1953 PREPRINT FOREST PRODUCTS RESEARCH SOCIETY 252

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The Absorption of Water, Swelling and Solubility of Free Films of Paint

F. L. BROWNE

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

Tests substantiating that free films of house paints soaked in distilled water absorb surprisingly large amounts of water are described. Amount is often more than 1 ½ times the weight of linseed oil that the film contains. When such films are young, swelling of many paints may cause expansion of surface area as much as 50 percent.

IT IS POPULARLY SUPPOSED that coatings of oil paints and of drying oils are inert or nearly inert to water. Because oil and water are practically insoluble in each other, it is easy to assume that the incompatibility continues after the oil has become oxidized, polymerized, and cross-linked into a gel structure. Nevertheless, more than 30 years ago English (*23*)[2] and German (*14, 29*) workers showed that films of linseed oil after drying absorb a third or even half of their weight when immersed in water for a few days, and Dunlap (*12, 13*) and later Browne (*4*) at the Forest Products Laboratory reported that coating wood with paint, varnish, or oil merely retards without preventing changes in moisture content of the wood. Since then there have been many publications on the absorption of water (*1, 2, 3, 8, 25, 26, 27, 39, 40*) and water vapor (*16, 17, 31*) by coatings of oils and paints and on the leaching of water-soluble ingredients from coatings (*11, 14, 20, 21*). Many of the studies were concerned with the evaluation of rust-protective paints and the mechanism of protection against corrosion for metal (*18, 19, 20, 24, 28, 32* to *38*, incl.). Most observations were made with coatings supported on glass or metal; few on free, unsupported films (*30, 31*). In all of the publications cited, swelling was measured in terms of the absorption of water by the films; no direct measurements of changes in dimensions are reported.

The loss of substance by leaching and the swelling and shrinking from gain and loss of water are surely significant properties of paint coatings about which more should be known before the behavior of paints on exterior woodwork and the chemistry of coating deterioration can be explored to full advantage. Such developments as checking, cracking, curling, flaking, and blistering clearly reveal the operation of sizeable stresses on the coatings. It is commonly assumed that the stresses originate outside the coatings, particularly in movement or development of fluid pressure within the wood surface that supports the paint. The discoveries that water swells many of the paints in common use to a much greater extent than it does wood and that painted surfaces on houses are continuously wet for long periods of time (*15*) strongly suggest that the destructive stresses may arise chiefly within the coatings themselves.

In order to limit the present studies to the behavior of the coating materials themselves without complications from the effects of the substrate, the tests were made on free unsupported films of clear drying oils and oil paints. All of the films swelled measurably when immersed in water, many of them very greatly. The swelling observed was the increase in area, calculated from precise measurements of increase in length and width of the films. (Convenient means were not found for measuring increase in thickness with sufficient precision to calculate volumetric swelling reliably, though it is hoped that some determinations of change in volume can be made in future work.) Films attached to a substrate, of course, cannot swell freely in length and width; length and width must remain fixed by the requirements of the substrate if separation is to be avoided, and any necessary adjustment of volume must be made by change in film thickness. In a substantially rigid medium such adjustment of volume by change in one dimension only necessarily develops internal stresses. By reason of such stresses it may be that films attached to substrates do not absorb so much water as the free films used in these studies, although the data reported in the literature indicate that any such difference is small.

Methods of Obtaining Free Films

Suitable substrates were coated with oil or paint by brushing or by drawing

How the length and width of a marked portion of a free film of paint held flat between glass plates were measured before and after swelling in water by use of a traveling microscope.

[1] Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

[2] Italic figures in parentheses refer to Literature Cited at end of the paper.

ABOUT THE AUTHOR: BROWNE, DR. FREDERICK L. B. Chem. degree in 1917 at Cornell University and the Ph. D. degree in colloid chemistry in 1921 at the University of Wisconsin. He first joined the staff of the Forest Products Laboratory in 1918–19 to develop casein glues for the wood airplanes of World War I. In 1921–22 he was a National Research Fellow at Wisconsin. He is one of the "iron men" of the Chemical Abstracts staff and has edited Section 2, General and Physical Chemistry, since 1929. Besides the American Chemical Society, he is a fellow of the American Association for the advancement of Science and the Wisconsin Academy of Sciences, Arts, and Letters, and is a member of Sigma Xi, of the American Society for Testing Materials, and FPRS.

down with a Bird doctor blade. The coatings were allowed to stand 10 days to dry and harden. Some were then stripped from the substrate for immediate testing, whereas others were exposed in an accelerated weathering machine or to natural weathering out of doors for desired periods of time, after which the coatings were stripped from the substrate for testing. Three kinds of substrate permitted the films to be stripped off at the desired time.

1. Flat tinplate (in pieces 3⅜ by 5⅛ inches) coated on one face held coatings well during natural or artificial weathering, after which free films could be stripped off readily by amalgamating the tin with mercury. Enough coating was scraped off near the edges of a specimen to expose tin, and the specimen was floated on mercury with the coated face down for about half an hour. With care, it was then possible to loosen the coating at one of its edges and slowly peel it from the metal without breaking the freed film, provided that the coating had not been weathered too long to permit moderate bending without breaking. Much trouble was experienced, however, in stripping unweathered coatings only 10 days old without seriously tearing the films. There might be less difficulty if the specimens with young coatings were chilled to 40° F. for stripping. In these studies the amalgamation process was used chiefly for specimens subjected to natural weathering.

2. Flat pieces of glass, metal, or paper coated with a thin layer of silicone parting agent DC–7 (Dow–Corning Co.) applied with a finger can be painted readily, will hold coatings for a limited period of natural or artificial weathering, and yet allow the films to be stripped off when needed for testing. Some of the films for these studies were prepared on siliconed paper. Shortcomings of the method were a graininess in the layer of silicone that was transmitted to the free films and a tendency for some paints to crack and to begin to peel from embrittlement at an earlier stage of natural or artificial weathering than they did on tinplate or on gummed paper. It is possible that both shortcomings might be overcome by coating the paper mechanically with a thinner and more nearly uniform layer of silicone than was possible with manual application.

3. Commercial gummed (dextrine mucilage) paper, previously saturated with linseed oil, proved the most convenient substrate for most of the present tests. Prior saturation of the paper with linseed oil was necessary because the layer of dextrine mucilage is readily permeable to the oil in paints; if the paper is allowed to draw oil through the dextrine the composition of the paint coating is altered undesirably. Gummed-paper specimens held most paints satisfactorily for 1,200 kilowatt-hours (about 360 hours of ultraviolet light with water spray for 1½ minutes in each 18 minutes), by which time all paints were chalking, most of them very freely, and were greatly embrittled, some to the point of cracking. To strip off the free films for testing, the specimens were placed in a room at 80° F. and 97 percent relative humidity for about 30 minutes to soften the oiled paper, plasticize embrittled coatings, and melt the dextrine mucilage. The films were then peeled from the oiled paper and placed face down on a glass plate while any mucilage clinging to the backs was quickly sponged off with moist absorbent cotton. Alternatively, the specimens were placed on a pad of damp blotting paper, paper-side down, and held flat under the weight of glass plates for half an hour before stripping off the films. A few very soft coatings, particularly those of raw linseed oil containing paint drier, required a special technique in which the specimens were immersed in water chilled to 40° F. for 15 to 30 minutes. The films were then stripped off by loosening the film at a corner of the specimen sufficiently to insert a finger tip, by placing the specimen coated side down in the cold water, and by holding the film firmly against the bottom of the glass water tray while the paper was carefully peeled off. Soft films are very much firmer at 40° F. than they are at 70° or 80° F. But too long a soaking period may blister coatings of paints that swell greatly, and the blisters may remain in the films after they have been stripped from the substrate.

Other Experimental Procedures

Tests were made with 32 coating materials. Four were clear (unpigmented) materials, namely, raw linseed oil, bodied linseed oil of viscosity Z3, bodied linseed oil of viscosity Z6, and a commercial alkyd-resin paint vehicle said to contain 77 percent drying oil and 16 percent phthalic anhydride by weight. These liquids were used also for the vehicles of 23 paints of varying pigmentation ground at the Forest Products Laboratory. Of the 23 laboratory paints, 18 were practicable house paints and 5 were single-pigment paints of scientific interest only. All of the linseed oils and oil paints contained lead-manganese naphthenate driers; the alkyd resin and alkyd-resin paints contained lead-cobalt naphthenate driers. The remaining 5 coating materials were trade-brand paints purchased in Madison in July 1952, of which 4 were products of large manufacturers with national distribution and 1 was a so-called "breather type" or "blister-resistant" paint made by a smaller manufacturer. All of the commercial paints had the formula printed on the label. In this report the composition of paints is expressed by volume in the short notation first described by Browne (5) and recently described in this Journal (6) and elsewhere (7).

Method of applying coatings of controlled thickness by use of a Bird doctor blade and suction plate.

For most of the experiments reported, paints were applied with a Bird film applicator or doctor blade drawn manually over a substrate held firmly on a Bird suction plate. With each paint, specimens were prepared in pairs, one with a draw-down with a blade that left a coating nominally 3 mils thick and the other with a 6-mil blade. Actual thicknesses, however, varied appreciably from the nominal. When made on gummed paper 8 by 10½ inches in size, such coatings were 3½ inches wide and 10½ inches long and were then trimmed to specimens 3½ inches by 8 inches by cutting off the uncoated parts of paper and the first and last parts of the draw-down, which might be of unrepresentative thickness. When made on tinplate the coatings covered nearly all of the surface of 3⅝ by 5⅛ inch specimens, which were not trimmed after coating.

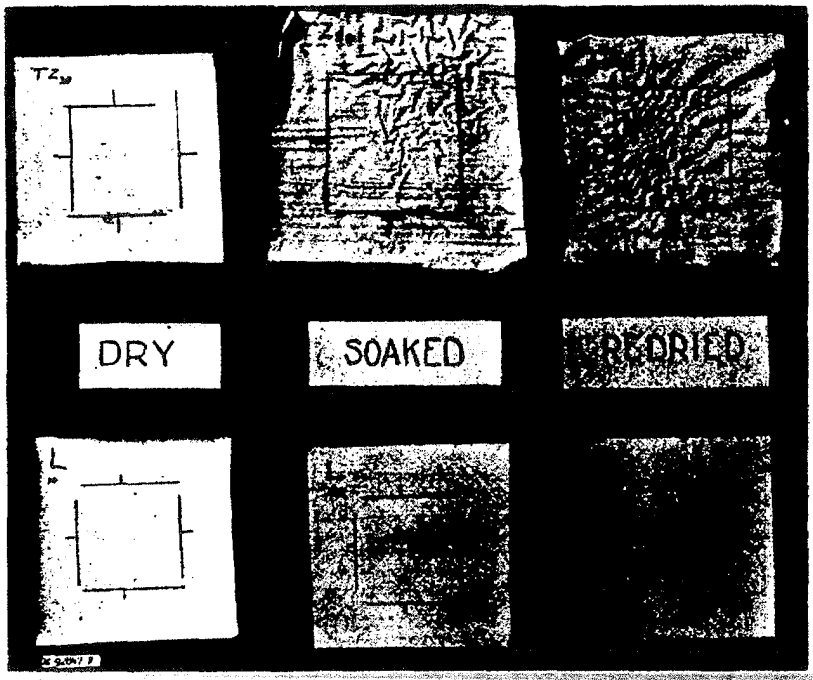
Although the 3-mil and 6-mil draw-downs made much thicker coatings than are usually spread at one time in practical painting, most of the paints dried without wrinkling and none wrinkled too seriously to be acceptable for testing. The clear liquids, however, wrinkled too badly for use. Clear liquids, therefore, were applied by brushing in a sufficient number of successive thin coats to build coatings thick enough for the purpose. Some of the paints for preliminary tests were also applied by brushing. In brush application, coating materials were always spread by stroking both longitudinally and crosswise for even application, but care was taken to see that the brushing ended with longitudinal strokes over all portions of the areas coated.

For exposure to weathering, specimens of coatings on tinplate and on siliconed paper were fastened with weather-resistant pressure tape to sheets of aluminum-painted plywood that were attached to outdoor test

Table 1.--The behavior of five kinds of films when soaked continuously in distilled water at 69.5° F. for periods of time up to 49 days

The films were 1.5 by 2.5 inches in size, of the thickness indicated below, and were 9 days old when they were stripped from gummed-paper substrates and submerged under distilled water. Negative values for swelling after redrying mean that the film shrank to less than the area before immersion.

Number of days immersed in water	Thinner films: Water absorbed (A)	Thinner films: Swelling (Increase in area) In water (ΔQ)	Thinner films: Swelling (Increase in area) Redried (ΔQ^1)	Thinner films: Solubility (Leached out by water) (B)	Thicker films: Water absorbed (A)	Thicker films: Swelling (Increase in area) In water (ΔQ)	Thicker films: Swelling (Increase in area) Redried (ΔQ^1)	Thicker films: Solubility (Leached out by water) (B)
	Milligrams	Percent	Percent	Milligrams	Milligrams	Percent	Percent	Milligrams
Raw linseed oil containing lead-manganese drier								
	Thickness 3.4 mils, initial weight 195.5 milligrams				Thickness 6.5 mils, initial weight 371.4 milligrams			
3	23	5	-0.5	4.7	34	4	-1.8	7.2
6	19	4	-1.0	4.7	46	9	+1.4	13.1
12	27	4	-1.4	9.7	48	6	- .9	13.7
20	45	5	-2.5	12.5	65	6	-1.1	18.5
32	149	12	-1.8	22.8	137	14	+1.1	18.1
49	148	9	.....	33.8	280	18	.....	38.9
Paint L, p/nv 0.30 (white lead paint)								
	Thickness 2.8 mils, initial weight 468.4 milligrams				Thickness 6.2 mils, initial weight 1034 milligrams			
3	27	10	.5	6.8	35	5	- .6	13.0
6	37	17	2.1	7.8	46	7	- .2	13.9
12	50	19	3.3	9.9	61	10	+ .3	18.5
20	57	22	4.3	12.2	73	11	+ .8	22.7
32	64	25	5.7	12.3	78	12	+ .8	23.4
49	74	24	6.0	14.1	90	12	+ .9	21.8
Paint T_{A20}, p/nv 0.30 (anatase titanium dioxide paint)								
	Thickness 2.1 mils, initial weight 141.6 milligrams				Thickness 4.9 mils, initial weight 705.5 milligrams			
3	59	20	+1.8	6.2	72	11	- .7	7.1
6	87	35	+4.2	7.6	114	17	+ .5	9.4
12	92	39	+6.0	11.6	152	22	+1.4	14.5
20	96	43	+3.1	14.9	158	21	+2.0	19.9
32	95	40	+ .4	21.2	177	21	+2.8	23.5
49	79	28	-2.9	30.6	158	20	+5.0	34.1
Paint Z, p/nv 0.30 (zinc oxide paint)								
	Thickness 2.5 mils, initial weight 365.2 milligrams				Thickness 5.6 mils, initial weight 811.2 milligrams			
3	59	70	25	10.1	284	47	16	12.7
6	.....	.....	.....	.....	400	68	26	17.7
12	.....	.....	.....	.....	416	68	25	20.3
20	.....	.....	.....	.....	362	61	23	26.0
32	.....	.....	.....	.....	342	58	21	29.9
49	.....	.....	.....	.....	365	59	23	35.0
Paint $TL_{20}Z_{20}$, p/nv 0.30 (titanium-lead-zinc paint)								
	Thickness 12.9 mils, initial weight 352.7 milligrams				Thickness 6.5 mils, initial weight 785.0 milligrams			
3	140	38	11	8.2	239	28	8	8.6
6	143	42	13	9.4	317	36	13	12.0
12	152	42	11	12.2	432	46	18	17.1
20	165	46	13	13.8	425	41	16	21.6
32	180	46	12	17.0	430	40	16	24.1
49	169	45	11	19.3	478	40	16	29.8



Effects of soaking in water and then redrying on free films of two different kinds of paint. The three films in the top row were of titanium-zinc paint (TZ_{20}, p/nv 0.30), the three on the bottom row were of pure white lead paint (L, p/nv 0.30). The two films in the left-hand column were dry and show the markings in drawing ink between which length and width were measured accurately with a traveling microscope. The two films in the center column had just been taken from water after soaking for three days and were still thoroughly wet. The two films in the right-hand column had been soaked in water and had then been allowed to dry out again. The rumpled films were flattened out for measurement by sandwiching them between sheets of glass.

racks facing south and sloped back at 45° from the vertical.

For exposure to artificial weathering, one set of specimens consisting of five commercial and five laboratory-made paints spread on gummed paper and on siliconed paper were exposed continuously to ultraviolet light from a flaming carbon arc covered by a globe of Corex D glass (Atlas Weatherometer) in complete dryness, that is, without use of water spray at any time. Samples were taken for test after 400, 800, and 1,600 kilowatt-hours' exposure. The results with this run, in which water-soluble products were allowed to accumulate in the films until the immersion tests, suggested that light without moisture fails to effect the visible changes in paint that are reasonably representative of natural weathering. It was therefore decided to use the water spray in the weathering machine after equipping the spray with special nozzles that produced a fine mist rather than jets of water impinging forcefully on the paint coating. The mist deposited water gently on the surfaces in sufficient quantity to wet the surfaces thoroughly and then to drain down over the specimens and drip copiously from the bottom edges. The specimens were sprayed in that way about three times every hour. Loss of soluble ingredients by such leaching was measured by weighing specimens of coated tinplate before exposure and after periods of 400, 800, and 1,200 kilowatt-hours of exposure. Specimens of the coatings on gummed paper exposed simultaneously were then used for stripping films for measurements of water absorption and swelling. There was, however, further loss of soluble ingredients from the free films during the immersion tests.

The usual procedure with specimens on gummed paper was as follows: Ten days after the coatings had been spread the specimens were trimmed to 3½ inches by 8 inches, as already described. Then a 2-inch length was cut off for testing before weathering. The 6-inch specimens remaining were mounted in the weathering machine and exposed for 400 kilowatt-hours (about 120 hours), after which another 2-inch length was cut off for testing. A third 2-inch length was cut off after 800 kilowatt-hours of weathering, and the remainder was available for testing after 1,200 kilowatt-hours, provided the coating was able to withstand that much weathering without cracking too seriously to be stripped and tested.

Free films, after being stripped from the substrate, were cut into test specimens either 2 inches by 2 inches in size (for the first run) or 1½ inches by 2½ inches in size. It was sometimes necessary to depart from the preferred dimensions when very soft young coatings or unusually brittle weathered coatings were torn or cracked in stripping or became cracked in weathering. As a rule, the 1½-inch dimension was the direction of stroking with brush or doctor blade during application and is therefore called the length of the specimen in this report. If the direction of stroking lay otherwise than parallel to the 1½-inch dimension, the direction was marked on the specimen with black drawing ink. Suitable reference marks were then ruled on the specimens in drawing ink to record two places, approximately 1 inch apart along the length and to points approximately 1 inch apart along the width, between which length and width could be measured exactly before and after immersion in water. The specimens were then placed in a desiccator over calcium chloride for at least 24 hours to dry them thoroughly.

The dried specimens were weighed with a chainomatic analytical balance. They were then sandwiched between 1½- by 3-inch microscope slides to hold them flat while the length and width between reference marks were measured precisely with a traveling microscope. The lightest specimens weighed more than 0.12 gram, and the heaviest no more than 1.2 grams; weights were recorded to 0.1 milligram. Length and width were measured to 0.001 inch. Specimens were then submerged in distilled water held at 69.5° F. in a thermostat. As a rule, one 3-mil and one 6-mil film of the same kind of paint were immersed in 300 ml. of water. Paints of different kinds were immersed in separate dishes because the water comes to a pH characteristic of the kind of paint and the absorption and swelling vary with change in pH. Submerged films were weighted down beneath pads of coarsely woven spun-glass cloth to keep some of them from curling too seriously.

Except when otherwise stated, films were immersed for 72 hours, after which they were removed, sandwiched between microscope slides while still thoroughly wet, and the length and width were then remeasured with the traveling microscope. The wet films were then pressed lightly between pieces of dry blotting paper or of paper toweling to remove free water from the surfaces and reweighed as rapidly as possible, always well within 1 minute after blotting, with the chainomatic balance. The films were then allowed to dry in the laboratory for 2 or 3 hours and were then placed

in a desiccator over calcium chloride for at least 30 hours. The films were then weighed for the third time and, when the data were desired, the length and width were measured for a third time.

There was, of course, an experimental uncertainty in the second weighings while the swollen films were still wet owing to the fact that water was being lost by evaporation during progress of the weighings. A tedious procedure leading to a different end-point has been proposed (*21*) for dealing with this difficulty, but the method used, which is similar to those of other careful workers (*17*) was considered preferable because the uncertainty was found to be a negligibly small fraction of the differences among paints.

The difference between the first and the last weighing of a film gave the weight of water-soluble ingredients extracted during the period of immersion in water, represented hereafter by S. The difference between the second and the third weighing gave the weight of water absorbed by the film and still retained after loss of the water-soluble ingredients, represented hereafter by A. The swelling in length, ΔL, and in width, ΔB, was obtained from the differences between the first and the second measurements of those dimensions. The increase in area of the marked portion of the film is represented by ΔQ. On redrying, most films shrank only part of the way back to their initial dimensions.

Preliminary Tests

1. Table 1 shows that free films of linseed oil and oil paints when continuously submerged in distilled water for 49 days undergo changes all the time and fail to reach a condition of equilibrium. The five coating materials were selected to represent widely different behavior. For each material two large specimens on gummed paper were prepared, one applied with the 3-mil and the other with the 6-mil doctor blade except for the clear linseed oil, which was applied by brushing. After 8 days for hardening, six small specimens were cut from each large specimen, marked, and dehydrated over calcium chloride. On the ninth day they were weighed and measured, and each set of six matched specimens was submerged in its own dish of distilled water held at 69.5° F. At each of the prescribed periods of immersion recorded in table 1, one specimen was drawn from each matched set to be weighed and measured while wet, redried over calcium chloride, and weighed and measured again.

None of the films ever reached a long period of constancy in weight and dimensions. The general course of events was a steady gain in absorption of water and swelling until maxima were reached, after which absorption and swelling declined. The 6-mil films of the two paints that contained zinc oxide attained their maxima relatively early, perhaps at 12 days, although the thinner film of titanium-lead-zinc paint continued to absorb and swell until the thirty-second day. The other paints and the clear linseed oil did not reach their maxima before the twentieth to thirty-second day. Some of them gave the highest readings on the forty-ninth and last day of test, but it may be presumed that on still longer immersion they, too, would begin to decline. On the other hand, the loss of water-soluble ingredients by films of all kinds and thicknesses continued steadily upward throughout the 49 days of test except for the pure white lead paint, for which the solubility was nearly constant from the twentieth to the forty-ninth day. When redried after immersion, the two paints containing zinc oxide retained a large part of the great increase in area they had experienced during immersion. Paints and oil that did not swell so much in water, on redrying, shrank more nearly, though seldom quite, to their original dimension; occasionally a zinc-free paint and frequently a clear oil film shrank back to less than its initial length and width (indicated in table 1 by minus signs). Loss of water-soluble ingredients readily accounts for such shrinkage.

The course of the absorption, swelling, and leaching in water suggests no one period of immersion that is more significant than any other. For the rest of this study a soaking period of 72 hours was selected because it has been used by some previous workers, is short enough for reasonable convenience in the conduct of the tests, and is not so long as to permit unduly serious chemical changes in the films while they are being tested.

2. The temperature of the water in which paint films are immersed markedly affects their absorption, swelling, and solubility, as is shown

Table 2.--Effect of temperature of soaking water on absorption, swelling, and solubility of films

The films were 2 by 2 inches in size, of the thickness indicated below, and were nearly 3 months old (stored indoors in a dry, dark place) when they were stripped from the substrates and tested by immersion in water for 72 hours.

Temperature of soaking water	Water absorbed (A)	Swelling (Increase in area) (ΔQ)	Solubility (Leached out by water) (S)
°F.	Milligrams	Percent	Milligrams
Paint L, p/nv 0.30 (white lead paint); thickness 6.8 mils, initial weight 1,207 milligrams			
33 to 36	9	1.3	2.2
72 to 75	20	2.2	6.8
88 to 98	34	2.6	12.6
Paint TZ_{20}, p/nv 0.30 (titanium-zinc paint); thickness 7.7 mils, initial weight 878 milligrams			
33 to 36	103	7	6.5
72 to 75	369	34	18.1
88 to 98	519	78	48.5

Table 3.—Effect of pH (degree of acidity or alkalinity) of soaking water on absorption, swelling, and solubility of films

The films were 2 by 2 inches in size, of the thickness indicated below, and were nearly 3 months old (stored indoors in a dry, dark place) when they were stripped from the substrates and tested by immersion in buffer solutions (citric acid and sodium phosphate) of the pH and concentration indicated; temperature 72° to 75° F.

Soaking solution		Water absorbed (A)		Swelling (ΔQ)		Solubility (leached out by solution) (S)	Buffer salts absorbed by film
pH	Concentration of buffer salts	In 19 hours	In 72 hours	In 19 hours	In 72 hours		
	Moles per liter	Milligrams	Milligrams	Percent	Percent	Milligrams	Milligrams
Paint L, p/nv 0.30 (white lead paint); thickness 6.0 mils, weight 1,067 milligrams							
6.0	0.030	11	29	1.9	2.9	1.2	3.1
7.0	.033	16	33	1.6	3.3	8.5	3.7
7.0	.066	14	43	1.7	2.4	9.8	3.2
8.0	.036	6	41	1.9	3.6	13.4	3.2
Paint TZ_{20}, p/nv 0.30 (titanium-zinc paint); thickness 4.7 mils, weight 534 milligrams							
6.0	.030	141	242	22	33.2	40	3.7
7.0	.033	90	(1)	22	(1)	71	.....
7.0	.066	218	(1)	28	(1)	0	39.4
8.0	.036	184	(1)	27	(1)	114	16.2

[1] In solutions of pH 7.0 or pH 8.0, films of TZ paint after 19 hours acquired such soft and tacky surfaces that they were no longer manageable for weighing and measuring while still wet.

Table 4.—Loss in weight and shrinkage of free films of five kinds when allowed to stand 53 days in the laboratory in preparation for tests reported in table 5

The films were 1.5 by 2.5 inches in size, of the thickness indicated, and were 7 days old when stripped from gummed paper substrates, marked, weighed, and measured, after which they stood 53 days before making final weighings and measurements. (Intermediate observations were made but are not tabulated.)

Kind of film	Thickness of film	Initial weight of film	Loss in weight	Shrinkage in— Length	Width	Area
	Mils	Milligrams	Milligrams	Percent	Percent	Percent
Linseed oil and drier	3.4	192	4.9	1.9	2.2	4.1
	6.1	347	7.5	1.6	1.4	3.0
Paint L, p/nv 0.30	2.9	482	3.6	.9	.9	1.8
	6.1	1,013	5.2	1.2	1.4	2.6
Paint T_{420}, p/nv 0.30	2.1	312	5.7	2.0	1.8	3.8
	4.8	696	9.5	2.7	2.5	5.3
Paint Z, p/nv 0.30	2.2	326	1.9	.4	.7	1.1
	5.5	800	3.7	1.1	1.1	2.2
Paint $TL_{20}Z_{20}$, p/nv 0.30	2.9	349	2.9	.8	1.2	2.0
	6.6	782	.2	.6	1.1	1.7

in table 2. In water at 88° to 98° F. (near body temperature) the changes in films of titanium-zinc paint were 5 to 10 times as great as they were in water at 33° to 36° F. (near freezing). For pure white lead paint, which is a more resistant paint to water, the effect of temperature was somewhat less marked, but the absorption, swelling, and solubility at the highest temperature were still 2 to 6 times those at the lowest temperature. It was therefore necessary in all subsequent tests to hold the water at constant temperature during immersion tests by keeping the dishes in a closely controlled water thermostat.

3. The degree of acidity or alkalinity, measured customarily in terms of pH, and the presence of soluble salts in the water in which paint films are immersed, greatly modify the absorption of water, swelling, and solubility of paints that contain zinc oxide, although the effects are less on paints that contain much white lead. Table 3 records tests made with films of pure white lead paint and of a titanium-zinc paint immersed in solutions buffered with mixtures of citric acid and sodium phosphate to hold the pH at 6.0, 7.0, and 8.0 with approximately 0.03 moles of solute per liter, and at pH 7.0 with double that concentration of solute. With white lead paint the absorption of water was slightly greater at pH 7.0 than at pH 6.0 or 8.0, but there was little or no effect on the swelling; solubility was very low at pH 7.0 and increased with pH, but it was still moderate at pH 8.0. A small quantity of buffer salts remained in the films after they were removed from the solutions and dried, the amount of which was determined by soaking the films in distilled water for 24 hours and then drying and weighing them again.

The films of TZ paint were seriously affected at pH 7.0 and 8.0 in a manner suggesting break-down of the gel structure. The films soon became softened, the surfaces became tacky enough to stick together where they came in contact, and there was obvious dislodgment of both pigment and vehicle from the surfaces. It was found possible to measure absorption and swelling only for the first 19 hours of immersion at pH 7.0 or 8.0. Swelling apparently did not vary greatly with pH, but the absorption of water varied greatly but unsystematically. Solubility increased greatly with pH, except for an anomaly in the more concentrated buffer solution of pH 7.0, where adequate differentiation between leaching of film substance and retention of buffer salts in the film proved experimentally diffi-

cult. The quantity of buffer salts retained in the film after removal and drying was much greater at pH 7.0 and pH 8.0 than at pH 6.0.

In another experiment a film of the TZ paint of initial weight of 483 milligrams was immersed in distilled water for 23 hours, when the absorption was found to be 117.3 milligrams (uncorrected for loss by leaching), and the swelling was 20.7 percent. While still wet, the film was then immersed for 24 hours in water kept saturated with sodium chloride. The film lost all of its absorbed water together with a loss of 12.9 milligrams by leaching while in the saturated salt solution, but it shrank back only part way, to a net gain over the original area of 4.3 percent.

Only a few exploratory tests have been made so far on the composition of the soaking water after films of paints have been soaked in distilled water for 3 days. It has been tentatively observed, however, that the soaking water after contact with pure white lead paint comes to pH 7.2, approximately, and contains only enough soluble lead compounds to be slightly discolored by hydrogen sulfide without precipitating an observable amount of lead sulfide. The soaking water from pure zinc oxide paint comes to pH 5.7, approximately, and contains enough soluble zinc compounds to yield a copious precipitation of zinc sulfide with hydrogen sulfide. The soaking water from pure titanium dioxide paint comes to a pH lower than 5.2 and is unaffected by hydrogen sulfide.

The pronounced effect of pH on the behavior of many paints made it advisable to use only distilled water for subsequent soaking tests and to avoid immersing films of more than one kind of paint in any one dish of distilled water.

4. To observe the rate at which films of coating materials change while kept under ordinary room conditions, the five materials reported in tables 4 and 5 were applied to gummed paper, each in nominal 3-mil and in nominal 6-mil thickness. Films were stripped, cut to size, and marked after 7 days of drying, which was about the earliest age at which all of them were hardened enough to

Table 5.--Effect of aging during storage indoors on the absorption of water, swelling, recovery after redrying, and solubility of films of five kinds of coating materials

The films were 1.5 by 2.5 inches in size, of the thickness indicated, were stripped from gummed paper 7 days after application, and were then stored for the additional times recorded in the first column before testing by immersion in distilled water at 69.5° F. for 72 hours. Negative values for swelling after redrying mean that the film shrank to less than the area before immersion.

Time in storage after stripping before test by immersion	Thinner films: Water absorbed (A)	Thinner films: Swelling (Increase in area) In water (AQ)	Thinner films: Swelling (Increase in area) Redried (AQ¹)	Thinner films: Solubility (Leached out by water) (S)	Thicker films: Water absorbed (A)	Thicker films: Swelling (Increase in area) In water (AQ)	Thicker films: Swelling (Increase in area) Redried (AQ¹)	Thicker films: Solubility (Leached out by water) (S)
Days	Milligrams	Percent	Percent	Milligrams	Milligrams	Percent	Percent	Milligrams
Linseed oil containing lead-manganese drier								
Thickness 3.4 mils, initial weight 192 milligrams					Thickness 6.1 mils, initial weight 353 milligrams			
0	28	5	-1.5	7.2	37	5	-1.4	10.0
5	.....	.....	.....	.....	25	5	- .4	10.6
12	20	3	- .7	5.8	22	4	-1.9	8.3
22	17	4	-1.3	6.7	27	3	-1.9	10.5
33	.....	.....	.....	.....	28	5	-1.8	11.9
53	81	10	- .9	10.8	30	5	-2.4	12.2
Paint L, p/nv 0.30 (white lead paint)								
Thickness 2.9 mils, initial weight 461 milligrams					Thickness 6.1 mils, initial weight 1023 milligrams			
0	27	9	+ .3	6.7	33	5	- .6	9.7
5	20	6	+ .4	7.1	30	4	- .8	10.8
12	19	7	0.	6.1	28	4	- .7	11.9
22	15	6	- .2	6.3	25	3	- .7	12.6
33	14	5	- .7	7.4	27	3	- .8	12.8
53	15	4	-1.1	6.4	24	3	- .8	12.3
Paint T_{420}, p/nv 0.30 (anatase titanium dioxide paint)								
Thickness 2.1 mils, initial weight 309 milligrams					Thickness 4.8 mils, initial weight 706 milligrams			
0	52	19	+1.3	7.0	74	10	- .6	10.0
5	47	18	+ .8	2.6	67	10	- .8	11.1
12	44	16	+1.1	5.3	66	9	- .3	10.3
22	39	15	+ .7	6.4	67	9	- .2	12.6
33	35	13	0	7.	64	9	- .5	12.1
53	32	10	- .6	8	103	10	0	17.1
Paint Z, p/nv 0.30 (zinc oxide paint)								
Thickness 2.2 mils, initial weight 316 milligrams					Thickness 5.5 mils, initial weight 795 milligrams			
0	68	40	3		332	58	25	14.7
5	56	38	4		283	55	24	13.9
12	62	38	7		251	45	17	11.1
22	61	36	7		230	41	17	12.4
33	61	34	7		230	40	16	9.0
53	61	31	6		217	37	16	10.2
Paint $TL_{20}Z_{20}$, p/nv 0.30 (titanium-lead-zinc paint)								
Thickness 2.9 mils, initial weight 351 milligrams					Thickness 6.6 mils, initial weight 791 milligrams			
0	167	47	16	10.5	245	31	11	17.3
5	137	42	14	7.0	203	24	7	12.6
12	125	34	10	4.8	178	18	5	10.9
22	99	28	8	4.4	160	18	6	10.1
33	88	26	7	5.4	144	16	4	9.7
53	79	24	8	4.9	124	15	5	10.0

be processed without damage. Six matched specimens for each material and thickness were prepared, weighed and measured, and then allowed to rest on a table top near a closed window of the laboratory with northern exposure. From each set of matched specimens one was taken immediately and one after 5, 12, 22, 33, and 53 days, respectively, for test by immersion in distilled water for 3 days.

All films except the 6-mil films of paint $TL_{20}Z_{20}$ lost in weight and shrank progressively throughout the period of storage before immersion in water. The 6-mil films of paint $TL_{20}Z_{20}$ gained slightly in weight for 33 days and swelled in area for 5 days before they began to decrease in weight and dimensions. All of the changes, however, were small when compared with the changes most paints undergo when immersed in water. Table 4 records the changes at the end of the 53-day storage period. Differences among the coating mate-

Table 6.--Absorption of water by free films of different coating materials during 72-hour immersion in distilled water at 89.5° F., both before and after exposure of the films to artificial weathering, expressed in percentage of the weight of linseed oil in the films

The films were 1.5 by 2.5 inches in size, of the thickness indicated, and were prepared on gummed paper. After 10 days for hardening, samples were stripped for the immersion test before weathering and the rest were exposed to ultraviolet light and periodic water spray in a weathering machine. Further samples were stripped for immersion tests after 400, 800, and 1,200 kilowatt hours of exposure, respectively. The weight of linseed oil in a 1.5- by 2.5-inch film 3.0 mils thick, W_o, is 171 milligrams; in a paint of p/nv 0.30 it is 120 milligrams, p/nv 0.36 it is 109 milligrams, p/nv 0.40 it is 102 milligrams.

Coating material	Pigment volume in paint p/nv	Thinner films: Initial thickness	Thinner films: Absorption of water, A/Wo, after exposure for indicated number of kilowatt-hours: 0	400	800	1200	Thicker films: Initial thickness	Thicker films: Absorption of water, A/Wo, after exposure for indicated number of kilowatt-hours: 0	400	800	1200
		Mils	Percent of the oil in film, by weight				Mils	Percent of the oil in film by weight			
Group 1 - Unpigmented coating materials											
Raw linseed oil	0	4.8	32	.....	62	42	6.5	21	11	12	12
Bodied linseed, Z3	0	6.3	9	5	16	22	15.5	4	5	6	8
Bodied linseed, Z6	0	6.4	7	11	16	33	16.0	3	4	6	8
Alkyd resin	0	4.1	8	6	10	13	7.6	6	4	5	7
Group 2 - Linseed oil paints free from zinc oxide											
Magnesium silicate	0.30	3.4	125	15	.....	.....	7.6	63	15	19	23
Calcium carbonate	.30	2.8	83	25	13	13	6.5	126	24	10	9
L	.30	3.0	18	26	29	28	6.4	12	11	13	15
L	.36	2.4	20	47	25	40	4.9	12	20	29	27
TL40	.30	3.1	74	13	13	.....	6.5	44	13	9	7
TL40	.40	2.6	58	22	25	.....	5.6	34	20	13	14
T420	.09	3.1	26	23	18	.....	4.2	20	32	12	10
T420	.30	2.1	49	15	16	.....	4.7	27	6	7	10
Average for group 2			57	23	20			42	18	14	14
Group 3 - Alkyd-resin paints											
T(are)	.30	3.4	44	18	12	9	4.6	42	23	19	17
T(are)	.36	2.9	57	32	13	10	3.9	73	32	27	12
T(are)	.40	2.9	79	29	14	13	4.3	79	39	26	13
Group 4 - Linseed oil paints containing zinc oxide and of p/nv 0.30											
Z	.30	2.6	149	114	67	67	5.9	96	40	25	20
LZ37	.30	3.2	100	69	.....	.....	6.6	70	32	21	23
$TL_{50}Z_{30}$	.30	3.2	130	68	43	28	6.6	84	40	20	15
$TL_{30}Z_{25}$	.30	3.2	130	81	54	62	6.8	78	39	22	19
$TL_{20}Z_{20}$	.30	3.3	127	61	41	37	6.7	86	37	22	16
$TL_{10}Z_{10}$	.30	3.3	154	59	51	48	6.3	96	36	24	16
TZ20	.30	3.3	142	90	75	71	6.8	97	46	43	25
Average for group 4			134	77	55	52		87	39	25	19
Group 5 - Linseed oil paints containing zinc oxide and of p/nv 0.30 or 0.40											
$TL_{30}Z_{25}$	.36	2.6	141	85	70	.....	5.6	69	47	26	21
$TL_{20}Z_{20}$	.36	2.7	148	79	51	46	5.6	86	49	26	24
$TL_{10}Z_{10}$	.36	2.9	142	62	49	45	6.1	82	39	23	17
TZ20	.36	3.0	178	82	70	61	5.9	106	59	46	43
TZ20	.40	3.0	173	81	67	.....	5.8	113	57	44	40
Average for group 5			156	78	61	51		91	50	33	31
Group 6 - Commercial paints											
No. 1 - TL_7Z_{23}	.35	2.9	137	74	56	50	6.1	87	41	28	28
No. 2 - $(TL_{23}Z_{18})_{134}$	.31	3.2	138	62	45	42	6.2	79	30	21	22
No. 3 - $(TZ_{19})_{126}$	.30	2.8	118	90	82	72	5.7	100	48	35	36
No. 4 - $(TZ_{16})_{122}$	.38	2.8	145	103	88	89	6.0	155	81	61	61
No. 5 - T_{139}(re)	.31	1.8	93	42	39	46	3.9	.....	33	26	29

rials were relatively small. In another preliminary test it was found that films of paint L and of paint TZ_{20} were still losing weight very slowly after 8 months in storage. Both of these films increased slightly in weight for about 50 hours after they were applied and then began to fall off steadily, but the loss after 8 months was only 27 milligrams for paint L and 17 milligrams for paint TZ_{20}.

Table 5 records the results of immersion tests made with the films after different periods of storage up to 53 days after stripping from the substrate (60 days after applying the coatings). Absorption of water and swelling diminished steadily for at least the first 3 weeks. After that time films of clear linseed oil and the thicker film of titanium dioxide paint began to increase again in absorption and swelling, whereas the other films continued to decline. The solubility of the films and the dimensional changes on redrying after immersion did not change very much for any of the films, although they diminished slightly with age for the films of zinc oxide and of titanium-lead-zinc paint. On the whole, differences among the paints at any age were much larger than the differences

Table 7.--Swelling (increase in surface area) of free films of different coating materials during 72-hour immersion in distilled water at 69.5° F., both before and after exposure of the films to artificial weathering

The measurements of swelling were made on the same films and at the same times as the measurements of absorption of water recorded in table 6. By way of comparison, flat-grain surfaces of southern yellow pine boards shrink 6.2 percent (practically all across the grain) in drying from the green condition to 6 percent moisture content. Most other softwoods shrink less than that.

Coating material	Pigment volume in paint p/nv	Swelling (increase in area)40, after exposure for indicated number of kilowatt-hours							
		Thinner films				Thicker films			
		0	400	800	1,200	0	400	800	1,200
		Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent
Group 1 - Unpigmented coating materials									
Raw linseed oil	0	22	.....	13	10	12	3	4	6
Bodied linseed, Z3	0	11	3	4	8	3	3	3	3
Bodied linseed, Z6	0	6	3	3	10	2	2	3	3
Alkyd resin	0	5	4	3	3	4	3	2	3
Group 2 - Linseed oil paints free from zinc oxide									
Magnesium silicate	0.30	27	4	.....	.....	16	3	8	10
Calcium carbonate	.30	26	11	3	4	54	9	2	2
L	.30	8	2	1	1	5	2	2	2
L	.36	8	3	2	1	4	2	2	2
TL40	.30	27	4	3	.....	15	4	2	2
TL40	.40	18	6	4	.....	8	6	3	4
T420	.09	13	8	7	.....	13	7	6	4
T420	.30	18	3	3	.....	10	2	1	1
Average for group 2		18	5	3		16	4	3	3
Group 3 - Alkyd-resin paints									
T(are)	.30	9	6	3	3	10	5	4	3
T(are)	.36	12	6	3	3	10	4	4	3
T(are)	.40	12	4	2	2	9	4	4	3
Group 4 - Linseed oil paints containing zinc oxide and of p/nv 0.30									
Z	.30	70	43	21	16	33	13	8	6
LZ37	.30	42	29	.....	.....	27	11	9	7
TL50Z30	.30	49	28	20	16	30	11	6	6
TL30Z25	.30	49	32	18	19	27	12	7	9
TL20Z20	.30	40	19	13	13	26	9	6	4
TL10Z10	.30	47	17	16	12	29	9	6	5
TZ20	.30	57	35	29	25	40	16	11	10
Average for group 4		51	29	19	17	30	12	8	7
Group 5 - Linseed oil paints containing zinc oxide and of p/nv 0.30 or 0.40									
TL30Z25	.36	46	27	13	.....	18	12	7	6
TL20Z20	.36	45	25	15	14	22	12	7	7
TL10Z10	.36	38	18	12	11	19	8	5	4
TZ20	.36	56	31	23	21	36	18	15	15
TZ20	.40	53	27	19	.....	30	20	14	17
Average for group 5		48	26	16	16	25	14	10	10
Group 6 - Commercial paints									
No. 1 - TL7 Z23	.35	38	24	17	14	24	10	18	9
No. 2 - (TL23Z18)134	.31	35	18	11	10	19	8	5	5
No. 3 - (TZ19)126	.30	26	20	17	21	17	8	6	7
No. 4 - (TZ16)122	.38	55	38	29	27	49	26	22	19
No. 5 - T139(re)	.31	3	2	1	1	.....	1	1	0.3

Table 8.--Swelling efficiency of water for the free films reported in tables 6 and 7

The swelling efficiency is the swelling recorded in table 7 divided by the absorption of water per unit weight of oil in the film recorded in table 6, that is, $\Delta V \div A/W_o$.

Coating material or group of materials as classified in tables 6 and 7	Average swelling efficiency for the group after exposure for indicated number of kilowatt-hours							
	Thinner films				Thicker films			
	0	400	800	1,200	0	400	800	1,200
	Percent				Percent			
Group 1 - Unpigmented materials	80	61	27	29	72	48	46	43
Group 4 - Zinc-containing paints of p/nv 0.30	39	39	35	35	37	31	31	35
Group 5 - Zinc-containing paints of p/nv 0.36 or 0.40	31	33	27	29	27	27	29	30
Group 6 - Commercial zinc-containing paints	28	30	27	27	25	25	25	27
Group 2 - Zinc-free paints other than white lead	34	30	23	28	38	29	31	29
Group 3 - Alkyd-resin paints	19	22	21	26	16	14	17	22
White lead paints, L p/nv 0.30 and 0.36	43	9	6	5	38	18	13	15
Commercial paint No. 5 ("breather type")	3	4	2	2	....	3	4	1

brought about by aging of any one kind of paint. For the subsequent studies, films were allowed to harden for 10 days after application before they were stripped from the substrate and were then submitted to immersion tests within 3 days.

Tests of 32 Oils and Paints Before and After Artificial Weathering

Large specimens of the 32 coating materials on substrates of gummed paper were prepared, each material in nominal 3-mil and 6-mil thicknesses. After 10 days for hardening, a small sample was cut from each large specimen to be stripped and tested immediately by immersion in water. The remaining portions of the large specimens were placed at once in the artificial weathering machine, operated with periodic spraying with water. Each large specimen was further sampled for stripping and testing after 400, after 800, and after 1,200 kilowatt-hours of exposure (approximately 5, 10, and 15 days of continuous operation). A second complete set of specimens spread on tinplate instead of gummed paper was exposed in the weathering machine at the same time in order to determine the weight of soluble material leached from each specimen by the water spray during the course of the artificial weathering.

Absorption of Water: The absorption of distilled water on 72-hour soaking of the free films before and after each stage of artificial weathering is reported in table 6. The weight of water absorbed by each free film is expressed in percentage of the weight of linseed oil in the film, that is, $100A/W_o$, where W_o is the weight of oil in the film. That is considered a more significant basis for comparing the different paints and film thicknesses than the absorption in milligrams of water, A, because absorption and swelling are believed to reside primarily in the oil in the film. It would be very misleading, of course, to express the absorption in percentage of the total weight of film in view of the great variation in specific gravity of different pigments. Thus the weight of a free film 1.5 inches long, 2.5 inches wide, and 3 mils thick is approximately 171 milligrams for unpigmented linseed oil, 270 milligrams for calcium carbonate paint of p/nv 0.30, and 499 milligrams for white lead paint of p/nv 0.30.

All of the free films tested absorbed distilled water in significant quantity. For all of the paints in which there were pigments, the newly prepared and unweathered films absorbed much more water than the artificially weathered films did. The first 400 kilowatt-hours of weathering usually effected greater reduction in swelling than the next 400 kilowatt-hours did, but the last 400 kilowatt-hours produced so little further change as to suggest that a minimum had been reached. Some films, in fact, absorbed more water after 1,200 than after 800 kilowatt-hours of exposure. Films of clear oils without pigments, with the possible exception of the bodied linseed oil of viscosity Z6, passed through a minimum of absorption after 400 kilowatt-hours and usually absorbed more water after 1,200 kilowatt-hours than they did before exposure to weathering.

The bodied linseed oils initially were much less absorptive than the raw linseed oil, but after weathering the differences became small. The alkyd resin was only slightly less absorptive than the bodied linseed oil of viscosity Z6.

Paint made with magnesium silicate in raw linseed oil absorbed more water than the unpigmented oil did, especially so before the films were weathered. On the other hand, the calcium carbonate paint, although high in absorption at the outset, became less absorptive than unpigmented oil after weathering. Pure titanium dioxide paint, T_{420}, was initially slightly more absorptive and, after weathering, slightly less absorptive than raw linseed oil.

Pure white lead paint, L, at the outset had a lower absorption than any other paint and a lower absorption than raw linseed oil. Weathering produced relatively little change in the absorption of pure white lead paint, so that, in the end, it still remained less absorptive or, in the thicker film, only slightly more absorptive than raw linseed oil.

Zinc oxide, on the other hand, whether the sole pigment in a paint or present to the extent of as little as 10 percent of the total pigment by volume, very greatly stimulated absorption of water by free films, particularly when the films were unweathered. Thus pure zinc oxide paint, Z, and titanium-zinc paint, TZ_{20}, absorbed about 5 times as much water initially as raw linseed oil did, and remained 2 to 4 times as absorptive after weathering. The presence of white lead along with zinc oxide usually reduced the absorptiveness somewhat, but the stimulating effect of zinc oxide was dominant over the

moderating effect of white lead even when there was 1.7 times as much white lead as zinc oxide in the paint.

Paints of pigment volume 0.36 or 0.40 usually absorbed a little more water in proportion to their oil content, although slightly less in proportion to their volume than the corresponding paints of pigment volume 0.30, despite the fact that much of the oil in the former was bodied oil, whereas all the oil in the latter was the more absorptive raw oil.

Of the five commercial paints tested, the four that contained zinc oxide proved high in absorption, comparably so with the laboratory-made paints of similar composition. The fifth commercial paint, advertised as resistant to moisture blistering, was decidedly less absorptive than the others but was more absorptive than the paints made in the laboratory with no lead or zinc pigments and alkyd-resin vehicle.

Swelling in Water: Table 7 records the swelling, ΔQ (increase in area of surface), of the free films caused by the absorption of water reported in table 6. In general, the swelling runs approximately parallel to the absorption of water, as would be expected. The relations already discussed for absorption therefore apply also to swelling, except that commercial paint No. 5 exhibited disproportionately low swelling for the amount of water it absorbed. Possible reasons for the peculiar behavior of this paint are discussed further on.

The swelling of the free paint films may well be compared with the swelling of wood on which such paints might be used. Flat-grain boards of southern yellow pine change 6.6 per-

Table 9.--Solubility of free films of different coating materials during 72-hour immersion in distilled water at 69.5° F., determined while making the measurements of absorption and swelling recorded in tables 6 and 7, and expressed in percentage of the weight of linseed oil in the films

Coating material	Pigment volume in paint p/nv	Solubility in water, B/Wo, after exposure for indicated number of kilowatt-hours: Thinner films: 0	400	800	1200	Thicker films: 0	400	800	1200
		Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent
Group 1 - Unpigmented coating materials									
Raw linseed oil	0	7.0	.....	9.6	10.9	3.9	2.5	2.0	7.0
Bodied linseed, Z3	0	4.0	2.6	4.7	7.0	1.4	1.2	2.0	3.0
Bodied linseed, Z6	0	3.4	2.3	3.9	7.9	1.0	.9	1.7	2.6
Alkyd-resin	0	7.0	2.9	3.4	4.4	3.2	.8	2.1	2.3
Group 2 - Linseed oil paints free from zinc oxide									
Magnesium silicate	0.30	7.5	5.8	.....	.....	3.6	3.0	5.5	5.6
Calcium carbonate	.30	14.5	11.1	5.9	7.1	9.7	4.7	2.3	2.7
L	.30	4.7	5.8	6.6	9.0	3.3	2.7	2.8	2.9
L	.36	6.8	4.9	10.7	12.0	4.4	2.8	4.3	4.7
TL40	.30	5.4	6.6	3.3	.....	4.4	2.8	2.2	2.0
TL40	.40	6.5	9.8	5.0	.....	3.5	5.1	3.1	4.8
T420	.09	4.4	5.5	5.8	.....	4.5	4.1	5.0	3.0
T420	.30	5.5	7.2	9.3	.....	3.9	2.0	3.5	5.0
Average for group 2		6.9	7.1	6.7		4.7	3.4	3.6	3.8
Group 3 - Alkyd-resin paints									
T(are)	.30	8.3	4.8	5.6	3.9	4.2	3.5	4.5	3.2
T(are)	.36	5.6	5.3	6.0	6.8	3.2	3.0	4.3	2.9
T(are)	.40	4.9	5.3	6.2	7.0	3.2	3.3	4.5	.7
Group 4 - Linseed oil paints containing zinc oxide and of p/nv 0.30									
Z	.30	11.2	7.5	3.9	16.0	3.8	2.7	2.1	2.2
LZ37	.30	6.3	9.5	.....	.....	2.6	1.5	1.5	2.1
TL50Z30	.30	5.8	5.6	6.4	3.0	3.4	3.4	3.2	2.7
TL30Z25	.30	5.7	5.7	7.5	5.3	2.7	2.7	2.7	1.5
TL20Z20	.30	5.5	5.4	6.1	3.5	.7	1.6	3.2	2.1
TL10Z10	.30	5.1	6.4	8.6	6.6	4.0	1.8	3.2	2.2
TZ20	.30	8.2	7.0	7.8	7.0	4.8	2.5	3.7	3.1
Average for group 4		6.8	6.7	6.7	6.9	3.1	2.3	2.8	2.3
Group 5 - Linseed oil paints containing zinc oxide and of p/nv 0.36 or 0.40									
TL30Z25	.36	5.1	7.3	7.8	.....	2.8	3.9	5.0	2.0
TL20Z20	.36	4.5	7.3	10.0	8.0	4.0	3.5	3.2	3.7
TL10Z10	.36	5.4	6.6	8.7	4.5	4.2	2.5	2.9	3.0
TZ20	.36	7.1	14.9	10.9	13.2	3.0	9.7	2.9	3.6
TZ20	.40	8.0	7.3	10.5	.....	3.8	6.7	3.8	6.4
Average for group 5		6.0	8.7	9.6	8.6	3.6	5.3	3.6	3.7
Group 6 - Commercial paints									
No. 1 - TL7 Z23	.35	27.5	9.1	7.8	9.6	5.1	3.5	3.3	4.2
No. 2 - (TL23Z18)134	.31	6.6	7.9	4.1	4.3	3.9	2.1	1.7	3.7
No. 3 - (TZ19)126	.30	12.1	13.8	7.9	12.3	4.3	5.2	4.4	5.8
No. 4 - (TZ16)122	.38	23.6	19.0	25.6	31.8	12.4	7.2	6.4	12.8
No. 5 - T139(re)	.31	9.2	11.4	9.3	16.1	.....	6.0	6.4	6.8

cent in width (across the grain) and practically not at all in length (along the grain) between 6 percent moisture content and the green or thoroughly water-soaked condition. The moisture content of exterior lumber is seldom as low as 6 percent. The change in area is therefore 6.6 percent of the dry dimensions or 6.2 percent of the green dimensions. Most other woods used on houses swell less than southern yellow pine. Thus free films of most paints when newly prepared swell more than wood does on changing from the air-dry to the water-saturated condition. After weathering for some time, zinc-free paints usually swell less than wood does. Paints containing zinc oxide swell several times as much as wood does when the paints are new, and swell as much or more than wood does even after they have become well weathered. Of course, the coatings of paint must conform to the wood in length and width as long as the coatings remain in place, and to do so the coatings must change sufficiently in thickness to meet the required volumetric changes, a process that necessarily involves severe internal stresses in a rigid body.

To check that conclusion, dry 1/24-inch yellow-poplar veneer was painted in one case with two coats of paint L, p/nv 0.30, making a coating 3.6 mils thick when dry, and in another case with two coats of paint TZ_{20}, p/nv 0.30, making a coating 4.8 mils thick when dry. Suitable specimens were marked for measurement of length, width, and coating thickness (by observation of sharply cut edges in a microscope with micrometer eyepiece) and were then soaked in water for 2 days and remeasured while still wet. In surface area both paint coatings swelled 10 percent, chiefly across the grain of the wood, which is the expected dimensional change for thin veneer of yellow-poplar. In thickness the coating of paint L shrank 0.2 mil, but that of paint TZ_{20} swelled 2.7 mils. The result was qualitatively in agreement with the data of table 7, which give the swelling in area as 8 percent for paint L and 57 percent for paint TZ_{20} in free films about 3 mils thick after soaking 3 days. At the end of the soaking period the coating of paint TZ_{20} was beginning to form tiny blisters, but that of paint L was still entirely sound.

Among the paints reported in table 7, paints L, TL_{40}, and commercial paint No. 5 are known from past tests on laboratory blistering boxes and from experience on houses to be highly resistant to failures by blistering and peeling under conditions of so-called excessive moisture. Work reported by a large paint-industry laboratory indicates that the leadless and zincless alkyd-resin paints, T(are), are similarly resistant to such conditions. All of these paints are characterized by a low degree of swelling in water. On the other hand, all of the zinc-containing paints, which have a high degree of swelling, are known from past experience to be sensitive to moisture blistering and peeling. It may well be, then, that the degree of swelling in water is a useful measure of the ease with which a paint yields to blistering and peeling of this kind.

During the immersion tests the free films of those paints that exhibited a low degree of swelling remained flat and free from troublesome curling. Even after redrying they could be kept flat provided the absorbed water was allowed to evaporate equally rapidly from both faces of the film. In contrast, free films of paints that swelled greatly always had a marked tendency to curl, particularly near the edges of the films, and required very careful handling to straighten them out between glass microscope slides sufficiently to measure the dimensions. Such curling became still more marked during redrying. These differences in behavior correspond to the characteristic performance of the paints during the later stages of normal weathering. Once cracking sets in, paints that swell greatly also curl markedly at the cracked edges and tend toward scaling in large pieces, whereas paints of low degree of swelling, if they crack at all, usually curl very little and tend toward crumbling or flaking in tiny particles.

Extreme curling during immersion in water was exhibited by heterogeneous films made up of consecutive coats of paints of widely different swelling tendencies. Thus free films were prepared by applying in one case two coats of paint L, p/nv 0.30, followed by two coats of paint TZ_{20}, p/nv 0.30, and in the other case two coats of the TZ_{20} paint, followed by two of paint L. When the free films were soaked in distilled water for a few days, both curled into tight rolls much like rolls of wrapping paper. The two films curled in opposite directions, so that in both cases the highly swellable TZ paint was on the outside of the curled roll and in both cases the direction of last brushing of the paints during application was parallel to the axis of the roll. After the films were soaked for a week, the two layers of paint in each film began to separate and the TZ layer became wrinkled until eventually it was an easy matter to pull the two layers completely apart.

Some Paints Possess Grain: When free films swell while immersed in water, the increase in width, ΔB, usually differs from the increase in length, ΔL. (The length is always the direction in which the brush or doctor blade was last moved during application.) The ratio $\Delta B/\Delta L$ is not exactly reproducible quantitatively among different films of the same kind or even in different sections cut from the same large film; slight variations in the manner of application or in the way the film is immersed in water apparently exert measurable effects. But such vagaries are small in comparison with certain large differences among paints according as they do or do not contain pigments of strongly anisotropic shape. Acicular (rod-shaped) pigments evidently become oriented with their long dimensions parallel to the last direction in which the liquid paint flows before it hardens, and they retain their orientation in the hardened film even after prolonged weathering. Such orientation of acicular pigments imparts grain to the paint films that is roughly analogous to the grain in wood. It has long been observed in paint exposure tests at the Forest Products Laboratory and elsewhere that many paints, including enamels that form coatings entirely free of brush marks, crack on weathering with the predominant direction of the cracks roughly parallel to the direction in which the paint was last brushed. Since the last brushing of paint is normally parallel to the grain of the wood, it has usually been assumed that the grain of the wood controlled the direction of paint cracking by reason of the greater swelling of wood across than with the grain. The discoveries that many paints swell more than wood does, swell more across than with the last direction of flow, and therefore possess a grain of their own, confirms this Laboratory's earlier observations that it is the grain of the paint rather than the grain of the wood on which the direction of paint cracking commonly depends.

The observations of grain in free films may be briefly summarized by the following list of approximate ratios of transverse to longitudinal swelling, $\Delta B/\Delta L$, which are averages for the number of closely agreeing paints or coating materials indicated:

Kind of coating material	$\Delta B/\Delta L$
Magnesium silicate in linseed oil	2.10
Five commercial paints (all contained magnesium silicate)	1.87
Paint T(are) with all extender magnesium silicate	1.73
Seven TLZ paints with all extender magnesium silicate	1.60
Calcium carbonate (No. 1) in linseed oil	1.49
Paint T(are) with half the extender magnesium silicate and half calcium carbonate (No. 2)	1.45
Three TZ_{20} paints with half the extender magnesium silicate and half calcium carbonate (No. 2)	1.17

Kind of coating material	ΔB/ΔL
Paints L, Z, T(re), and LZ(re) with no extender	1.12
Paint T(re) with all extender calcium carbonate (No. 8)	.96
Four unpigmented vehicles (linseed oils and alkyd resin)	.95

Magnesium silicate (fibrous talc) is a markedly acicular pigment; it clearly imparted grain to all the paints in which it was used, including all five of the commercial paints. Calcium carbonate No. 1 was a pigment of very high oil absorption and an appreciable degree of acicularity that imparted significant grain to paint; but calcium carbonates No. 2, low in oil absorption, and No. 3, very low in oil absorption, were granular and imparted little or no grain to paint. All of the opaque pigments used, white lead, zinc oxide, and titanium dioxide, were effectively granular enough to produce little or no grain in paint, though some of them are available in somewhat acicular grades.

Swelling Efficiency of Water: In order to study the relation between degree of swelling and the quantity of water absorbed per unit weight of oil in the films, a factor that may be called the swelling efficiency was computed for all of the films listed in tables 6 and 7. The swelling efficiency is defined as the swelling in surface

Table 10.--Loss in weight by leaching with water spray during exposure of coatings on tinplate to artificial weathering, expressed as percentage of the weight of linseed oil in the films

Coating material	Pigment volume in paint p/nv	Thinner films: Thickness	Thinner films: Loss by leaching per unit weight of oil after exposure for indicated number of kilowatt-hours: 400	800	1,200	Thicker films: Thickness	Thicker films: Loss by leaching per unit weight of oil after exposure for indicated number of kilowatt-hours: 400	800	1,200
		Mils	Percent	Percent	Percent	Mils	Percent	Percent	Percent
Group 1 - Unpigmented coating materials									
Raw linseed oil	0	6.1	15.9	22.2	28.1	12.3	10.3	14.7	17.8
Bodied linseed, Z3	0	5.8	9.9	12.7	16.3	12.7	5.7	7.6	9.1
Bodied linseed, Z6	0	6.0	7.6	10.0	12.7	13.4	5.1	6.2	7.8
Alkyd-resin	0	6.3	4.2	6.2	6.4	11.8	2.9	3.9	3.6
Group 2 - Linseed oil paints free from zinc oxide									
Magnesium silicate	0.30	4.8	13.7	21.8	28.4	7.7	9.8	14.2	18.2
Calcium carbonate	.30	3.1	18.3	31.2	39.8	6.2	9.8	15.7	20.2
L	.30	4.2	13.0	21.1	27.0	7.2	7.2	11.9	16.2
L	.36	4.2	10.2	14.4	18.8	5.0	8.8	12.5	16.2
TL40	.30	4.9	14.0	23.7	31.0	7.7	7.6	13.0	16.8
TL40	.40	4.0	17.4	31.4	39.0	5.2	12.9	23.2	29.5
T420	.09	4.2	17.4	29.8	41.2	6.3	11.5	20.6	29.0
T420	.30	5.9	12.5	18.0	21.8	8.4	7.9	10.6	13.4
Average for group 2			14.6	23.9	32.1		9.4	15.2	19.9
Group 3 - Alkyd-resin paints									
T(are)	.30	3.4	5.6	7.8	11.8	6.9	1.9	1.4	1.9
T(are)	.36	4.3	5.1	7.4	7.3	6.2	3.6	5.3	6.6
T(are)	.40	4.2	5.3	8.3	10.3	6.1	4.0	5.6	6.6
Group 4 - Linseed oil paints containing zinc oxide and of p/nv 0.30									
Z	.30	2.8	8.9	19.9	26.5	6.8	3.0	5.8	8.1
LZ37	.30	4.6	3.9	8.4	11.6	8.2	1.3	4.0	5.1
TL50Z30	.30	5.0	4.8	6.1	7.6	8.4	2.3	2.6	3.1
TL30Z25	.30	5.4	4.8	7.0	9.3	7.6	2.8	4.0	5.5
TL20Z20	.30	4.7	5.3	6.8	8.9	7.9	3.2	3.4	3.9
TL10Z10	.30	3.9	8.1	11.5	14.6	6.5	4.5	5.8	7.2
TZ20	.30	4.1	6.4	11.3	14.4	8.2	1.8	3.8	4.6
Average for group 4			6.0	10.1	13.3		2.7	4.2	5.4
Group 5 - Linseed oil paints containing zinc oxide and of p/nv 0.36 or 0.40									
TL30Z25	.36	2.9	11.0	19.8	25.6	7.1	4.2	6.4	8.9
TL20Z20	.36	4.1	2.1	11.0	13.5	6.4	4.1	5.1	6.3
TL10Z10	.36	3.6	8.9	12.8	16.0	6.7	4.1	5.8	7.2
TZ20	.36	4.0	6.1	11.3	14.0	6.2	3.2	6.6	8.1
TZ20	.40	4.0	6.0	12.0	14.9	6.1	3.6	7.5	9.3
Average for group 5			6.8	13.4	16.8		3.8	6.3	8.0
Group 6 - Commercial paints									
No. 1 - TLZ23	.35	3.8	6.1	12.9	18.8	6.5	2.8	5.5	8.1
No. 2 - (TL23Z18)134	.31	4.6	5.0	8.6	12.1	7.0	1.8	2.5	5.6
No. 3 - (TZ19)126	.30	3.8	8.0	8.3	12.5	6.4	2.4	3.5	5.5
No. 4 - (TZ16)122	.38	4.2	4.9	9.8	14.5	7.0	2.3	4.5	7.0
No. 5 - T139(re)	.31	2.3	4.5	14.2	18.3	4.0	4.9	9.8	11.4

area, ΔQ, divided by the quantity of water absorbed per unit weight of oil in the film, A/W_o, that is, $\Delta QW_o/A$. Examination of the tabulated data then showed that the coating materials fell into certain groupings within which the swelling efficiencies were essentially the same. The groupings of coating materials were those that already appear in tables 6 and 9, except that the pure white lead paints in group 2 and commercial paint No. 5 differed from the other paints in their groups. Accordingly, table 8 lists the average swelling efficiencies for each group with the two exceptions omitted and listed separately.

All materials except commercial paint No. 5 and the alkyd-resin paints were swelled more efficiently by water when the films were freshly prepared than after weathering. Most of the reduction in efficiency from weathering was accomplished in 400 to 800 kilowatt-hours of exposure; often the efficiency after 1,200 kilowatt-hours was slightly higher than it had been after 800 kilowatt-hours. For the alkyd-resin paints, the initial swelling efficiency was lower than that of other paints except commercial paint No. 5, but the swelling efficiency for the alkyd-resin paints increased slightly after weathering. For thick films, the swelling efficiency was nearly always slightly lower than it was for thinner films, but the difference largely disappeared after weathering.

Unpigmented films were subject to higher swelling efficiency than other films when freshly prepared and, in the thicker films, throughout the weathering periods. For zinc-containing paints of pigment volume 0.30, the efficiency was slightly higher than for otherwise similar paints of pigment volume 0.36 or 0.40, but the differences in swelling efficiency were small among the zinc-containing paints of the higher pigment volume, the commercial zinc-containing paints, and the zinc-free paints other than weathered pure white lead paint.

Conspicuously unusual results were obtained with pure white lead paint and with commercial paint No. 5. For the latter, the swelling efficiency of water was slight at any stage in life. For the former, the swelling efficiency was as high as for other paints when freshly prepared, but on weathering the swelling efficiency for the thinner films of paint L quickly dropped to values nearly as low as those for commercial paint No. 5. The thicker films of white lead paint on weathering were swelled more efficiently than the thinner films but were far less swellable than other paints. "Breather-type" paints, such as commercial paint No. 5, are said to be physically porous by reason of voids in such pigments as diatomaceous silica or of interstices left unfilled by the vehicle. If so, they have a capacity for holding free water or for taking up part of the swelling of the oil internally without change in external dimensions. It is conceivable that white lead paint becomes physically porous on weathering because it is known that once it has passed well into the chalking stage the surface can no longer be restored to a glossy condition by rubbing as can be done with most other paints. MacGregor (*22*) postulated the development of such porosity during the weathering of some paints, although he did not believe that it occurs in white lead paint. At any rate, the low swelling efficiency of commercial paint No. 5 and of weathered paint L indicates clearly that such paints take up water in a manner that causes less swelling than is brought about in other paints.

Thickness of Free Films: In calculating the swelling efficiencies in table 8 it is tacitly assumed either that the thickness of free films does not change during swelling or that the thickness always changes proportionately to the area. The first assumption is certainly incorrect. The second may be true within reasonable limits but must be considered uncertain. For that reason some of the smaller differences in swelling efficiency recorded in table 8 may be misleading because they may be due chiefly to variations in the participation of thickness change in the total volumetric swelling.

It was hoped that it would be possible to measure changes in thickness as well as in length and width in these experiments, but all techniques tried so far for measuring swelling in thickness have proved too inexact for quantitative purposes. Plans for future work therefore include direct measurements of volumetric swelling of at least some of the paints and unpigmented vehicles.

All film thicknesses reported in the tables were calculated from the weight of the film, its area, and the density of the nonvolatile ingredients of the coating material while still in the liquid condition. Such computation involves an underestimation of the density of the coating material when dried and an overestimation of the film thickness because air-drying materials become measurably more dense during the process of drying (*9, 10*). Existing data, however, are inadequate for calculating the densities of the films after drying and weathering. For films of unpigmented raw linseed oil, the correction probably amounts to several tenths of a mil, but for the pigmented films, the corrections would be smaller. Actual measurements of thicknesses of the films before immersion in water confirmed the expected order of magnitude of the discrepancies.

Solubility of Free Films in Water: The quantity of soluble materials leached from the films during the determinations of absorption of water and swelling is recorded in table 9. All films tested yielded soluble materials. Thin films yielded more, in proportion to their oil content, than thick films of the same kind, as might well be expected from the greater specific surface of the thinner films. On the average, the solubility remained about as great after weathering as it was before, even though the weathering cycle involved enough spraying with water to remove much soluble material before the weathered films were subjected to immersion tests. This fact, together with the steady increase in solubility during the prolonged immersion tests reported in table 1, suggests that most, if not all, of the soluble substances reported in tables 1 and 9 were formed by reactions that took place while the films were immersed in water rather than before immersion.

The soluble ingredients leached from the unpigmented oils and from paints with insoluble, chemically inert pigments such as magnesium silicate and titanium dioxide, clearly originate in decomposition of the oxidized linseed oil in the films. The extract can be recovered from the soaking water by evaporation to dryness and is then seen to be an amorphous, glossy, amber-colored deposit that looks much like the clear material found under paint blisters of the "glossy-backed" type. When the paint contains white lead, the extract contains no more than a faint trace of lead, but the extract from paints containing zinc oxide has a substantial content of zinc, presumably as zinc salts of organic acids.

The differences in solubility among the various kinds of films recorded in table 9 were not large enough to require discussion at this time, except to point out that commercial paint No. 4 proved exceptionally high in solubility both initially and after weathering, and commercial paints Nos. 1 and 3 were unusually high when tested in the thinner films. No reason for such peculiar behavior is evident in the formulas printed on the labels of the paints.

Leaching of Coatings During Artificial Weathering: Much larger proportions of soluble substance were leached from many of the coatings by the water spray while in the weather-

ing machine than were extracted from the free films subsequently when they were immersed in water. Leaching during weathering was determined by exposing coatings applied on tared tinplate in the weathering machine side by side with the coatings on gummed paper, and by drying and weighing the coated tinplate specimens after each period of exposure. The leaching losses, expressed in percentage of the linseed oil in the coating, are reported in table 10.

Leaching losses were greater from thin than from thick coatings of the same kind of paint. Since the quantity of soluble material increased markedly during each successive interval of weathering, it is evident that the process of solubilization went on during the weathering, for all soluble material in the coatings when weathering began would surely have been extracted within the first 400 kilowatt-hours of exposure. Higher losses in the weathering machine than in 3-day immersion periods indicates that solubilization goes on faster when ultraviolet light and water act together than when water acts alone. (During one period of 400 kilowatt-hours, or 5 days, in the weathering machine the total time of subjection of the coatings to running water could not have exceeded half a day.)

Leaching losses from coatings free from zinc oxide, including white lead paint and unpigmented raw linseed oil, were notably greater than the losses from paints that contained zinc oxide. The result offers an explanation of the observation by Browne and Laughnan (6, 7) that white lead paint and titanium-lead paint waste away in coating thickness during the intervals between repaintings more rapidly than mixed-pigment paints that contain zinc oxide.

Tests of 10 Paints After Natural Weathering

Ten paints, the five commercial paints and five of those made in the laboratory, were applied in three-coat work by brushing on substrates of tinplate and of paper coated with silicone and were then exposed to natural weathering for 5½ months, from September 1952 to February 1953, facing south and sloped back at an angle of 45° from the vertical. At the end of the weathering period samples were cut, stripped from the substrates, and tested by immersion in distilled water for 72 hours. The results are reported in table 11.

The absorption, swelling, and solubility of the films exposed to natural weathering were reasonably similar to those obtained with the same paints by artificial weathering, tables 6, 7, and 9. All of the paints except pure white lead and commercial paint No. 5 were still swelling much more than southern yellow pine does even after weathering. At least for the present, it may be assumed that artificial weathering brings about changes in paint films of much the same kind as occur during natural weathering. Further results of natural weathering will be obtained when a longer period of time has elapsed. It is not possible to establish the relative rate of change by artificial and natural weathering, but the results suggest that 5½ months over a winter period are equivalent to no more than 400 kilowatt-hours in the artificial-weathering cycle used.

Table 11.--Absorption of water, swelling, and solubility of free films of five commercial and five laboratory-made paints after natural weathering for 5-1/2 months

The films were 1.5 by 2.5 inches in size, of the thickness indicated. For each paint averages are reported for four films, of which two were exposed on tinplate and two on siliconed paper. Free films were tested by immersion in distilled water at 69.5° F. for 72 hours.

Kind of paint	Pigment volume -in paint p/nv	Thickness of film	Absorption of water based on weight of oil in film A/W_o	Swelling (Increase in area) ΔQ	Swelling efficiency $\Delta QW_o/A$	Solubility, based on weight of oil in film S/W_o
		Mils	Percent	Percent	Percent	Percent
Commercial paints						
No. 1-TL_7Z_{23}	0.35	5.0	163	51	31	13.1
No. 2-$(TL_{23}Z_{18})_{134}$	.31	4.8	130	33	25	9.4
No. 3-$(TZ_{19})_{126}$	.30	4.0	128	24	18	15.2
No. 4-$(TZ_{16})_{122}$	.38	4.5	104	30	29	20.8
No. 5-T_{139}(re)	.31	2.5	99	5	4	6.7
Laboratory-made paints						
L	.30	3.3	23	2	8	6.4
LZ_{37}	.30	3.6	91	35	24	7.4
TZ_{20}	.30	3.9	126	46	36	12.7
TZ_{20}	.36	4.7	112	32	29	10.8
TZ_{20}	.40	3.6	100	26	26	11.0

Tests of Certain Paints After 16 Years of Natural Weathering

In 1936 a series of exposure tests was started at Madison in which wood panels were painted with 12 kinds of house paint and each paint was repainted at intervals, always with the same kind of paint used originally, until 1948, when painting ceased for 4 years while the results were being observed. As pointed out in other publications, (6, 7), most of the painting programs led to coatings of excessive thickness, which, if the paint contained zinc oxide, produced cross-grain cracking, curling, and scaling in relatively large pieces. Late in 1952 large chips of eight kinds of paints were collected for test by immersion in water. No paint free from zinc oxide yielded paint chips large enough for such study.

The chips collected were of various sizes and of irregular shapes. It therefore was not possible to cut them into the 1.5- by 2.5-inch or 2- by 2-inch specimens usually preferred; instead, chips were used very nearly in the sizes and shapes in which they were available. The chips selected were marked, dried, weighed and measured, immersed in distilled water for 72 hours, again weighed and measured while wet, dried over calcium chloride, and weighed and measured once more. The results are reported in table 12, in which the paints are listed in the order of decreasing content of white lead.

Although part of the paint in each of the chips was 16 years old and all of it was at least 4 years old, the chips still absorbed about as much water as

roughly similar paints did after moderate exposure to artificial weathering, as recorded in table 6. The swelling and swelling efficiency of water for the 16-year old paints were somewhat lower than the values in tables 7 and 8 for much younger paints; but when due account is taken of the great thickness of the old chips, their swelling cannot be considered much less striking than that of the younger paints after moderate weathering. Even after 16 years and in excessive thickness of film, some paints still swell more than flat-grain surfaces of southern yellow pine.

Conclusions

Free films of house paints when soaked in distilled water absorb surprisingly large amounts of water, often more than 1½ times the weight of linseed oil that the films contain. As a rule, the absorption of water causes marked swelling, which in free film finds expression in expansion of the surface area that for many paints may amount to more than 50 percent when the films are still young. Such swelling is several times as much as that of flat-grain surfaces of wood between the air-dried and the water-soaked conditions. Coatings firmly attached to wood must, of course, conform to the surface dimensions of the wood; the larger swelling of the coating must be accomplished by increase in coating thickness. Such accommodation of the dimensions of the swollen coating to the requirements of the substrate necessarily gives rise to large stresses within the coating, which, no doubt, have direct bearing on the phenomena of cracking, curling, and flaking in the normal weathering of coatings and on such abnormalities of coating behavior as blistering and peeling. Besides the absorption and swelling, water causes a leaching of water-soluble ingredients from paint films, apparently developed, at least in large part, by chemical reactions occurring while the paint films are in contact with water. Still larger losses of soluble ingredients occur during the weathering of paint coatings through the combined action of ultraviolet light and spraying with water.

For paint of any one kind, absorption and swelling are greatest when the free films have been freshly prepared. They decrease slightly with age even when the films are kept indoors in subdued light under dry conditions. Absorption and swelling usually decrease markedly on weathering either naturally or artificially, but even after 16 years of weather exposure some paints may still swell in water more than wood does.

Table 12.—Absorption of water, swelling, and solubility of paint chips from coatings exposed for 16 years on a test fence at Madison, Wis.

The paint chips were collected in 1952 from naturally loosened coatings of the "1936 Paint Maintenance Tests," which have been previously published (6, 7). The coatings on wood had been maintained by painting in 1936 and repainting at intervals until 1948, when the last coats of paint had been applied. The chips were of varying sizes and of the measured thicknesses indicated. They were tested by immersion in distilled water at 69.5° F. for 72 hours.

Kind of paint	Pigment volume in paint p/nv	Thickness of film (measured)	Absorption of water, based on weight of oil in film A/W_o	Swelling (increase in area) ΔQ	Swelling efficiency $\Delta QW_o/A$	Solubility, based on weight of oil in film S/W_o
		Mils	Percent	Percent	Percent	Percent
LZ_{23}	0.29	17.5	36	1.7	5	2.7
LZ_{37}	.29	13.4	18	1.6	9	1.7
$(LZ_{30})_{80}$	.29	10.3	35	3.2	9	2.7
$(TL_{28}Z_{28})_{116}$	.29	9.3	23	5.5	24	1.2
$(LZ_{15})_{33}$	.36	18.1	31	4.4	14	2.7
$(SL_{11}Z_{23})_{75}$	.29	15.1	48	12.9	27	2.7
$(TZ_{23})_{107}$	.29	11.3	54	7.6	17	2.9
$(TZ_{66})_{207}$(e)	.19	10.0	26	4.2	19	1.5

Paints in which there are markedly acicular (rod-shaped) pigments swell anisotropically and, in that sense, possess grain. The grain is produced by orientation of the acicular particles during the last stroking of the paint when it is being applied. As in wood, swelling is greater across the grain of the paint than it is along the grain. Grain in paint often expresses itself in the pattern of cracking or other defects that show up later when the paint becomes embrittled with age.

Although the absorption and swelling of free paint films clearly originate in the oil vehicle, they are markedly affected by the pigments, especially if the pigments are chemically reactive. Thus zinc oxide imparts greatly increased absorption and swelling, much greater than the absorption and swelling of films of unpigmented linseed oil. Such chemically inert pigments as titanium dioxide and magnesium silicate alter the absorption and swelling of oil only moderately. On the other hand, white lead markedly reduces both absorption and swelling, especially after the paints have begun to weather. When the paint contains both zinc oxide and white lead, the augmenting effect of the zinc oxide predominates even when the proportion of zinc oxide is relatively low.

There is evidence that paints of the so-called breather type, which are claimed to be unusually resistant to blistering and peeling by reason of a porosity of their coatings, may in fact make coatings with internal void spaces capable of holding free water without a proportionate swelling or, perhaps, of accommodating much of the swelling internally rather than externally. One of the commercial paints, which dried entirely without gloss, was found to absorb a substantial amount of water without undergoing much swelling in consequence. Likewise, pure white lead paint, after it had become weathered, swelled much less than would normally result from the amount of water it absorbed. It may well be that the resistance of such paints to moisture blistering comes from the low swelling rather than from the alleged ability to breathe by letting moisture readily pass out from the substrate through the coating.

Further studies of the absorption of water, swelling, and solubility of free films of house paints offer promise of explaining many of the phenomena of paint behavior that have so far been subject to great diversity of opinion, and of furnishing a tool for the search for better paints. But until such further studies have been made, and particularly until a connection between swelling of free films and blistering

of paint coatings has been established by direct experiment, it would be unwise to evaluate paints for practical use on the basis of the absorption of water and swelling of their free films.

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