given paint, the relation between time and thickness is not sharply defined, as might be expected from the observed irregularity in penetration. Blistering does not occur until penetration is well advanced, but may occur before penetration is complete.

3. Penetration occurs faster in coatings of high water absorption, such as zinc oxide paint, than in coatings of low absorption, such as white lead paint. Weathered coatings are usually penetrated more rapidly and blistered sooner than are unweathered coatings of similar paint. The relations between time of penetration and thickness of coating and between penetration and water absorption are also more obscure.

4. The mechanism of blistering in these tests is largely osmotic, because the blistering occurs much sooner where the water-soluble cobalt chloride and methyl cellulose are interposed between coating and glass than elsewhere.

5. Measurements of the specific permeability of paint films to water vapor (Payne cup method at 70° F.) revealed that permeability and water absorption bear little or no relation to each other. Both high and low permeabilities were found among highly absorptive films and also among films of low absorption. As groups, oil and oleoresinous paint films are very much less permeable to water vapor than are latex paints, yet the range in water absorption of the latex paints falls within the range for oil and oleoresinous paints. If water absorption affords an indication of the resistance of a paint to moisture blistering, permeability to water vapor does not, at least within the range of permeabilities of the oil and oleoresinous paints.

6. During permeability tests in Payne cups, paint films absorbed much less moisture than when they were soaked in water. The amounts were roughly parallel, however. Such absorption in Payne cups may be high when the permeability is low, and may be low when the permeability is relatively high.

7. In oil and oleoresinous vehicles, both white lead and zinc oxide make paint films of lower permeability than is obtained with titanium dioxide, antimony oxide, or magnesium silicate. White lead and antimony oxide impart low water absorption, however, whereas zinc oxide imparts very high water absorption. In latex vehicles, permeability is high with any of these pigments, and both white lead and zinc oxide tend to cause higher water absorption than titanium dioxide or magnesium silicate. Among the vehicles tested, phenolic-resin varnish made paint films that were usually low in both permeability and water absorption. Raw linseed oil vehicle favored high permeability and high absorption, bodied linseed oil held an intermediate position for both permeability and absorption, and alkyd-resin vehicle developed intermediate permeability but even greater absorption than raw linseed oil.

8. The specific permeability of all paint films increases rapidly with temperature. Study of films of 12 paints, however, showed that the logarithm of the permeability constant, which considers differences in vapor pressure, is linearly related to the reciprocal of the absolute temperature, which is to be expected of films that are not too hydrophilic and do not swell too much. Latex films differ strikingly from most oil or oleoresinous films in that their permeability constant is not only much higher, but also decreases as temperature rises. There were two oil paints, however, for which the permeability constant decreased with rising temperature. For such films, the solubility of water vapor in the film probably falls as temperature rises.

9. A device was constructed, based on an Asbeck-Van Loo cell for measurement of critical pigment volume, to study the ability of paint films to "breathe" in the sense of permitting air to pass through under a pressure difference of 0.38 atmosphere. Films of linseed oil paints within the range of pigment volume practicable for house paints are incapable of such breathing. Films that can be penetrated by air under a pressure gradient can be made with pigment volumes well above the critical pigment volume. A commercial "breather-type" paint was found to be impenetrable by air until its film had been weathered. Impenetrable films may become porous enough to breathe after they have been weathered, but some paint films remain impenetrable after 15 days of artificial weathering. Films of latex paints made at pigment volumes suitable for exterior use are impenetrable, or nearly so, provided that the films are free from vacuoles left when foamy paint hardens. Vacuoles may make the films penetrable or leave them still impenetrable, depending on whether the vacuoles are connected with one another or remain isolated.

10. The permeability of paint films to water vapor is not governed by the presence of pores through which air can pass under a pressure gradient. Films highly permeable to water vapor may be entirely impenetrable by air. On the other hand, latex films of very high penetrability by air because of vacuoles may be no more permeable to water vapor than other latex films that are impenetrable to air.

Literature Cited

1. Asbeck, W. K. and M. Van Loo. 1949. Critical pigment volume relationships. Indus. and Eng. Chem. 41: 1470–5.
2. Bell, S. H. 1955. The structure of paint films. Jour. of the Oil and Colour Chemists' Assoc. 38: 595–618.
3. Blackmore, P. O. 1956. Film formation, film properties, and film deterioration. Jour. of the Oil and Colour Chemists' Assoc. 39: 23, 24.
4. Broeker, J. F. 1955. Development of exterior coatings for wood. Paint, Oil and Chemical Review 118 (11): 16, 17, 20.
5. Browne, F. L. 1953–56. Swelling of paint films in water. Paper I. Jour. of For. Prod. Res. Soc. III (5): 108–24; Paper II. Jour. of For. Prod. Res. Soc. IV (6): 391–400; Paper III. For. Prod. Jour. V (1): 92–6; Paper IV. For. Prod. Jour. V (2): 142–6; Paper V. For. Prod. Jour. V (3): 192–200; Paper VI. For. Prod. Jour. VI (4): 152–9; Paper VII. For. Prod. Jour. VI (6): 235–40; Paper VIII. For. Prod Jour. VI (8): 312–118; Paper IX. For. Prod. Jour. VI (10): 453–8.
6. Brubaker, D. W. and Kurt Kammermeyer. 1952. Separation of gases by means of permeable membranes. Indus. and Eng. Chem. 44: 1465–74. Flow of gases through plastic membranes. Indus. and Eng. Chem. 45: 1148–52.
7. Doty, P. M., W. H. Aiken and Hermann Mark. 1944. Water vapor permeability of organic films. Indus. and Eng. Chem., Anal. Ed. 16: 686–90.
8. Dunn, E. J., Jr. 1954. Moisture resistance of paint films. Official Digest, Federation of Paint and Varnish Production Clubs 26 (353): 387–407.
9. Dunn, E. J., Jr. 1956. Physical properties of latex films. Official digest, Federation of Paint and Varnish Production Clubs 28 (378): 564–89.
10. Eckhaus, Sigmond, Irvin Wolock and B. L. Harris. 1953. Porosity of paint films. Water vapor adsorption and per-

meability. Indus. and Eng. Chem. 45: 426–8.
11. Fabre, G. 1955. The permeability of plastics. Industrie Plastiques Modernes (Paris) 7 (4): 33–5, (5): 41–3, (6): 35–8.
12. Gardner, H. A. 1934. Primers for wood. Indus. and Eng. Chem. 26: 1272–3.
13. Harris, B. L. and A. Bialecke. 1952. Permeability to water of thin unsupported films of pure drying oils. Official Digest, Federation of Paint and Varnish Production Clubs No. 335: 884–7.
14. Herzog, P. C. and A. E. Gilchrist. 1955. Emulsion vapor barrier coating compositions. U. S. Patent 2,709,689.
15. Hess, Manfred. 1951. Paint film defects, their causes and cure, p. 105. Reinhold (New York).
16. James, D. M. 1956. Experiments on paint adhesion under moist conditions. Jour. of the Oil and Colour Chemists' Assoc. 39: 39–62.
17. Kittelberger, W. W. and A. C. Elm. 1946–47. Water immersion testing of metal protective paints. Indus. and Eng. Chem. 38: 695–9, 39: 876–81.
18. Kuzmak, J. M. and P. J. Sereda. 1955. The blistering of paint in the presence of water. Canadian Jour. of Technology 33: 67–76.
19. MacGregor, J. R. 1952. The unexplored field of exterior paint. Official Digest, Federation of Paint and Varnish Production Clubs No. 335: 869–80.
20. Mayne, J. E. O. 1950. The blistering of paint films. Jour. of the Oil and Colour Chemists' Assoc. 33: 312–16, 538–47.
21. Morgan, P. W. 1953. Structure and moisture permeability of film-forming polymers. Indus. and Eng. Chem. 45: 2296–2306.
22. New York Paint and Varnish Production Club. 1937. Scientific Section Circular 546, Amer. Paint and Varnish Manufacturers' Assoc.
23. Nicholson, A. and H. A. H. Jenkins. 1955. The blistering of paint films on steel. Paint Manufacturer 25:303.
24. Othmer, D. F. and G. J. Frohlich. 1955. Correlating permeability constants of gases through plastic membranes. Indus. and Eng. Chem. 47: 1034–40.
25. Payne, H. F. 1944. Adsorption, permeability, water resistance, and structure of organic surface coatings. Chapter 7 in vol. 4 of Protective and Decorative Coatings by J. J. Mattiello, Wiley (New York).
26. Pragst, W. 1956. Report of some experiments on the question of the humidity blocking action of coatings. Farbe und Lack 62: 145–51.
27. Rains, H. G. and G. L. E. Wild. 1955. Passage of water through a paint film. Jour. of the Oil and Colour Chemists' Assoc 38: 800–2.
28. Taylor, J. 1955. Treated rutile-type titanium dioxide pigments and their properties. Jour. of the Oil and Colour Chemists' Assoc. 38: 233–49.
29. Thomas, A. M. and W. L. Gent. 1945. Permeation and sorption of water vapor in varnish films. Proc. Physical Soc. (London) 57: 324.
30. Turner, J. H. W. and S. Hodgson. 1956. Composition-property relationships in high-polymer emulsions. Jour. of the Oil and Colour Chemists' Assoc. 39: 114–28.
31. Vannoy, W. G. 1952. Blister-resistant house paints. Amer. Paint Jour. 36 (32): 82, 84–7.
32. Waack, Richard, N. H. Alex, H. L. Frisch, Vivian Stannett and Michael Szwarc. 1955. Permeability of polymer films to gases and vapors. Indus. and Eng. Chem. 47: 2524–27.
33. Weinmann, Kurt. 1955. Water vapor permeability of varnish and synthetic films and its relation to swelling and stability in dampness. Farbe und Lack 61: 315–23.
34. Wirth, W. R., II. 1956. Study of the permeability and blistering of five exterior house paints. Amer. Paint Jour. 40 (35): 72–110.
35. Woodbridge, R. J. 1955. Evaluation of emulsion paints. Jour. of the Oil and Colour Chemists' Assoc. 38: 285–99.