Swelling of Paint Films in Water, II[1]

Absorption and Volumetric Swelling of Bound and Free Films Before and After Weathering

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Previous methods of studying swelling of paint films in water were improved by including measurements of volumetric swellings of both free films and bound films (coatings on glass). The new technique leads to more precise measurements and discloses information about the structure of the paint coatings.

A TECHNIQUE for measuring the volumetric swelling of bound films of house paint coated on glass as well as of free films was developed to supplement the measurements of absorption of water, swelling in area, changes on redrying, and loss of soluble ingredients previously described for free films. Although bound films absorb and swell somewhat less than free films do, films of some paints still display great sensitivity to water. Both artificial and natural weathering usually reduce absorption and swelling below the values for unweathered films; but the reduction takes place during the first few months of natural weathering or the equivalent and, thereafter, remains nearly constant for at least 16 years. Unweathered films swell at least 1 cubic centimeter for each gram of water absorbed; weathered films swell less, sometimes much less than 1 cubic centimeter for a gram of absorbed water. Swelling and redrying or weathering may develop voids within the films that can hold free water that does not contribute to swelling.

Introduction

A previous paper (3) reported measurements of the absorption of water by free films of house paints, the swelling of the films in surface area caused by absorption of water, the shrinking on subsequent redrying, and the loss of soluble ingredients while soaking in water. Some paints were found to swell several times as much as wood does, whereas others swell less than wood. Data were also presented on the effects on absorption and swelling of film thickness, time of contact with water, temperature and acidity or alkalinity of the water, aging of the films before soaking in water, and exposure of the paints to both natural and artificial weathering before testing them in water. But direct measurements of the changes in film thickness were not precise enough to permit calculation of the volumetric swelling.

Since the earlier paper was written, the experimental technique has been improved to measure directly the volume of the paint films before and after soaking in water and after redrying. From the changes in volume and in area, the changes in thickness can be calculated precisely. Volumetric swelling was measured both for free films and for coatings on glass (bound films). Volumetric swelling proves to be even more instructive than swelling in area. Among different paints, the volumetric and the areal swelling are not necessarily proportional to each other. Moreover, the volumetric swelling sometimes reveals changes in the internal structure of paint films that are not evident from the areal swelling.

The volume of a free film of paint was measured by weighing the film in air and again in distilled water (4). The difference in weight was the water displaced. Within the precision possible in this work, it was permissible to consider that a displacement of 1 gram of water at room temperature (70° to 75°) represented a volume of 1 cubic centimeter. The film of paint was weighed in air and in water immediately before immersion in water for the soaking test. Then, at the end of the soaking period, it was weighed in water and again in air after removing free water clinging to the surfaces. Finally, it was weighed in air and water for the third time after it had been redried in a desiccator over calcium chloride. Thus the initial volume, the swollen volume, and the volume after redrying and the densities in each of the three conditions could be calculated. The volume of coatings on glass was determined in a similar way by subtracting the previously determined weights of the glass in air and in water.

By use of a chainomatic balance, it was possible to immerse, weigh, and remove a dry film from the water in 140 to 260 seconds. Tests showed that in 5 minutes, even the most highly absorptive paints take up no more than 1 percent of the water they absorb in 3 days of soaking.

Changes in length and width of the free films were measured before and after swelling and after redrying as in the work previously reported (3). From the volume and area of the film, the thickness at each stage of the soaking tests was easily computed.

Paints and Vehicles Tested

The paints tested were chosen from the list of those used in the experiments on swelling in area previously published. The composition of the paints is expressed by volume in the short notation first described by Browne (1) and more recently described in this journal (2). Two clear vehicles without any pigment were tested; namely, raw linseed oil containing lead-manganese naphthenate drier and bodied linseed oil of viscosity Z6 containing the same kind of drier. Single-pigment paints made in the laboratory were as follows:

Magnesium silicate in raw linseed oil, pigment volume (p/nv) 0.30

[1] A contributed paper.

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

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Basic carbonate white lead in raw linseed oil, paint L, p/nv 0.30
Anatase titanium dioxide in raw linseed oil, paint T_{420}, p/nv 0.30
Zinc oxide in raw linseed oil, paint Z, p/nv 0.30

Of the single-pigment paints, only the white lead paint was a practicable house paint; the others are of scientific interest only. Multiple-pigment paints, all of them practicable house paints but made in the laboratory, were as follows:

Paint TL_{40}, p/nv 0.30, anatase titanium dioxide, basic carbonate white lead, magnesium silicate, and calcium carbonate in raw linseed oil
Paint LZ_{37}, p/nv 0.30, basic carbonate white lead and zinc oxide in raw linseed oil
Paint $TL_{60}Z_{30}$, p/nv 0.30,)
Paint $TL_{30}Z_{25}$, p/nv 0.30,)
Paint $TL_{20}Z_{20}$, p/nv 0.30,)
Paint $TL_{10}Z_{10}$, p/nv 0.30,)
anatase titanium dioxide, basic carbonate white lead, zinc oxide, and magnesium silicate in raw linseed oil; same ingredients but differing proportions
Paint TZ_{20}, p/nv 0.30, anatase and rutile titanium dioxide, zinc oxide, magnesium silicate, and calcium carbonate in raw linseed oil
Paint TZ_{20}, p/nv 0.36, the same pigments as paint TZ_{20}, p/nv 0.30, but in a mixture of raw and bodied linseed oil

Commercial paints of open formula were tested as follows:

No. 1—TL_2Z_{23}, p/nv 0.35, leaded zinc oxide, titanium-calcium, titanium dioxide, and magnesium silicate in raw and bodied linseed oil
No. 2—$(TL_{23}Z_{18})_{134}$, p/nv 0.31, basic carbonate white lead, basic silicate white lead, zinc oxide, titanium dioxide, and magnesium silicate in linseed oil
No. 3—$(TZ_{19})_{126}$, p/nv 0.30, zinc oxide, titanium dioxide, and magnesium silicate in linseed and soya oils
No. 4—$(TZ_{16})_{122}$, p/nv 0.38, zinc oxide, titanium dioxide, and magnesium silicate in bodied linseed oil
No. 5—T_{112}(re), p/nv 0.39, titanium dioxide, mica, magnesium silicate, and aluminum stearate in tung oil varnish and bodied linseed oil

Commercial paints 1 to 4 were chosen because they are widely sold in all parts of the United States and are reasonably representative of the range in composition of the commercial first-grade paints with which the public is familiar. Commercial paint No. 5, although not yet so well known, was of particular interest for this study because it is a so-called breather-type of paint that is unusually resistant to moisture blistering.

Methods of Experiment

Unpigmented oils were applied by brushing in successive coats until enough had been applied, determined by weighing, to form a coating of the desired thickness. Pigmented paints were applied by drawing down manually with a Bird doctor blade over a substrate held firmly on a Bird suction plate. Each paint was applied in a single coat at a predetermined wet-film thickness achieved when necessary by use of suitable shims.

Coatings were allowed to dry in the laboratory near a closed window that faced north. Drying continued for 10 days, after which those to be weathered were mounted in an Atlas Weatherometer or on suitable racks placed on a roof of the Laboratory, where the coatings were exposed to natural weather, facing south and sloped back at an angle of 45° from the vertical. Coatings that were not weathered were tested immediately after the 10-day drying period.

Bound Films (Coatings on Glass): In order to compare the absorption of water and swelling of bound films with free films, a rigid substrate that is not measurably affected by water was needed. Glass was chosen for the purpose. Microscope slides 45 mils thick, 1½ inches wide, and 3 inches long were measured for exact thickness with an Ames dial gage and sorted into matched sets actually 46, 45.5, or 44.5 mils thick, plus or minus 0.2 mil. Close control of slide thickness was necessary to permit control of wet-film thickness while applying paint with the doctor blade. Each of the selected microscope slides was marked with an identification number, carefully cleaned and dried in a dessicator over calcium chloride, and then weighed in air and again when submerged in distilled water at the temperature of the room in order to determine its volume by displacement.

After the coatings on glass had been applied and had dried for 10 days, those for testing before weathering were promptly subjected to the soaking test. The others were weighed to determine the initial coating weight. They were then fastened by suitable clips to aluminum-painted plywood backboards of a size to fit the slots in the drum of an Atlas Weatherometer, and the artificial weathering was started. For the purpose of these experiments, the artificial-weathering cycle consisted of constant exposure to visible and ultraviolet light from a flaming carbon arc filtered through Corex D glass, which passes only that portion of the ultraviolet spectrum that is present in normal sunshine out of doors. As the Weatherometer drum rotated, the test specimens passed three times an hour under specially designed sprays that wet the painted surfaces gently with a fine mist of water in sufficient quantity to drain down and drip copiously from the bottom edges of the specimens. After passing the sprays, the water left clinging to the paint evaporated before the specimens moved more than halfway around to the position of the water sprays.

Test data are given in tables 1, 2, 3, and 4. When the data for tables 1 and 3 were obtained, Madison city water, which is very hard, was supplied to the sprays in the Weatherometer. As will be discussed farther on, this led to false results with some paints for the loss in weight during weathering. For that reason, the Weatherometer was later equipped with a tank and pump to supply distilled water to the sprays. The data in table 2 were obtained in the revised Weatherometer.

One set of specimens was exposed in the Weatherometer until the watt-hour meter registered 600 kilowatt-hours, which required about 7½ days. A second set of specimens was exposed for 1,200 kilowatt-hours, or about 15 days. On removal from the Weatherometer, the specimens were dried over calcium chloride and submitted to the soaking test. From the weight before exposure in the Weatherometer and the first weighing in air to start the soaking test, the change in weight of the paint coating during artificial weathering was computed.

Free Films: The paints and oils that were tested as films bound on glass, where the changes in volume necessarily took place entirely by changes in thickness of coating, were tested also as free films that could change in all three dimensions. The free films were prepared by spreading the paints as coatings on gummed paper that had previously been saturated with linseed oil and allowed to dry. For any 1 paint, the coatings on glass and those on gummed paper were always made on the same day, and the 2 types of specimens were taken through the program of exposure and testing contemporaneously. It was practicable to expose the coatings on gummed paper in the Weatherometer without loss of adhesion because the periods of exposure to water spray were too short for the dampness to penetrate through the coatings to soften the layer of gum.

The free films were stripped from the gummed paper after the 10-day drying period for unweathered specimens or after exposure in the Weatherometer by soaking in water for a few minutes until the gum was dissolved. From the free films, test specimens 1½ by 2½

Table 1.--Data for bound films (coatings on glass) of 2 vehicles and 8 paints, each in 2 coating thicknesses, before and after artificial weathering--changes in density while drying and while weathering, changes in weight while weathering (hard water used in Weatherometer water sprays), absorption of water, volumetric swelling, and swelling efficiency when soaked in distilled water for 3 days, changes in volume on redrying, and weight of soluble ingredients lost while soaking

Paint or clear vehicle (density of nonvolatile while liquid)	Time exposed to artificial weathering	Weight change while weathering S_1/V_o	Before soaking: Density	Before soaking: Film thickness T_o	Absorption of water A/V_o	Swelling in volume ΔV_s	Swelling efficiency $\Delta V_s V_o/A$	Redried: change in volume ΔV_r	Weight loss while soaking S_2/V_o
	Days	Percent		Mils	Percent	Percent	Percent	Percent	Percent
Raw linseed oil (0.933)	0		1.15	2.7	17.5	18.3	104	-3.7	4.6
	0		1.11	5.5	10.3	10.7	104	-2.6	2.8
	7-1/2	-33.1	1.20	2.0	27.6	25.5	93	-4.2	7.6
	7-1/2	-16.5	1.15	5.1	10.8	9.9	92	-2.2	3.5
	15	-72.4	1.25	1.4	40.3	38.0	94	-6.6	8.1
	15	-27.2	1.16	5.1	10.9	10.3	94	-2.6	2.9
Bodied linseed oil, Z6 viscosity (0.970)	0		1.12	2.5	10.6	12.0	113	-2.9	3.1
	0		1.10	5.3	5.7	6.7	117	-1.7	1.5
	7-1/2	-22.1	1.19	2.1	26.8	23.8	89	-3.1	6.2
	7-1/2	-13.2	1.15	4.6	13.3	11.5	87	-1.1	3.2
	15	-42.6	1.23	1.8	38.0	34.5	91	-3.3	5.4
	15	-18.3	1.16	4.6	13.4	12.5	94	-1.9	2.8
Magnesium silicate, p/nv 0.30 (1.515)	0		1.70	3.3	40.7	41.9	103	-2.9	3.2
	0		1.64	6.4	17.0	17.8	105	-1.5	1.1
	7-1/2	-11.0	1.82	2.9	11.2	9.4	84	-2.0	3.8
	7-1/2	-5.1	1.73	6.5	7.4	6.6	89	-1.0	1.6
	15	-19.4	1.94	2.6	10.0	7.9	79	-2.8	4.2
	15	-8.1	1.74	6.4	7.0	6.2	89	-1.1	1.2
Basic carbonate white lead, L, p/nv 0.30 (2.705)	0		3.00	3.5	8.1	8.7	107	-2.0	3.0
	0		2.90	6.8	4.4	5.3	120	-1.3	1.0
	7-1/2	-6.3	3.22	3.0	17.0	15.6	92	-1.8	3.2
	7-1/2	-3.8	3.02	6.9	7.7	7.2	94	-.7	1.3
	15	-12.2	3.39	2.7	18.3	15.8	87	-1.5	3.6
	15	-5.3	3.08	6.5	10.6	10.0	94	-1.1	1.1
Titanium dioxide, anatase type, T_{420}, p/nv 0.30 (1.820)	0		2.02	2.6	23.5	24.9	106	-3.0	3.4
	0		1.92	6.8	7.3	8.2	112	-1.3	.8
	7-1/2	-29.5	2.86	2.6	10.5	8.6	82	-1.3	2.7
	7-1/2	-7.2	2.00	7.1	4.6	3.2	70	-.6	1.0
	15	-33.0	2.40	2.6	13.0	10.2	79	-3.0	4.8
	15	-12.3	2.08	6.7	4.6	3.6	78	-1.1	1.3
Zinc oxide, Z, p/nv 0.30 (2.345)	0		2.51	2.8	62.7	62.0	99	+1.2	2.3
	0		2.44	6.1	21.9	22.5	103	-.4	.1
	7-1/2	+2.8	2.57	2.2	26.9	21.9	82	-.8	2.7
	7-1/2	+2.3	2.48	6.8	9.2	8.4	91	0	.7
	15	-2.1	2.74	2.8	18.5	16.9	91	-1.8	4.2
	15	+2.9	2.52	6.5	8.3	8.1	98	-1.5	.8
Titanium-lead-zinc, $TL_{50}Z_{30}$, p/nv 0.30 (2.370)	0		2.56	3.8	26.6	27.0	101	-.4	1.1
	0		2.46	8.3	17.5	17.9	102	-.2	0
	7-1/2	+2.0	2.64	3.8	14.0	12.7	91	-1.1	1.5
	7-1/2	+3.3	2.50	8.2	6.1	5.4	89	-.6	1.5
	15	+7.1	2.70	3.9	13.4	7.9	59	-1.9	3.1
	15	+4.4	2.55	8.0	6.5	5.9	91	-.1	.4
Titanium-zinc, TZ_{20}, p/nv 0.36 (1.870)	0		2.00	3.6	31.6	31.3	99	-1.3	1.4
	0		1.96	6.7	18.4	18.8	102	-.8	.4
	7-1/2	+7.6	2.05	3.5	18.9	16.4	87	-2.4	2.8
	7-1/2	+3.2	2.01	6.6	11.7	11.2	96	-1.5	1.7
	15	+12.1	2.14	3.4	21.2	19.1	90	-2.0	3.9
	15	+5.0	2.05	6.5	13.1	12.2	93	-.5	1.0
Commercial paint No. 1, TL_7Z_{23}, p/nv 0.35 (2.005)	0		2.14	4.4	30.4	30.5	100	-1.5	1.9
	0		2.11	7.9	18.8	19.2	102	-1.0	.6
	7-1/2	+5.7	2.18	4.7	20.1	18.9	94	-8.3	8.0
	7-1/2	+2.0	2.15	8.8	8.1	7.3	90	-.5	1.2
	15	+2.0	2.28	4.3	14.5	12.9	89	-1.2	3.4
	15	+2.1	2.18	8.5	8.2	7.7	94	-.6	.9
Commercial paint No. 5, T_{112}(re), p/nv 0.39 (1.688)	0		1.85	3.1	16.3	17.2	106	-1.6	1.5
	0		1.82	4.9	10.6	11.3	107	-1.6	1.0
	7-1/2	-4.9	1.92	3.2	9.0	7.7	86	-1.9	3.1
	7-1/2	-3.9	1.87	5.3	7.6	6.4	84	-1.0	1.7
	15	+4.3	2.00	3.1	9.9	5.5	56	-1.4	4.3
	15	+2.1	1.93	5.2	6.3	3.2	51	-.4	2.1

inches were cut with a template and razor blade. Each specimen was marked in black drawing ink with an identification mark and suitable reference lines for measuring length and width under a traveling microscope. The specimens were then dried over calcium chloride before starting a soaking test.

Coatings on gummed paper have the disadvantage that the changes in weight of the coatings while undergoing weathering cannot be measured reliably because the paper, the linseed oil in the paper, and perhaps the gum undergo changes in weight at the same time. In later work, therefore, coatings for exposure either in the Weatherometer or to natural weathering were spread on tinplate. The tinplate specimens could be weighed before and after exposure with reasonable assurance that any change in weight occurred in the coating. After exposure and reweighing, the coatings were stripped from the tin-

Table 2.--Data for free films of 2 vehicles, 11 laboratory-made, and 5 commercial paints before and after artificial weathering for 15 days and after natural weathering for 6 months and for 12 months--losses in weight while weathering (distilled water used in Weatherometer water sprays), changes in density, absorption of water, swelling in volume, area, and thickness and swelling efficiency when soaked in distilled water for 3 days, changes in volume, area, and thickness on redrying, and weight of soluble ingredients lost while soaking

Paint or clear vehicle (density of nonvolatile while liquid)	Weathering: Kind	Weathering: Time	Weight loss while weathering: S_1/V_o	Before soaking: Density	Before soaking: Film thickness T_o	Absorption of water: A/V_o	Swelling increase: In volume ΔV_s	Swelling increase: In area ΔQ_s	Swelling increase: In thickness ΔT_s	Swelling efficiency $\Delta V_s V_o/A$	Redried change: In volume ΔV_r	Redried change: In area ΔQ_r	Redried change: In thickness ΔT_r	Weight loss while soaking S_2/V_o
		No.	Percent		Mils	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent
Raw linseed oil (0.933)	None	0		1.11	3.1	21.8	22.0	9.8	10.8	101	-6.0	-4.9	-1.3	5.8
	Artificial	1/2	(1)	1.17	3.7	20.4	20.5	4.4	15.5	100	-2.2	-1.7	+.3	2.9
	Natural	6	80.4	1.16	2.7	24.2	16.6	8.7	9.7	69	-2.0	-3.8	+1.9	6.1
	....do....	12	92.0	1.22	2.5	25.0	28.3	3.3	24.4	113	-10.4	-2.5	-8.0	6.8
Bodied linseed oil, Z6 viscosity (0.970)	None	0		1.10	3.6	9.0	9.2	6.1	1.4	102	-4.9	-2.6	-2.2	5.1
	Artificial	1/2	(1)	1.16	4.1	26.1	27.5	10.1	14.9	98	-.7	+2.1	+.2	1.8
	Natural	6	41.4	1.19	3.2	7.5	8.3	4.1	1.3	110	-3.3	-.1	-2.8	2.8
	....do....	12	41.1	1.19	3.3	8.2	7.7	2.4	2.1	94	-3.2	-1.1	-1.5	3.1
Magnesium silicate, p/nv 0.30 (1.515)	None	0		1.68	2.9	56.2	56.1	15.9	31.5	100	-3.8	+2.2	-6.1	4.5
	Artificial	1/2	19.0	1.89	2.4	9.9	9.8	5.0	6.7	99	-2.1	-3.4	+.1	3.4
	Natural	6	33.8	1.80	3.9	6.4	6.7	2.2	2.5	105	-2.5	-.3	-2.3	2.1
	....do....	12	39.6	1.81	3.8	6.7	6.4	1.6	2.6	96	-2.6	0	-2.6	1.7
Basic carbonate white lead, L, p/nv 0.30 (2.705)	None	0		2.84	3.9	10.7	10.8	6.0	1.6	101	-3.3	+1.0	-3.6	4.8
	Artificial	1/2	21.0	3.21	5.5	12.4	12.3	2.0	10.0	99	-1.2	-.8	+.2	1.8
	Natural	6	26.5	3.28	3.9	11.0	8.8	3.9	5.1	80	+2.0	+.4	+1.5	2.7
	....do....	12	28.3	3.28	4.1	10.8	6.9	3.0	3.2	64	-.9	0	-1.0	3.5
Titanium-lead, TL_{40}, p/nv 0.30 (2.010)	None	0		2.22	4.0	29.3	29.9	12.7	11.8	102	-3.9	+1.6	-5.3	5.1
	Artificial	1/2	(2)											
	Natural	6	51.6	2.67	3.1	27.2	26.3	9.1	17.0	97	-.3	+2.7	-2.6	1.8
	....do....	12	53.7	2.65	3.3	28.2	27.0	8.4	16.4	96	-.8	+1.3	-2.1	2.3
Titanium dioxide, anatase type, T_{420}, p/nv 0.30 (1.820)	None	0		2.02	2.7	25.6	25.3	13.5	6.9	99	-4.1	+1.0	-4.7	5.2
	Artificial	1/2	55.1	2.12	5.6	10.2	9.5	2.5	6.2	93	-1.3	-.7	0	2.3
	Natural	6	85.2	2.32	2.9	20.9	18.1	7.4	8.8	87	-2.4	-.8	-1.4	2.9
	....do....	12	107	2.39	2.8	12.8	9.1	3.2	3.5	71	-2.3	-.9	-1.1	4.7
Zinc oxide, Z, p/nv 0.30 (2.345)	None	0		2.48	3.7	74.6	74.6	42.7	20.0	100	-3.9	+9.4	-12.0	5.6
	Artificial	1/2	12.1	2.77	2.2	40.0	32.4	11.7	18.9	81	+.6	+2.2	-.5	8.2
	Natural	6	16.3	2.54	4.1	44.4	38.3	14.5	20.9	86	+29.4	+2.6	+26.5	7.5
	....do....	12	15.8	2.58	4.0	33.8	29.7	14.6	12.6	88	-.8	+4.3	-4.9	7.3
Lead-zinc, LZ_{37}, p/nv 0.30 (2.563)	None	0		2.74	3.9	68.0	81.0	32.6	24.0	119	-2.8	+6.4	-8.5	4.6
	Artificial	1/2	7.7	2.84	4.2	37.6	34.6	20.0	32.7	92	-2.0	+7.6	-1.7	1.7
	Natural	6	20.7	2.94	4.0	42.5	37.8	19.5	14.9	89	+22.5	+2.6	+20.0	7.1
	....do....	12	21.8	2.90	4.1	41.3	36.6	19.3	12.3	89	-3.1	(3)		8.3
Titanium-lead-zinc, $TL_{50}Z_{30}$, p/nv 0.30 (2.370)	None	0		2.52	3.9	61.2	60.5	33.5	19.3	99	-2.0	+7.7	-9.0	3.8
	Artificial	1/2	13.0	2.74	3.4	36.6	34.8	13.7	34.0	95	-1.0	+4.2	-.9	2.5
	Natural	6	16.3	2.69	3.9	38.1	37.0	17.2	14.6	97	-2.9	+5.0	-7.4	6.9
	....do....	12	20.2	2.68	4.0	36.6	34.5	18.0	11.4	94	-3.0	+5.9	-8.2	7.1

plate by floating them face down on mercury until the tin became amalgamated and the coatings could be stripped off. The free films were then cut to size, marked, and equilibrated over calcium chloride in preparation for soaking tests.

Methods of Expressing Results

During exposure to natural or artificial weathering, there is normally a loss of weight of coatings by leaching of water-soluble ingredients and sometimes by erosion (chalking). Some paints reported in table 1 gained in weight during artificial weathering for a reason that is explained farther on. In either case, the change in weight, which was the difference in weight of coating in grams immediately before exposure and afterward, is represented by the symbol S_1. There was a further loss in weight from all coatings and films during the 3-day soaking test that was revealed by the difference in weight in air just before immersion in water and the weight in air after redrying over calcium chloride. This loss in weight in grams from leaching of soluble ingredients is represented by the symbol S_2.

All coatings and films absorbed water during the 3-day soaking test. The absorption of water in grams, represented by A, was the difference between the weight in air on removal from water and the weight after redrying over calcium chloride. If the initial rather than the final dry weight were taken for the subtrahend, the absorption would be underestimated by the weight of soluble ingredients lost during the soaking. By the method used, there is still a small error from loss of volatile ingredients other than water during the period of redrying in a dessicator, but such loss of volatile matter is much less than the loss of soluble substances while soaking.

The great variation in density among the paints and vehicles studied raises a problem of finding a meaningful method of expressing comparative results for absorption of water, A, and the losses, S_1 and S_2. In the previous paper (3), A and S_2 were reported in percent by weight of the oil present in the film calculated on the assumption that the film at the time of test retained the same percentage of oil as the nonvolatile portion of the liquid paint from which the film had been made. The assumption is at best a reasonable approximation for unweathered films and becomes decreasingly reliable as the films are weathered. Volumetric measurements offer a much better basis of expression; namely, the volume in cubic centimeters of the film or coating at the beginning of the soaking test, represented by the symbol V_o. Accordingly, the absorption of water is now reported as $(A/V_o) \times 100$, which is the percent by volume if 1 gram of water is taken as 1 cubic centimeter. The losses S_1 and S_2 are expressed similarly; $(S/V_o) \times 100$, or the grams of substance of unknown composition lost per 100 cubic centimeters of film.

During the 3-day soaking in water, the initial volume V_o increased to a larger volume V_s; and when the film was redried, the volume shrank to V_r. As a rule, V_r was less than V_o, presumably by the volume of soluble ingredients leached out while soaking. In such cases, the percent swelling in volume, ΔV_s, was calculated as $100\ (V_s - V_r)/V_o$; and it was observed that the density of the redried film returned nearly to the density before soaking or

Table 2.--Data for free films of 2 vehicles, 11 laboratory-made, and 5 commercial paints before and after artificial weathering for 15 days and after natural weathering for 6 months and for 12 months--losses in weight while weathering (distilled water used in Weathermeter water sprays), changes in density, absorption of water, swelling in volume, area, and thickness and swelling efficiency when soaked in distilled water for 3 days, changes in volume, area, and thickness on redrying, and weight of soluble ingredients lost while soaking--continued

Paint or clear vehicle (density of nonvolatile while liquid)	Weathering: Kind	Weathering: Time	Weight loss while weathering: ing S_1/V_o	Before soaking: Density	Before soaking: Film thickness T_o	Absorption of water A/V_o	Swelling increase: In volume ΔV_s	Swelling increase: In area ΔQ_s	Swelling increase: In thickness ΔT_s	Swelling efficiency $\Delta V_s V_o/A$	Redried change: In volume ΔV_r	Redried change: In area ΔQ_r	Redried change: In thickness ΔT_r	Weight loss while soaking: ing S_2/V_o
		Mo.	Percent		Mils	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent
Titanium-lead-zinc, $Ti_{30}Z_{25}$, p/nv 0.30 (2.110)	None	0		2.25	3.9	69.2	67.8	33.3	84.8	98	-1.5	+8.6	-9.4	4.8
	Artificial	1/2	9.2	2.40	4.4	32.1	31.1	15.0	30.7	97	-.4	+4.6	-.2	.9
	Natural	6	11.1	2.38	5.3	37.7	35.5	16.6	34.8	94	-1.6	(3)	(3)	6.5
	....do....	12	24.3	2.40	3.9	39.2	35.3	15.1	16.0	90	-1.7	+5.4	-6.9	7.4
Titanium-lead-zinc, $Ti_{20}Z_{20}$, p/nv 0.30 (1.960)	None	0		2.10	3.7	71.0	70.5	31.5	88.6	99	-1.8	+8.0	-8.9	3.0
	Artificial	1/2	10.3	2.27	4.3	42.4	40.1	18.3	40.0	95	+.9	+7.3	+.9	1.8
	Natural	6	19.1	2.20	3.6	49.0	44.1	15.2	25.2	90	+14.5	+2.9	+11.6	5.7
	....do....	12	15.6	2.22	4.1	41.4	38.2	14.3	19.3	93	-2.1	+4.6	-6.4	6.3
Titanium-lead-zinc, $Ti_{10}Z_{10}$, p/nv 0.30 (1.900)	None	0		1.92	4.1	59.3	59.5	27.3	84.0	100	-2.4	+6.7	-8.7	3.7
	Artificial	1/2	12.7	2.15	3.9	38.8	36.8	15.6	35.8	95	+1.2	+8.6	+1.0	1.5
	Natural	6	27.5	2.03	3.4	54.6	47.0	18.2	24.3	86	+29.2	+6.0	+22.5	7.6
	....do....	12	27.9	2.06	3.8	43.4	40.6	13.8	22.1	94	-2.1	+4.3	-6.0	5.8
Titanium-zinc, TZ_{20}, p/nv 0.30 (1.728)	None	0		1.86	4.0	118	109	56.7	31.8	93	-2.3	+17.4	-17.2	5.3
	Artificial	1/2	8.2	1.93	4.6	48.3	45.7	21.0	45.5	95	+2.2	+10.8	+2.2	1.6
	Natural	6	16.6	1.95	4.4	69.0	68.6	28.4	31.6	99	+30.9	(3)	(3)	6.4
	....do....	12	20.0	1.95	4.1	61.8	60.1	27.2	23.2	97	-3.6	+11.6	-13.5	7.4
Commercial paint No. 1, Ti_7Z_{23}, p/nv 0.30 (2.005)	None	0		2.16	3.4	92.0	91.0	36.3	37.3	99	-3.4	+10.5	-12.4	7.5
	Artificial	1/2	(1)	2.26	2.2	46.9	45.4	18.3	22.4	97	-.9	+5.8	-6.4	4.2
	Natural	6	15.5	2.24	4.9	63.0	59.7	27.5	25.0	95	+1.3	+13.4	-10.6	5.8
	....do....	12	18.1	2.25	5.2	48.7	46.6	19.8	22.2	96	-1.1	+9.9	-9.6	5.0
Commercial paint No. 2, $(Ti_{23}Z_{18})_{134}$, p/nv 0.31 (1.960)	None	0		2.10	3.6	72.4	71.4	25.8	33.9	99	-3.0	+8.0	-9.9	4.9
	Artificial	1/2	(2)											
	Natural	6	11.3	2.19	5.8	47.2	45.2	15.1	26.5	96	+1.3	+5.2	-3.4	2.4
	....do....	12	22.0	2.21	4.7	46.0	42.7	15.4	23.4	93	-.4	+7.5	-7.4	3.4
Commercial paint No. 3, $(TZ_{19})_{126}$, p/nv 0.30 (1.745)	None	0		1.87	3.1	90.5	92.0	22.1	53.8	102	-4.7	+4.8	-9.1	9.5
	Artificial	1/2	(2)											
	Natural	6	13.4	1.95	4.8	82.0	77.7	7.5	65.5	95	+15.7	+1.0	+15.1	8.1
	....do....	12	16.5	1.95	4.9	38.8	36.2	6.7	25.3	94	-2.7	+1.8	-4.0	9.0
Commercial paint No. 4, $(TZ_{16})_{122}$, p/nv 0.38 (2.000)	None	0		2.18	3.4	84.2	84.3	44.1	22.0	100	-8.4	+13.5	-18.5	19.9
	Artificial	1/2	(2)											
	Natural	6	18.4	2.23	3.8	41.6	27.3	8.4	18.3	66	+2.5	-.2	+2.7	34.5
	....do....	12	21.2	2.26	3.9	42.5	40.3	8.5	24.1	95	-6.0	-.5	-5.4	27.4
Commercial paint No. 5, T_{112}(re), p/nv 0.39 (1.688)	None	0		1.92	1.6	23.2	24.1	5.5	14.5	104	-3.7	-.4	-4.0	4.2
	Artificial	1/2	(1)	2.08	1.6	11.0	4.0	2.0	1.3	36	+1.2	0	+1.2	6.4
	Natural	6	48.5	2.06	1.9	10.3	9.4	2.5	4.7	91	-2.5	+.3	-2.6	2.9
	....do....	12	62.6	2.06	2.0	10.1	9.7	2.0	4.1	96	-3.3	-.6	-2.6	3.2

[1] Not determined.

[2] These paints were not tested after artificial weathering with distilled water in the Weathermeter sprays.

[3] Data lacking because the redried films were too badly curled and too brittle to permit measurements.

became slightly greater. But with films of some paints, the redried volume V_r was greater than the initial volume V_o, and the density after redrying remained significantly less than the density before soaking, despite loss of soluble ingredients. To avoid gross underestimation in such cases, the volumetric swelling was calculated by the formula $\Delta V_s = 100(V_s - V_o)/V_o$. The percentage change in volume after redrying was always calculated from the formula $\Delta V_r = 100(V_r - V_o)/V_o$. It was negative or positive accordingly as V_r was greater or less than V_o.

The relation between the percent absorption, A/V_o, and the volumetric swelling, ΔV_s, was conveniently studied by computing the swelling efficiency, which was ΔV_s divided by A/V_o times 100, expressed in percent. As a rule, the swelling efficiency was not far from 100 percent, which meant that each gram of water absorbed increased the volume of the film by 1 cubic centimeter. After weathering, the swelling efficiency tended to decrease somewhat, and for a few paints it decreased markedly. There are paints not included in these tests for which the swelling efficiency is less than 100 percent even before weathering. Low values of swelling efficiency indicate that the film contains voids that can take up water without causing any swelling, a condition that was predicted from theoretical considerations by MacGregor (7).

Changes in area of free films were calculated from the changes in length and width between lines ruled on the surface of the films about an inch apart in the central portion of the films. Curling at the edges of films that swell greatly made it impracticable to make measurements between edges. It was shown in the previous paper that films of many paints swell more across the grain of the paint, determined by the last direction of flow of the paint during application, than with the grain. After computing the percentage change in area of the marked portion of the films, the change in total area was calculated on the assumption that the whole film changed in the same proportion as its marked central portion. Taking Q_o, Q_s, and Q_r as the areas before soaking, after soaking, and after redrying, respectively, the areal swelling, ΔQ_s, and the change in area on redrying, ΔQ_r, were computed analogously to the changes in volume from the formulas: $\Delta Q_s = 100(Q_s - Q_r)/Q_o$ if Q_r was less than Q_s, or $\Delta Q_s = 100(Q_s - Q_o)/Q_o$ if Q_r was greater than Q_o and $\Delta Q_r = 100(Q_r - Q_o)/Q_o$.

The thickness of the film in mils (1 mil = 0.001 inch) before soaking was calculated from the volume and area, $T_o = 61\ V_o/Q_o$ where V_o is in cu. cms., Q_o in square inches, and 61 is a con-

Table 3.--Data for free films of 2 vehicles and 8 paints, each in 2 coating thicknesses, before and after artificial weathering--changes in density while drying and while weathering, absorption of water, swelling in volume, area, and thickness and swelling efficiency when soaked in distilled water for 3 days, changes in volume, area, and thickness on redrying, and weight of soluble ingredients lost while soaking

Paint or clear vehicle (density of nonvolatile to artificial while liquid)	Time exposed to weathering	Before soaking: Density	Before soaking: Film thickness T_o	Absorption of: water A/V_o	Swelling increase: In volume ΔV_s	Swelling increase: In area ΔQ_s	Swelling increase: In thickness ΔT_s	Swelling efficiency $\Delta V_s V_o/A$	Redried change: In volume ΔV_r	Redried change: In area ΔQ_r	Redried change: In thickness ΔT_r	Weight loss while soaking S_2/V_o
	Days		Mils	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent
Raw linseed oil (0.933)	0	1.11	3.1	21.8	22.0	9.8	10.8	101	-6.0	-4.9	-1.3	5.8
	0	1.11	5.6	10.8	11.0	6.5	1.1	102	-5.2	-1.6	-3.6	5.2
	7-1/2	1.20	1.7	45.6	38.3	25.8	21.2	84	+.4	-14.4	+17.0	9.4
	7-1/2	1.17	3.9	16.1	16.5	6.2	6.6	103	-3.5	+1.2	-4.6	5.0
	15	(1)										
	15	1.17	3.7	20.4	20.5	4.4	15.5	100	-2.2	-1.7	+.3	2.9
Bodied linseed oil, 26 viscosity (0.970)	0	1.11	3.6	9.0	9.2	6.1	1.4	102	-4.9	-2.6	-2.2	5.1
	0	1.10	5.4	7.5	8.0	5.4	1.3	107	-3.7	-2.2	-1.5	3.4
	7-1/2	1.18	3.1	45.2	44.8	16.1	23.1	99	-1.5	+3.7	-4.9	4.0
	7-1/2	1.15	4.7	18.5	18.6	6.2	9.5	100	-2.3	-.3	-2.3	3.2
	15	(1)										
	15	1.16	4.1	28.1	27.5	10.1	14.9	98	-.7	+2.1	+.2	1.8
Magnesium silicate, p/nv 0.30 (1.515)	0	1.68	2.9	56.2	56.1	15.9	31.5	100	-3.8	+2.2	-6.1	4.5
	0	1.65	6.7	33.0	33.1	11.8	16.8	100	-2.8	+1.2	-4.0	2.9
	7-1/2	1.82	2.6	7.2	7.0	3.2	1.9	97	-2.1	-.6	-1.9	3.4
	7-1/2	1.71	6.5	5.1	5.3	1.7	3.1	104	-.6	0	-.6	.6
	15	1.89	2.4	9.9	9.8	5.0	6.7	99	-2.1	-3.4	+.1	3.4
	15	1.74	6.3	5.8	5.2	1.9	2.9	90	-.5	0	+.3	.6
Basic carbonate white lead, L, p/nv 0.30 (2.705)	0	2.98	2.8	10.0	9.2	4.7	1.1	92	-3.9	-.2	-3.6	6.1
	0	2.98	6.4	6.5	6.6	3.6	2.3	101	-2.0	-1.0	-1.1	2.6
	7-1/2	3.28	2.5	19.1	19.1	2.0	15.7	100	-1.8	-.8	-1.2	2.9
	7-1/2	3.10	6.1	7.5	7.9	1.8	4.9	105	-1.7	-.3	-1.5	1.8
	15	3.47	2.1	13.4	10.7	1.8	10.0	80	-.1	-.8	+.6	3.6
	15	3.21	5.5	12.4	12.3	2.0	10.0	99	-1.2	-.8	+.2	1.8
Titanium dioxide, anatase type, T_{420}, p/nv 0.30 (1.820)	0	2.02	2.7	25.6	25.3	13.5	6.9	99	-4.1	+1.0	-4.7	5.2
	0	1.97	6.7	12.2	12.5	7.5	3.4	102	-2.6	-1.0	-1.9	2.5
	7-1/2	2.34	2.1	8.8	9.6	3.6	5.3	109	-1.7	-1.0	-1.0	3.8
	7-1/2	2.07	6.0	4.3	4.2	2.2	1.7	98	-.5	-.3	-.3	1.1
	15	(1)										
	15	2.12	5.6	10.2	9.5	2.5	6.2	93	-1.3	-.7	0	2.3
Zinc oxide, Z, p/nv 0.30 (2.345)	0	2.46	2.5	96.7	96.5	65.9	16.8	100	-3.5	+24.6	-22.4	6.3
	0	2.46	6.2	46.4	46.2	24.9	16.0	100	-1.5	+5.1	-6.0	1.9
	7-1/2	2.70	2.4	46.2	41.0	13.7	24.6	89	+2.6	+2.8	0	6.1
	7-1/2	2.51	6.2	9.2	9.4	4.5	4.7	102	0	+.4	-.5	.6
	15	2.77	2.2	40.0	32.4	11.7	18.9	81	+.6	+2.2	-.5	8.2
	15	2.53	5.7	10.0	8.8	3.0	5.3	88	-.4	+.1	-.2	1.1
Titanium-lead-zinc, $TL_{50}Z_{30}$, p/nv 0.30 (2.370)	0	2.53	2.9	61.5	61.1	38.0	15.6	99	-2.1	+10.2	-10.7	3.7
	0	2.51	7.1	30.8	30.8	15.2	12.4	100	-1.3	+1.8	-3.1	1.3
	7-1/2	2.65	2.8	27.3	32.2	11.4	17.7	118	-.9	+3.1	-4.0	2.5
	7-1/2	2.57	7.0	10.0	9.7	5.6	3.6	97	-.4	+1.0	-1.3	.5
	15	2.71	2.6	33.2	30.9	17.4	8.5	93	+.8	+5.6	-2.3	2.8
	15	2.58	6.6	8.5	7.9	3.3	5.0	93	0	-.1	+.5	.5
Titanium-zinc, TZ_{20}, p/nv 0.36 (1.870)	0	2.00	2.5	90.3	86.8	58.5	18.0	96	-.3	+20.1	-17.0	5.0
	0	1.97	5.6	44.9	44.4	23.8	15.3	99	-1.6	+4.6	-5.7	2.3
	7-1/2	2.08	2.3	60.8	58.8	18.8	33.8	97	+15.3	+4.6	+10.0	2.9
	7-1/2	2.00	5.6	16.9	16.1	5.8	10.0	95	-.2	-.5	+.2	1.1
	15	2.87	2.2	71.0	69.3	21.4	39.8	98	+4.7	+6.0	+.5	2.9
	15	2.03	5.4	18.4	17.6	6.7	10.8	96	+.5	+1.3	0	1.0
Commercial paint No. 1, TL_7Z_{23}, p/nv 0.30 (2.005)	0	2.15	2.5	71.2	67.5	36.6	22.7	95	+1.8	+10.1	-7.5	6.9
	0	2.15	5.6	39.1	38.8	15.3	19.0	99	-1.8	+2.5	-4.1	2.8
	7-1/2	2.25	2.3	43.0	43.6	20.3	18.7	101	-.8	+7.4	-7.7	2.1
	7-1/2	2.18	5.8	12.2	12.0	4.6	6.7	98	-.3	+.5	-.9	.8
	15	2.26	2.2	46.9	45.4	18.3	22.4	97	-.9	+5.8	-6.4	4.2
	15	2.18	5.4	14.8	14.0	6.2	7.2	95	-.5	+.9	+.2	1.3
Commercial paint No. 5, T_{112}(re), p/nv 0.39 (1.688)	0	1.92	1.6	23.2	24.1	5.5	14.5	104	-3.7	-.4	-3.6	4.2
	0	1.84	3.9	19.9	20.5	4.0	14.1	103	-2.5	-.4	-2.3	2.3
	7-1/2	2.03	1.6	7.6	.6	2.3	0	8	-3.5	-.2	-3.2	3.5
	7-1/2	1.89	4.3	7.0	6.4	1.6	3.7	91	-1.5	-.3	-1.6	2.0
	15	2.08	1.6	11.0	4.0	2.0	1.3	36	+1.2	0	+1.2	6.4
	15	1.92	4.2	7.6	4.5	2.0	2.4	59	+1.0	0	+1.0	2.5

[1] These films were too badly damaged by weathering to be stripped from the gummed paper substrate as free films suitable for soaking tests.

version factor to give the answer in mils. For films bound on glass, the thickness necessarily changed during soaking and redrying by the same percentage as the change in volume, provided the coating remained attached to the glass substrate. But free films usually change in area as well as in thickness. The thickness when swollen was therefore calculated from the formula

$T_s = 61\ V_s/Q_s$, and the thickness after redrying from the formula

$T_r = 61\ V_r/Q_r$. The percent change in thickness on swelling was

$\Delta T_s = 100(T_s - T_o)/T_o$, and the percent change on redrying was

$\Delta T_r = 100(T_r - T_o)/T_o$.

Comparison of Bound and Free Films Before and After Artificial Weathering

Table 1 records the results of experiments with bound films (coatings on glass), and table 3 the contemporaneous results with free film of the same vehicle and paints. Each vehicle or paint was tested both bound and free in two different thicknesses of film because thin films change more rapidly or to greater extent than thick films. In making comparisons, therefore, both thick and thin films should be considered and allowance made for variations in thickness.

Changes in Density: The 10-day-old coatings of all of the vehicles and paints were markedly higher in density than the nonvolatile portion of the liquid coating material from which they were made. Part of the increased density came from absorption of oxygen while drying, but others (4, 5) have shown that most of it came from contraction in volume, which for raw linseed oil after 10 days may amount to nearly 13 percent (4). On weathering, the density of the coatings continued to increase materially. Part of the increase in density on weathering of the pigmented coatings may be attributed to loss of volatile and soluble products of decomposition of the linseed oil vehicle, and to the leaving behind of a higher proportion of the pigments, which are much denser than the vehicle. But there was also some loss of pigment by chalking or by leaching of soluble salts formed by reaction of some pigments with decomposition products of the vehicle. After allowance for such losses, however, it is clear that much of the increase in density was due to further contraction in volume of the coatings.

The increase in density while drying was often slightly more for thin coatings than for thick ones. The difference was greater for coatings on glass than for coatings on gummed paper. Such effect of coating thickness was to be expected because the oxygen necessary for drying enters the coating at its surface, affects the top of the coating sooner than the bottom, and takes longer to penetrate to the bottom of a thick than of a thin coating. The gummed paper substrate may have been somewhat permeable to oxygen, whereas the glass substrate was not. On weathering, thin coatings always gained in density more rapidly than thick coatings; particularly so when the coating contained opaque pigments to keep the light of the Weatherometer from penetrating readily to the bottom of the coating.

Absorption of Water: Free films nearly always absorbed more water during the 3-day soaking test than bound films on glass of the same paint and comparable thickness. The few exceptions to this rule were with paints of relatively low absorption, and the differences between the free and bound films were small. Although both faces of the free films were exposed to water, whereas water had access to 1 face only of the bound films, the period of exposure, 3 days, was so long in consideration of the thinness of films tested that it is very difficult to attribute the greater absorption by free films to the greater area of surface exposed. There was ample time for water to penetrate to the center of the thickest films. Moreover, the differences between free and bound films are as striking for the thinner films of each paint as they are for the thicker films. The more probable explanation, therefore, is that restraint of the bound films by their attachment to the glass substrate developed internal stresses of sufficient magnitude to reduce the absorption of water below the quantity taken up when the film was free to swell in all three directions.

Nevertheless, even bound films of some paints absorb surprisingly large quantities of water. The greatest absorption recorded was nearly 63 percent by volume for the unweathered thinner film of zinc oxide paint. The corresponding free film absorbed 90 percent. The smallest absorption by a bound film was 4.4 percent by the thicker unweathered film of white lead paint for which the corresponding absorption by the free film was 6.5 percent. Unweathered films of raw linseed oil absorbed 17.5 percent for the thicker and 10.3 percent for the thinner films when bound, compared with 21.8 percent for the thinner, and 10.8 percent for the thicker film when free.

Table 4.--Data for chips of naturally loosened paint from coatings on wood applied on a test fence at Madison, Wis., in 1936, maintained by periodic repainting with the last repainting in 1948, collected in 1952, and kept indoors until tested in 1954

Paint	Density	Film thickness T_o	Absorption of water A/V_o	Swelling in volume ΔV_s	Swelling efficiency $\Delta V_s V_o/A$	Redried: change in volume ΔV_r	Weight loss while soaking B_2/V_o
		Mils	Percent	Percent	Percent	Percent	Percent
Lead-zinc, LZ_{23}	2.80	17.5	23.7	21.0	89	+0.2	1.6
Lead-zinc, LZ_{37}	2.87	13.4	23.4	18.1	77	-1.5	2.2
Lead-zinc-inert, $(LZ_{30})_{80}$	2.74	10.3	26.5	21.3	80	-1.3	2.1
Lead-zinc-inert, $(LZ_{15})_{33}$	2.32	18.1	18.8	17.3	92	+.8	.4
Titanium-lead-zinc, $(TL_{28}Z_{28})_{116}$	2.67	9.3	29.9	26.9	90	-.7	1.6
Titanium-zinc, $(TZ_{23})_{107}$	2.33	11.3	45.2	41.4	91	+1.1	2.9
Titanium-zinc, $(TZ_{66})_{207}$(e)	2.20	10.0	30.6	26.6	87	-.8	1.7
Lithopone-lead-zinc, $(8L_{11}Z_{23})_{75}$	2.31	15.1	24.5	21.7	89	-.6	1.7

The absorptions by different kinds of paints and by thick and thin films of any one paint when in the bound condition ran parallel, at least qualitatively, to the corresponding absorptions by the free films. Thus, if one paint took up more water than another when bound, it did so also when free. Thin films always absorbed more water than thick films of the same paint whether the films were bound or free.

Artificial weathering increased the absorption of both bound and free films of unpigmented raw linseed oil and bodied linseed oil at comparable film thickness. White lead paint exhibited the same effect of weathering, but at a lower level of absorption. All of the other paints absorbed much less water after weathering than they did before. The first 7½ days of artificial weathering usually effected a greater change in absorption than the second 7½ days did; in fact, there was often a minimum of absorption after 7½ days of weathering and a slight increase again after 15 days.

Swelling in Water: The volumetric swelling, ΔV_s, of all of the unweathered vehicles and paints in tables 1 and 3 paralleled and approximated reasonably closely the absorption of water. For unweathered, bound coatings, the swelling efficiencies were between 99 and 120 percent, and for free coatings between 92 and 107 percent. The exceptionally high and exceptionally low values were for films of very low absorption and swelling, for which the experimental errors were therefore greatest. All of the water absorbed by the unweathered films, therefore, resulted in swelling, presumably because there were no voids in the films that could

become filled with water without increase in film volume. The fact that the swelling efficiency often slightly exceeded 100 percent may be attributed for the present to underestimation of the absorption because of evaporation of absorbed water while the soaked films were being weighed in air; although the possibility that the volumetric swelling does at times actually exceed the volume of water absorbed will be considered in a subsequent publication in this series.

After weathering, the swelling efficiency of bound films was always less than 100 percent. For commercial paint No. 5, the efficiency dropped as low as 51 percent. A similar trend was evident for the free films, but it was not so marked, except for commercial paint No. 5, and it was not so consistent. Some of the water absorbed by weathered films often fails to cause swelling, presumably because voids have been developed within the weathered films that take up water without changing the volume. Apparently, bound films, which can swell or shrink in thickness only, reveal the porosity developed by weathering more fully than do the free films, which can swell and shrink in three dimensions. The approximate equality in density of bound and free films indicates that they are about equally porous before immersion in water for the soaking test; but when the wet films, plasticized by the absorbed water, dry out again afterward, the free films may be able to draw together and collapse the pores more nearly completely than the bound films can.

For free films, the volumetric swelling was distributed between areal swelling and swelling in thickness. The distribution, however, was not in fixed proportions. Thus, for the thin, unweathered film of magnesium silicate paint, the volumetric swelling was 56.1 percent, the areal swelling 15.9 percent, and the swelling in thickness 31.5 percent; whereas, for the thin, unweathered film of titanium-lead-zinc paint, the corresponding figures were 61.1, 38.0, and 15.6 percent, respectively. Such variations appear throughout table 3 not only among paints but between weathered and unweathered films of the same kind of paint. In the previous paper (3) it was shown that many films swell much more across than with the grain of the paint.

Recovery on Redrying: On redrying after the soaking test, both bound and free films usually shrank to a volume slightly less than their initial volume before soaking. The loss in volume may be attributed to the loss of soluble ingredients by leaching during the soaking period. Quantitative comparison of the volumetric shrinkage with the leaching loss is not possible in the absence of knowledge of the density of the soluble ingredients. Usually the leaching loss in grams per 100 cubic centimeters was slightly greater than the percent shrinkage in volume, which agrees with the presumption that the soluble ingredients had a density greater than 1.

One of the 60 bound films in table 1, and 10 of the 60 free films in table 3 retained a larger volume after redrying than the volume before soaking, although all of them experienced loss of soluble ingredients during the soaking. Of the 11 films that remained somewhat swollen after redrying, 9 were films that had been weathered, and all 11 of them were films that exhibited less than 100 percent swelling efficiency in the soaking test. Eight of the 11 films were of paints that contained zinc oxide and were more brittle and less distensible than the other paints. It may be concluded at least tentatively, therefore, that the residual swelling left after redrying indicates voids left within the films after evaporation of the water with which they had been filled while the films were wet.

Failure of free films to return on redrying to their initial dimensions before soaking was much more frequent in the measurements of area than in those of volume. Of the 60 free films in table 3, there were 28 for which the area, when redried, exceeded the area before soaking. Twenty-two of the 28 were among the 24 films of paints that contained zinc oxide. The paints of highest absorption and swelling on soaking appear to be the ones most likely to retain swollen area after redrying. The harder, less distensible paints of high absorption and swelling thus seem to shrink more readily in thickness than in area when they dry out again. The results agree with phenomena that have long been observed in the moisture blistering of paints. Formation of blisters necessarily involves an increase in area of film. After the wet condition passes and the blistered paints dry again, the more distensible kinds of paint often draw down to a surface so level that the blistered area can no longer be seen; whereas, the less distensible paints often leave a rumpled surface, a sort of "double-chin" effect that clearly reveals the blistered area. Similiarly, in normal weathering of paints when cracking and curling occur, it can often be seen that, if the curled paint could be rolled out flat again, the parts on either side of the crack would have to overlap.

Both in swelling and in redrying of free films, measurements of changes in area alone prove inadequate and may lead to conclusions at variance with the understanding obtainable when the volumetric changes are measured also. When both volumetric and areal changes are observed, significant information is revealed about the internal structure of the films and the nature of the stresses that must be set up within them.

Loss in Weight While Soaking: The loss in weight of paint films during the 3-day soaking period were discussed in the previous paper (3). The loss arises from leaching of water-soluble substances probably formed by decomposition of the paint oils, chiefly during the soaking period. They can be recovered from the soaking water by evaporation. They consist of organic matter, together with inorganic constituents if the paint contained pigments partly soluble in water or capable of forming soluble salts with organic acids. In this paper, it is sufficient to point out that bound films yielded solubility losses of the same order of magnitude as those from free films. Thick films lost less in proportion to their volume than did thin films of the same kind of paint, whether the films were bound or free.

Comparison of Artificial and Natural Weathering

Table 2 reports results with free films of 2 unpigmented oils, 11 laboratory-made paints, and 5 commercial paints when tested before weathering, after artificial weathering for 15 days, and after natural weathering for 6 months and for 12 months. The 6-month period of natural weathering was from May to October 1953, inclusive, which included the summer months; the 12-month period was the extension through April 1954, which included the winter season.

Weight Losses While Weathering: Losses in weight during weathering, either artificial or natural, were substantial. Paint T_{420}, in which anatase titanium dioxide was the sole pigment, lost 107 grams per 100 cubic centimeters of weathered film after 12 months of natural weathering. But much of the loss by paint T_{420} was pigment because it was chalking very freely by the end of the exposure period. Although other paints chalked observably, none of them was chalking freely enough to attribute much of their weight loss to erosion of pigment. For most paints, the losses are believed to consist chiefly of volatile organic products of oxidation and to leaching of soluble decomposition products of the paint oils and soluble metal salts of such products. Raw linseed oil lost 92 grams per 100 cubic centimeters of weathered film after 12 months' natural weathering; bodied linseed oil lost a little less than half as much. Paint TL_{40} and commercial paint No. 5, which was pigmented with titanium dioxide and extending pigments, lost somewhat more than bodied linseed oil but less than raw linseed oil. Magne-

sium silicate paint lost a little less than bodied linseed oil; and pure white lead paint, paint L, lost less than magnesium silicate paint. All paints that contained zinc oxide lost less than pure white lead paint, but the lowest loss after 12 months' natural weathering was 15.6 grams per 100 cubic centimeters of weathered film of paint $TL_{20}Z_{20}$. These findings agree with measurements of the rate loss of coating thickness in practical exposure tests (2).

In natural weathering, most of the loss in weight took place during the first 6 months. After 12 months, the losses were usually greater but only slightly so. This is strong evidence that the weight losses consist chiefly of leachings of soluble decomposition and reaction products, rather than mechanical attrition by chalking or erosion. Oxidation takes place most rapidly in young films and slows down as they get older. Erosion, on the other hand, is negligible in young films and speeds up as they age. To be sure, the first 6-month period of natural weathering included the summer period during which paint deterioration proceeds more rapidly than in winter, but the 6-month losses approach the 12-month losses too closely to be attributed largely to the difference between summer and winter seasons.

In artificial weathering for half a month, the weight losses were smaller, usually much smaller, than the losses in natural weathering. The shorter period of time for artificial weathering may be partly responsible for the difference, but another and perhaps more important factor is the brevity of the periods of exposure to water in artificial weathering. Each spraying with water, during which soluble ingredients could be leached out, lasted only a few minutes, after which the films had time to dry thoroughly before again reaching the sprays. The time was insufficient for the water to affect more than a thin, superficial layer of the paint films. Other workers (6) also have pointed out that customary cycles of artificial weathering fail to provide long enough periods of exposure to wet conditions.

In table 1, bound films of paints containing zinc oxide usually gained in weight during exposure to artificial weathering. Losses by other paints were usually much less than the losses for the same paints recorded in table 2. The gains by the zinc oxide paints were clearly abnormal and were traced to deposits from the hard water used in the Weatherometer sprays. The metal clips by which the test specimens were held in the Weatherometer drum became coated with the deposits. This source of error was corrected by equipping the Weatherometer with a tank and pump to supply distilled water to the sprays for the experiments recorded in table 2.

Absorption of Water: Weathered films of pigmented paints, except pure white lead paint, absorbed less water when soaked than the unweathered films of the same paints, whether the weathering was artificial or natural. On the whole, artificial and natural weathering did not differ greatly in their effects on absorption. If there was any real difference between them, after making reasonable allowances for differences in film thickness, the difference was that absorption by artificially weathered films was more often slightly less than slightly more than the absorption by similar naturally weathered films. At any rate, the results indicate that half a month of artificial weathering ages the films fully as much as a year of natural weathering, at 45° facing south, though it does not follow that the chemical and physical effects of the 2 methods of weathering are the same in all respects.

Swelling and Swelling Efficiency: No significant differences were observable in the effects of artificial and natural weathering on the swelling and swelling efficiency of paint films. Before weathering, the swelling efficiency was usually close to or slightly greather than 100 percent; and after weathering of either kind, the efficiency as a rule was slightly less, sometimes markedly less than 100 percent. Likewise, the distribution of the volumetric swelling between area and thickness changes was about the same for artificial and for natural weathering.

Shrinking on Redrying: When redried after soaking, all unweathered films returned to less than the volume before soaking, presumably because of leaching of soluble ingredients. After artificial weathering, films of 5 paints, chiefly paints that contained zinc oxide, retained after redrying slightly more than their initial volume. All films naturally weathered for 12 months returned after redrying to less than the initial volume; but of the films naturally weathered only 6 months, those of 10 paints had larger-than-initial volume after redrying. The residual swelling was small for 3 zinc-containing paints and pure white lead paint; but it was large, from 14.5 to 30.9 percent, for 6 paints, namely, paints Z, LZ_{21}, $TL_{20}Z_{20}$, $TL_{10}Z_{10}$, TZ_{20}, and commercial paint No. 3. Large residual swelling after redrying was usually associated with low swelling efficiency during soaking. The area of films of all zinc-containing paints, except commercial paint No. 4, was always larger after redrying than it was before soaking, even for unweathered films.

Thus, the behavior of zinc-containing paints on redrying after soaking suggests that their physical condition after 6 months of natural weathering is farther away from the unweathered condition than is the condition after 12 months of weathering. On the other hand, it has already been pointed out that the data for loss in weight while weathering suggest that the chemical composition changes greatly during the first 6 months, but not much more during the next 6 months. But it may be that the physical condition that determines the ability to shrink again after becoming swollen in water, oscillates beteween limits during weathering, or that it depends more on the weather conditions for a few days immediately before sampling than on the total time of exposure to weathering.

Solubility While Soaking: Artificially weathered films lost less weight from leaching of soluble ingredients during soaking than the corresponding unweathered films did, except for the pure zinc oxide paint and commercial paint No. 5. Naturally weathered films of bodied linseed oil, all zinc-free paints, and commercial paints Nos. 1, 2, and 3 also lost less soluble material than the corresponding unweathered films. But naturally weathered films of raw linseed oil, all laboratory-made paints that contained zinc oxide, and commercial paint No. 4 had more soluble material than the corresponding unweathered films. (The laboratory-made paints were made with raw linseed oil, but the commercial paints contained substantial proportions of bodied drying oils.) Solubility was higher in naturally weathered than in artificially weathered films of all paints for which the data are available for such comparison, except pure zinc oxide paint and commercial paint No. 5.

It appears, then, that artificial weathering tends to reduce solubility below that of unweathered films. Natural weathering, on the other hand, seems to increase the solubility of films of raw linseed oil and of paints containing zinc oxide unless they also contain much bodied oil. For bodied linseed oil and zinc-free paints, the solubility after natural weathering, though less than that of unweathered films, is not so low as it is in artificially weathered films. More should be known about the chemistry of paint weathering before an explanation is offered for these facts.

Chips of 16-Year-Old Paint

An opportunity to measure the volumetric swelling of some very old paint films was afforded by a test-fence study of paint maintenance programs started at Madison, Wis., in 1936, the results of which have been published (2). The paint coatings were renewed by repainting at intervals, always with the same kind of paint, until 1948. After that, they were all allowed to stand without

further repainting until 1952 to provide a period for observing the outcome critically. The thicker coatings of many of the paints were then scaling badly enough to permit collection of samples of free films large enough to test for absorption of water and volumetric swelling. The chips were collected in the spring of 1952 and kept indoors until the measurements were made in January 1954.

The results are reported in table 4. All of the paint chips available for study were more than 9 mils thick, one of them 18.1 mils thick. The absorption and swelling measured, then, are for films of excessive thickness and presumably are much lower than the absorption and swelling of similar films of normal thickness, say 5 mils. All chips available were of paints that contained zinc oxide and that were therefore high in absorption and swelling. Zinc-free paints, even in excessively thick films, did not loosen and scale in pieces large enough to afford samples suitable for measurement.

The absorption of water ranged from 18.8 percent for paint $(LZ_{15})_{33}$ to 45.2 percent for paint $(TZ_{23})_{107}$. Absorption by the 2 paints in which there was no white lead was greater than the absorption by any of the 6 paints in which there was white lead. Although the absorptions were lower than for comparable paints in table 2 that received natural weathering for 1 year, the differences were no greater than might be accounted for by the much greater thickness of the 16-year-old films. Thus, it appears that most of the reduction in absorption caused by weathering of paint films occurs in the first year, or perhaps even in the first 6 months.

Volumetric swelling of the 16-year-old films was always less than the absorption of water, and the swelling efficiency was therefore less than 100 percent. The efficiencies ranged from 77 to 92 percent. The 16-year-old paints did not differ greatly from 1-year-old paints in swelling efficiency. Moreover, the shrinkage of the swollen films on redrying and the loss of soluble ingredients during the 3-day soaking period were about the same for the 16-year-old as for the 1-year-old films.

Conclusions

1. A technique was developed for measuring the volumetric swelling both of free films and of coatings of house paints bound on glass when soaked in distilled water for 3 days, and the shrinkage of the free and bound films when dried again after soaking. The volumetric measurements in conjunction with measurement of the absorption of water, the changes in area, and the loss of soluble ingredients by leaching previously reported add materially to the understanding of the action of water on house paints of different kinds. Paints were tested before exposure to weathering and after exposure to artificial and to natural weathering.

2. Bound films absorbed somewhat less water and swelled correspondingly less than free films, although the absorption and swelling of bound films of some paints were surprisingly large. The bound films, which could swell in thickness only, were perhaps unable to adjust their volume to the full extent of swelling and remained under greater internal stresses than the free films. Free films changed in length, width, and thickness.

3. Thick films, whether bound or free, absorbed less water and swelled less than otherwise similar thin films.

4. Unweathered films, either bound or free, usually swelled at least 1 cubic centimeter in volume for each gram of water absorbed. Artificial weathering in a Weatherometer reduced the absorption and swelling. Weathered films tended to swell less, sometimes much less than 1 cubic centimeter for each gram of water absorbed. It may be that the weathered films become porous and are able to hold some free water that causes no swelling in addition to the swelling water.

5. When redried after soaking, most films shrank to a somewhat smaller volume than they had before soaking. The loss in volume is attributed to loss of soluble ingredients by leaching during the soaking. Practically all films suffered loss in weight from this source. But a few films, chiefly of highly absorptive paints in which there was zinc oxide, were slightly greater in volume after redrying despite loss of soluble ingredients. This seems to be further evidence of the development of voids within some films.

6. All films lost weight substantially during either artificial or natural weathering. The losses were much larger in natural than in artificial weathering. In natural weathering, the major portion of the loss took place during the first 6 months. The loss in weight is attributed chiefly to leaching of soluble ingredients, rather than to mechanical erosion or chalking, because few paints were chalking very freely within the first 6 months of natural weathering.

7. In artificial weathering, the use of hard water in the Weatherometer sprays led to low measurements of weight loss; in fact, some paints that contained zinc oxide actually gained in weight. Evidently, there were gains in weight from deposition of the salts present in the hard water, which partly or wholly overbalanced the losses of soluble ingredients from the paint films. Such abnormal results were corrected by supplying distilled water to the Weatherometer sprays.

8. Absorption and swelling of films were reduced fully as much by 15 days of artificial weathering as by 12 months of natural weathering.

9. Chips of paint films from a test-fence study of paint-maintenance programs were available for examination. The paints had been maintained by repainting homogeneously at intervals throughout the period from 1936 to 1952, with the last repainting in 1948. The absorption and swelling of the 16-year-old paint chips, when reasonable allowance was made for their excessive thicknesses, was comparable with the absorption and swelling of similar paints when weathered for only 1 year. It seems, then, that the reduction in absorption and swelling of paint films caused by weathering takes place during the first few months and thereafter remains nearly constant for at least the next 15 years.

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