Swelling of Paint Films in Water IX. Effects of Temperature During Soaking and Film Formation, and Repeated Soaking and Drying

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Tests showed that free films of most linseed oil paints, both artificially weathered and unweathered, absorb more water, swell more, and lose more soluble material as the temperature of the water in which they are soaked increases. Higher temperature during formation of films reduces absorption of water and swelling of unweathered films. Coatings of paints on glass continue to absorb water, swell, and lose soluble material when subjected to as many as 15 cycles of soaking followed by re-drying.

Materials and Procedure

FIVE SINGLE-PIGMENT PAINTS made with unbodied linseed oil at a pigment volume of 0.30 were used in the tests. The five pigments were basic carbonate white lead, antimony oxide, rutile titanium dioxide, zinc oxide, and magnesium silicate. Of these, the first two make paints that are low and the last three make paints that are high in absorption and swelling.[2] Antimony oxide was chosen for one of the paints because it seems to have unusual properties. The other four pigments are widely used in commercial paints.

The experimental procedures and methods of calculating results were the same as those described in a previous paper.[3] To make unweathered free films, the paints were spread on gummed paper by doctor blade and suction plate. For weathered free films, the paints were spread on tinplate by doctor blade and suction plate, exposed to artificial weathering for 15 days, and then stripped from the tinplate by amalgamation. Coatings on glass were spread by doctor blade. In all cases, the films were intended to be about 4 mils thick when dry.

After the paints were spread, they were allowed to harden and form films in a laboratory at 70° to 80° F. in daylight from glass windows that face north. Unweathered films were 10 days old when the soaking tests began. Weathered films were 10 days old when placed in the weatherometer for 15 days, and were 26 days old when the soaking tests began.

For films formed at low temperature, the freshly spread paints were placed in a cold room at 36° F. and 80 per cent relative humidity, where they remained in subdued artificial light for three days. At the end of that time, the white lead and zinc oxide paints were thoroughly hardened, the titanium dioxide and magnesium silicate paints were hardened at the surface but still soft underneath, and the antimony oxide paint was still wet.

All of the specimens were then moved to the laboratory at 70° to 80° F., where all paints became thoroughly hardened by the fifth day. For films formed at high temperature, the freshly spread paints were placed in an incubator at 160° F and 20 per cent relative humidity, where they remained in subdued artificial light for three days. They were then moved to the laboratory at 70° to 80° F. When 10 days old, one set of coatings formed at 36° F. and one formed at 160° F. were stripped, cut into films, and started in the soaking test. Other sets of coatings were placed in the weatherometer for 15 days, then stripped, cut into films, and subjected to soaking when 26 days old.

For soaking tests, free films or coatings on glass were submerged in distilled water in crystallizing dishes and held usually at 70° F. in a water thermostat for three days. Exceptions were free films for soaking at 32° F., for which the submerged films were placed in a refrigerator for three days; free films for soaking at 119° F., for which the submerged films were placed in an incubator for three days; and coatings on glass, for which the specimens were immersed in water in a large glass dish at the temperature prevailing in the laboratory (70° to 80° F.).

Temperature of Soaking Water

The first paper in this series[4] reported the effect of temperature of the soaking water on absorption, areal swelling, and solubility of unweathered free films of two kinds of linseed oil paint. Since the effect proved large, it was desired to extend the observations to more paints, to include volumetric swelling, and to study weathered as well as unweathered films.

Results of the new tests on temperature of soaking water are reported in Table 1.

All films, except those of antimony oxide paint and weathered magnesium silicate paint, absorbed much less water when soaked at 33° and much more water when soaked at 119° than they did when soaked at 70° F. Absorption at 119° was from 1.9 to 8.4 times the absorption at 33°. For example, unweathered titanium dioxide films absorbed 6.1 per cent of water at 33°, 26.5 per cent at 70°, and 51.3 per cent at 119° F.

On the other hand, the films of antimony oxide paint and of weathered magnesium silicate paint were relatively insensitive to changes in temperature of the soaking water. Absorption by unweathered antimony

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

[2] Browne, F. L. 1955. Swelling of paint films in water, V. Effects of different pigments. For. Prod. Jour. V (3):192-200. 1955.

[3] Browne, F. L. 1956. Swelling of paint films in water, VI. Effect of different oil or oleoresinous vehicles. For. Prod. Jour. VI (4):152-9.

[4] Browne, F. L. 1953. The absorption of water, swelling, and solubility of free films of paint. Jour. of FPRS. III (5):108-24.

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Table 1.—EFFECT OF TEMPERATURE OF SOAKING WATER ON THE BEHAVIOR OF FREE FILMS OF UNWEATHERED AND WEATHERED LINSEED OIL PAINTS OF PIGMENT VOLUME 0.30

Pigment in linseed oil, pigment volume 0.30 (density of nonvolatile)	Weight loss while weathering, S_1/V_0	Temperature of soaking water	Density of film: Dry	Swollen in water	Redried	Initial thickness of film, T_0	Absorption of water, A/V_0	Swelling: In volume $(\Delta V)_s$	In area $(\Delta A)_s$	In thickness $(\Delta T)_s$	Swelling efficiency, $\frac{(\Delta V)_s V_0}{A}$	Redried: Volume $(\Delta V)_R$	Area $(\Delta A)_R$	Thickness $(\Delta T)_R$	Loss in weight while soaking, S_2/V_0
	Gm. per 100 cc.	°F.				Mils	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Gm. per 100 cc.
FILMS BEFORE WEATHERING															
Basic carbonate white lead (2.70)		33	2.88	2.85	2.91	3.7	2.5	3.0	0.9	1.6	120	-1.8	-0.4	-1.3	1.9
		70	2.87	2.77	2.92	3.9	7.4	7.7	2.7	5.1	104	-2.9	-.7	-2.1	3.6
		119	2.87	2.68	2.94	3.8	24.9	15.6	3.9	10.4	105	-4.3	0	-4.4	6.3
Antimony oxide (2.38)		33	2.56	2.54	2.59	3.7	2.3	2.7	1.6	1.1	117	-1.7	-.8	-.8	1.6
		70	2.55	2.55	2.60	3.9	2.3	2.5	2.7	0	109	-3.2	-.7	-2.6	3.5
		119	2.54	2.56	2.61	3.9	2.8	3.0	2.3	.5	107	-5.2	-2.3	-2.6	6.2
Rutile titanium dioxide (1.91)		33	2.06	2.01	2.08	4.1	6.1	6.9	5.1	1.7	113	-1.4	-1.0	0	1.1
		70	2.06	1.86	2.10	4.1	26.5	27.0	13.5	12.4	102	-3.0	+2.0	-4.9	2.8
		119	2.07	1.73	2.10	4.0	51.3	50.1	25.4	20.6	98	-4.2	+7.4	-10.7	6.5
Zinc oxide (2.33)		33	2.46	2.22	2.48	4.2	21.2	20.7	6.8	12.6	98	-1.3	+.5	-1.7	1.8
		70	2.46	1.89	2.49	3.8	67.5	66.3	21.0	37.7	99	-3.2	+4.8	-7.8	5.5
		119	2.47	1.83	2.41	3.6	80.4	75.2	24.0	40.0	94	-1.6	+9.3	-9.7	9.3
Magnesium silicate (1.51)		33	1.65	1.59	1.67	3.8	11.3	11.9	5.3	6.6	105	-2.0	+.5	-2.1	1.8
		70	1.64	1.47	1.67	4.4	39.7	40.2	14.1	23.2	101	-3.6	+2.4	-6.1	3.6
		119	1.65	1.38	1.67	4.0	70.1	70.4	20.3	41.5	100	-5.7	+5.0	-10.4	7.0
FILMS AFTER WEATHERING															
Basic carbonate white lead (2.70)	11.7	33	3.03	2.98	3.04	3.8	3.3	3.5	1.3	1.6	106	-1.2	-1.1	+.3	1.4
		70	3.04	2.92	3.02	3.9	6.8	5.4	.8	4.6	79	-.2	+.4	-.5	2.8
		119	3.06	2.91	3.07	3.5	10.1	9.1	.7	8.3	90	-1.9	+.1	-2.0	5.3
Antimony oxide (2.38)	30.4	33	2.95	2.94	2.97	3.3	2.9	2.3	1.2	.6	79	-.6	-.4	0	.6
		70	2.85	2.81	2.86	4.6	2.9	2.7	1.6	.9	93	-.7	-.8	+.5	.8
		119	3.04	3.05	3.09	2.7	3.7	2.5	1.8	.7	68	-2.6	-1.1	-1.5	3.8
Rutile titanium dioxide (1.91)	24.7	33	2.34	2.29	2.35	3.2	4.8	4.7	2.8	1.9	98	-.5	-.4	0	.9
		70	2.30	2.22	2.32	3.6	7.6	7.9	3.5	4.8	104	-1.3	-.8	-.8	1.1
		119	2.32	2.23	2.34	3.6	9.1	9.0	4.0	4.7	99	-1.9	-1.8	+.3	2.2
Zinc oxide (2.33)	13.0	33	2.54	2.47	2.56	3.7	11.1	7.6	3.2	4.6	69	+.6	-1.2	+.5	1.0
		70	2.56	2.20	2.56	3.7	40.0	34.1	7.5	24.0	85	-.2	+4.2	-4.0	1.5
		119	2.56	1.97	2.41	3.9	70.7	63.7	20.2	36.0	90	+4.5	+6.2	-1.5	3.7
Magnesium silicate (1.91)	29.0	33	1.84	1.79	1.84	3.6	7.6	7.5	1.8	5.6	96	-.8	+.5	-1.3	1.1
		70	1.84	1.76	1.84	3.5	10.4	10.8	1.3	9.8	104	-1.4	+.9	-2.0	2.1
		119	1.84	1.78	1.85	3.6	9.7	9.9			98	-2.6			3.6

oxide films was 2.3 per cent at 33° and 70°, and 2.8 per cent at 119°; absorption by weathered antimony oxide films was 2.9 per cent at 33° and 70°, and 3.7 per cent at 119°. Unweathered magnesium silicate films absorbed 11.3, 39.7, and 70.1 per cent of water at 33°, 70°, and 119° F., respectively, whereas the corresponding weathered films absorbed only 7.8, 10.4, and 9.7 per cent at the same respective temperatures. The reason for such wide variation in sensitivity of films to changes in temperature of the soaking water is not yet evident.

The density of all films except some of those of antimony oxide paint decreased on soaking approximately in proportion to the amount of water absorbed. Thus the decrease in density was greater at the higher soaking-water temperature. The apparent exception of antimony oxide films is attributable to the fact that the loss of soluble material exceeded the absorption of water by those films that failed to diminish in density.

When the soaked films were redried, they all regained or exceeded their density before soaking except the weathered white lead film soaked at 70° and the weathered and unweathered zinc oxide films soaked at 119° F. The exceptions were films for which low swelling efficiency[5] and low residual shrinkage[6] or even expansion in volume after redrying indicated the development of porosity within the films.

At all temperatures of soaking water, the volumetric swelling of the films paralled the absorption of water. Thus, swelling was much greater at 119° and less at 33° than at 70° F., except for the unweathered and weathered films of antimony oxide paint and weathered films of magnesium silicite paint already noted in the discussion of absorption. Departure from exact parallelism between volumetric swelling and absorption is indicated by the swelling efficiency.

Among unweathered films, swelling efficiency was distinctly higher at 33° and lower at 119° than at 70° F., except for zinc oxide films, for which the swelling efficiency was lowest at 119° but was nearly the same at 33° and 70°. The efficiency was less than 100 per cent for zinc oxide films at all temperatures and for titanium dioxide film at 119°, but was 100 per cent or more for all other unweathered films. Among weathered films, the swelling efficiency was less than 100 per cent for all films except white lead at 33° and titanium dioxide and magnesium silicate at 70° F. There seems to be no consistent relation between swelling efficiency and temperature of soaking water for the weathered films.

When they were redried, all unweathered films and all weathered films except that of zinc oxide soaked at 119° F. shrank to less than the volume before soaking, because of loss of soluble material. The loss in volume was almost directly proportional to the solubility for films of any one paint at the three temperatures, provided that the swelling efficiency gave no evidence of development of porosity in the films.

The slope of the graph relating loss in volume to solubility was nearly the same for unweathered films of antimony oxide and of magnesium silicate paint, but was somewhat less for unweathered films of white lead paint, which suggests that the soluble material from white lead films differs in density from the soluble material from antimony oxide and magnesium silicate films. When one or more of the

[5] Swelling efficiency is the swelling in volume expressed in percentage of the absorption of water by volume. For unweathered films pigmented below their critical pigment volume, the swelling efficiency is usually 100 per cent or slightly greater. Swelling efficiency less than 100 per cent generally means that the film is porous enough to hold some water that causes no swelling.

[6] Loss of soluble ingredients when films are soaked in water usually causes a proportional loss in volume when the films are dried again. But if the films become porous or increase in porosity when redried, the residual shrinkage is less than the loss in soluble ingredients would indicate or there may even be an increased volume after redrying.

Table 2.—EFFECT OF TEMPERATURE DURING DRYING OF LINSEED OIL PAINTS OF PIGMENT VOLUME 0.30 ON THE BEHAVIOR OF FREE FILMS OF THE UNWEATHERED AND WEATHERED PAINTS WHEN SOAKED IN WATER

Pigment in linseed oil, pigment volume 0.30 (density of nonvolatile)	Temperature at which paint dried	Weight loss while weathering, B_1/V_0	Density of film: Dry	Soaked in water	Redried	Initial thickness of film, T_0	Absorption of water, A/V₀	Swelling: In volume $(\Delta V)_s$	In area $(\Delta S)_s$	In thickness $(\Delta T)_s$	Swelling efficiency, $(\Delta V)_s$ / V_0 / A	Redried: Volume $(\Delta V)_R$	Area $(\Delta S)_R$	Thickness $(\Delta T)_R$	Loss in weight while soaking, B_2/V_0
	°F.	Gm. per 100 cc.				Mils	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Gm. per 100 cc.
FILMS BEFORE WEATHERING															
Basic carbonate white lead (2.70)	36		2.86	2.70	2.90	3.8	10.5	10.9	2.6	8.4	104	-2.6	-0.3	-2.3	3.5
	75		2.87	2.77	2.92	3.9	7.4	7.7	2.7	5.1	104	-2.9	-.7	-2.1	3.6
	160		2.95	2.91	2.98	3.8	3.4	3.4	.6	2.9	100	-1.7	-.2	-1.3	2.5
Antimony oxide (2.38)	36		2.56	2.55	2.60	3.9	2.4	2.7	1.9	.8	112	-3.0	-1.6	-1.5	3.2
	75		2.53	2.55	2.60	3.9	2.3	2.5	2.7	0	109	-3.2	-.7	-2.6	3.5
	160		2.60	2.59	2.60	4.1	1.5	1.0	.7	0	67	-.9	-.7	-1.0	2.1
Rutile titanium dioxide (1.91)	36		2.05	1.83	2.09	4.3	28.5	29.4	12.7	15.3	103	-3.2	+2.4	-5.6	2.9
	75		2.06	1.86	2.10	4.1	26.5	27.0	13.5	12.4	102	-3.0	+2.0	-4.9	2.8
	160		2.16	2.15	2.18	3.9	3.1	3.1	2.2	1.0	100	-2.1	-.6	-1.5	2.7
Zinc oxide (2.33)	36		2.46	1.80	2.48	4.2	85.3	84.1	18.1	54.2	99	-3.0	+7.2	-9.6	6.3
	75		2.46	1.89	2.49	3.8	67.5	66.3	21.0	37.7	99	-3.2	+4.8	-7.8	5.5
	160		2.58	2.44	2.59	3.6	10.3	10.2	4.6	5.5	99	-1.1	+.2	-1.4	1.9
Magnesium silicate (1.51)	36		1.67	1.41	1.69	3.8	64.5	64.5	18.0	39.0	100	-3.3	+4.7	-7.8	3.9
	75		1.64	1.47	1.67	4.4	39.7	40.2	14.1	23.2	101	-3.6	+2.4	-6.1	3.6
	160		1.71	1.67	1.71	3.8	6.5	6.4	2.4	4.0	99	-1.9	+.1	-1.9	2.9
FILMS AFTER WEATHERING															
Basic carbonate white lead (2.70)	36	12.6	3.06	2.98	3.04	3.7	5.4	4.0	.4	3.6	74	-.3	-.3	+.3	2.6
	75	11.7	3.04	2.92	3.02	3.9	6.8	5.4	.8	4.6	79	-.2	+.4	-.5	2.8
	160	10.2	3.12	3.00	3.04	3.7	5.3	4.7	.4	4.6	85	+1.9	-.6	+2.7	1.9
Antimony oxide (2.38)	36	32.5	2.90	2.86	2.91	3.0	2.4	2.7	1.9	1.7	112	-.6	-.8	0	1.6
	75	30.4	2.85	2.81	2.86	4.4	2.9	2.7	1.6	.9	93	-.7	-.6	+.5	.8
	160	19.0	2.90	2.87	2.91	3.2	2.6	2.5	2.0	.3	96	-.5	-.6	0	1.3
Rutile titanium dioxide (1.91)	36	20.3	2.30	2.23	2.30	3.4	5.3	5.9	3.3	2.4	111	-1.1	-1.3	0	1.1
	75	24.7	2.30	2.22	2.32	3.6	7.6	7.9	3.5	4.8	104	-1.3	-.8	-.8	1.1
	160	10.7	2.28	2.24	2.30	3.8	4.4	4.6	2.8	1.9	105	-1.1	-1.3	0	.9
Zinc oxide (2.33)	36	10.9	2.39	2.30	2.39	3.7	88.0	85.0	5.6	28.0	89	-.3	+1.3	-1.3	1.1
	75	13.0	2.36	2.20	2.36	3.7	40.0	34.1	7.5	24.0	85	-.2	+4.2	-4.0	1.5
	160	7.6	2.68	2.54	2.67	3.5	10.2	9.4	2.1	7.1	92	0	-.4	+.6	.3
Magnesium silicate (1.51)	36	32.8	1.84	1.80	1.87	3.1	6.2	7.0	2.0	5.1	113	-2.3	+.1	-2.6	1.7
	75	29.0	1.84	1.76	1.84	3.5	10.4	10.8	1.3	9.2	104	-1.4	+.9	-2.0	2.1
	160	27.7	1.89	1.84	1.90	3.0	6.0	6.5	2.4	4.3	108	-1.9	-.4	-1.7	2.0

films of any one paint became porous when it was redried, the relation between loss in volume and solubility was no longer linear, as was to be expected.

The changes in area and thickness of films during soaking and redrying were related to the changes in volume in much the same manner that was observed in previous studies.

All films, without exception, yielded less soluble material to the soaking water at 33° and more soluble material at 119° than at 70° F. The temperature coefficient of solubility was therefore positive in all cases. For the unweathered films, the coefficient ranged from 0.051 to 0.087, and for the weathered films it ranged from 0.015 to 0.045 gram per cubic centimeter of film for each degree of temperature.

Temperature During Formation of Films

Practical experience with house paint has long indicated that paint coatings are affected adversely by low temperature and high humidity during the period of hardening after the paint has been spread and that, conversely, coatings may be improved if the hardening takes place at temperatures somewhat higher than usual. It was therefore desirable to determine how the temperature during film formation affects the subsequent behavior of the films when they are soaked and redried.

Results of the tests with films formed at different temperatures are reported in Table 2.

The absorption of water by unweathered films was always greater for films formed at 36° and less for films formed at 160° than for films of the same composition formed at 75° F. For antimony oxide films, which did not harden during the three days at the lowest temperature, the differences were slight and the absorption was small at all three temperatures.

All other unweathered films absorbed much less water when formed at 160° than at 75°, and usually absorbed much more when formed at 36° than at 75°. Thus, zinc oxide films absorbed 85.3, 67.5, and 10.3 per cent of water when formed at 36°, 75°, and 160° F., respectively. No film formed at high temperature absorbed more than 10.3 per cent of water. After the films had been weathered, however, the absorption fell to approximately the level of the unweathered films formed at 160° except for the zinc oxide paint, for which weathered films formed at 36° and 75° still absorbed more than twice as much water as the film formed at 160° F. Thus, formation of films (other than those of zinc oxide) at 160° seems to have much the same effect on absorption as weathering.

Formation of films at 160° F. caused a distinctly greater increase in density over that of the nonvolatile components of the paint than occurred during formation at lower temperatures, but films formed at 75° were little if any greater in density than those formed at 36°. Weathering always caused a further increase in density in which the advantage of films formed at the highest temperature over those formed at the lower temperatures was retained by all paints except titanium dioxide.

Loss in weight of films during weathering was always less, usually markedly less, for films formed at 160° than for those formed at 75° or 36° F. The density of the films diminished approximately in proportion to the amount of water absorbed, but was regained or exceeded when the films were redried, except for weathered films of white lead and the film of zinc oxide formed at 160° F. The exceptional films all had low swelling efficiencies that were indicative of porosity.

For unweathered films, the volumetric swelling was nearly equal to the absorption of water; that is, the swelling efficiency was nearly 100 per cent. The greater deviations from 100 per cent by the antimony oxide films

cannot be considered exceptions because absorption and swelling were too low for an accurate calculation of efficiency. For weathered films of white lead and of zinc oxide, the swelling efficiency was always less than 100 per cent, but for films of titanium dioxide and of magnesium silicate it remained somewhat more than 100 per cent. The temperature at which films are formed therefore seems to have little or no effect on swelling efficiency. Similarly, the temperature at which films are formed does not appear to alter significantly the usual pattern of behavior with respect to shrinkage and distribution of the volumetric changes between area and thickness.

The solubility during soaking was about the same for unweathered films formed at 36° as for those formed at 75°, but was always somewhat less for those formed at 160° F. Among weathered films, decreased solubility for films formed at 160° was found in the cases of white lead, titanium dioxide, and zinc oxide paints, but not in those of antimony oxide and magnesium silicate paints.

Repeated Soaking and Drying of Bound Films

Paint coatings bound to a nonswelling substrate such as glass cannot swell or shrink in length or width and must accomplish practically all their volumetric changes by change in thickness alone. It was shown previously[7] that such constraint reduces the absorption and swelling of bound coatings to about four-fifths of the changes in corresponding free films. Presumably the constraint develops greater internal stresses within bound coatings than within free films. It seemed desirable to learn whether repeated reversal of the internal stresses tends to disrupt the structure of coatings with consequent increase in porosity.

It was also of interest to learn whether all soluble material is leached from coatings during the first few soakings in water. Bound coatings were more suitable for these tests than free films, both because of the greater internal stresses and because free films often curl too much or become too fragile for repeated soaking tests.

Results of the tests of repeated soaking and redrying of coatings on glass are reported in Table 3. All specimens were subjected to 15 cycles of soaking in distilled water for three days, followed by drying for two to five days. Complete sets of weighings and measurements were made during each of the first five cycles, during the tenth cycle, and during the fifteenth cycle. Data for the third and fourth cycles are omitted from Table 3 because they follow closely the trends from the second to the fifth cycle. There was, of course, a lapse of about 90 days from the beginning of the first to the end of the fifteenth cycle. The last two columns of Table 3 record the cumulative or overall changes in volume and weight of the coatings from the beginning of the first to the end of the fifteenth cycle.

The density of 10-day-old coatings was always reasonably close to that of 10-day-old free films of the same paints in Table 1. During the soaking tests with unweathered coatings, the density usually increased as soluble material was lost from the coatings. The unweathered zinc oxide films, however, gained in density during the first cycles, after which their density decreased and their swelling efficiency gave evidence of a marked increase in porosity.

Weathered coatings either decreased in density appreciably (zinc oxide), decreased slightly (white lead, magnesium silicate), remained unchanged (titanium dioxide), or increased very slightly (antimony oxide) during the 15 cycles.

The change in density depended on the extent to which the loss of soluble material was offset by gain in volume by the development of porosity. The density always decreased for both unweathered and weathered coatings when they were soaked, and it was regained or exceeded when they were redried unless the coating failed to shrink as much as its combined loss in volume of water and of soluble material.

Among the unweathered coatings, the absorption of water by white lead and by antimony oxide remained at nearly the same low levels and the absorption by magnesium silicate at nearly the same high level throughout the 15 cycles of soaking and redrying. The absorption by coatings of zinc oxide or of titanium dioxide, however, was significantly greater in the first or in the first and second cycles than in subsequent cycles, but leveled off to a relatively constant absorption for the later cycles, which for the zinc oxide coating at least was still high. Weathered coatings of all paints changed very little in absorption during the 15 cycles.

The swelling efficiency of both unweathered and weathered zinc oxide coatings showed the expected downward trend from the first to the fifteenth cycle of soaking and redrying. This, together with the downward trend in density and the slight cumulative shrinkage or expansion in volume after redrying, clearly reveals an increasing porosity of the coatings during the progress of the cycles.

Weathered coatings of white lead and perhaps of antimony oxide showed a similar downward trend in swelling efficiency, but the unweathered coatings did not. Likewise, weathered coatings of titanium dioxide and of magnesium silicate fell below 100 per cent efficiency by the fifteenth cycle, although they were still above 100 per cent at the tenth cycle. The unweathered coatings of titanium dioxide and of magnesium silicate remained above 100 per cent efficiency through the 15 cycles.

The evidence indicates, therefore, that zinc oxide coatings, even before weathering, tend to become steadily more porous with each cycle of soaking and drying, and that weathered coatings of most paints also become porous if the cycles are repeated often enough.

Unweathered coatings lost more soluble material in the first cycle of soaking than in any later cycle. Nevertheless, there was always a further loss in each additional cycle that became nearly constant in amount after the fifth or at least by the tenth cycle. If all of the soluble material were present in the 10-day-old coatings before the first soaking, there should be a steady decrease in solubility from cycle to cycle until all soluble material was removed. It may be concluded, therefore, that solubilization goes on continually in the unweathered coatings as a result of advancing age or hydrolysis while in contact with water.

Weathered coatings yielded less soluble material than unweathered films in the first soaking in water. From the second through the tenth cycles, the solubility of weathered coatings was approximately the same as that of the corresponding unweathered coatings, but by the fifteenth cycle, the solubility of weathered coatings fell to 0 to 0.3 gram per 100 cubic centimeters of coating. It is therefore possible that still further repetitions of the cycles would bring the weathered coatings to a point at which no further soluble material could be extracted, but the persistence of losses through at least 14 to 15 cycles indicates that solubilization continues to go on for some time after the soluble matter present before the first cycle has been extracted.

The last two columns of Table 3 show that all unweathered coatings suffered a cumulative loss in volume and loss in weight during the 15 cycles of soaking and drying. Except for the zinc oxide coatings, the loss in volume was only slightly less than the loss in

[7] See footnote 2.

weight, as would be expected if the loss in volume was due entirely to loss of soluble material of density only slightly greater than 1. For the four paints other than zinc oxide, the density of the soluble material indicated by the ratio of weight loss to volume loss was between 1.07 and 1.21 that is, it did not exceed the density of hardened films of 10-day-old unpigmented linseed oil. Such concordance of weight and volume losses, together with swelling efficiencies generally above and seldom far below 100 per cent, indicates that the coatings of the four paints were able to swell and shrink repeatedly without serious impairment of their internal structure.

Unweathered coatings of zinc oxide, however, lost only 1.6 per cent in volume for a weight loss of 10.8 grams per 100 cubic centimeters. The ratio of weight loss to volume loss was 6.7, more than 2-½ times the density of the paint coating when 10 days old. Since zinc oxide paints yield significant quantities of zinc salts to the soaking water, the density of the soluble products from such paints is probably higher than that from most other paints, but it must be far short of 6.7. Thus, the high ratio of weight loss to volume loss of the zinc oxide coatings confirms the development of porosity indicated by low swelling efficiency.

Since the swelling efficiency was 96 per cent in the first cycle, when the loss of soluble material was 4.8 grams per 100 cubic centimeters, and fell off strikingly in subsequent cycles, when the solubility remained fairly constant at 0.4 to 0.6 gram per 100 cubic centimeters, it seems reasonable to conclude that the stresses from repeated swelling and shrinking impaired the internal structure of the zinc oxide coatings and was at least partly responsible for the development of porosity.

Among weathered coatings, those of white lead and of zinc oxide gained slightly in volume by the end of the fifteenth cycle. Coatings of the other three paints lost volume, but the loss was much less than that of the corresponding unweathered coatings, and the ratio of weight loss to volume loss was 2.0 to 3.1. By the fifteenth cycle, the swelling efficiency of weathered coatings was always less than 100 per cent. It seems, then, that the internal structure of all of the weathered coatings was damaged in a manner causing porosity by repeated swelling and shrinking.

All test specimens of white lead, antimony oxide, and titanium dioxide coatings remained firmly adherent to

Table 3.—REPEATED SOAKING AND REDRYING OF COATINGS OF LINSEED OIL PAINTS OF PIGMENT VOLUME 0.30 ON GLASS BEFORE AND AFTER WEATHERING

Pigment in linseed oil, pigment volume 0.30 (density of nonvolatile)	Number of cycles of soaking in water and redrying	Weight loss while weathering, S_1/V_0	Density of coating: Dry	Soaked in water	Redried	Initial thickness of coating, Y_0	Absorption of water, A/V_0	Swelling in volume, $(\Delta V)_s$	Swelling efficiency, $\frac{(\Delta V)_s}{A} Y_0$	Redried volume, $(\Delta V)_R$	Loss in weight while soaking, S_0/V_0	Total change, first to fifteenth soaking: In volume	In weight
		Gm. per 100 cc.				Mils	Percent	Percent	Percent	Percent	Gm. per 100 cc.	Percent	Gm. per 100 cc.
COATINGS BEFORE WEATHERING													
Basic carbonate white lead (2.70)	1	.....	2.87	2.82	2.90	3.7	4.6	4.4	96	-1.1	1.1		
	2	.....	2.90	2.82	2.92	3.6	5.0	6.1	122	-1.9	.5		
	5	.....	2.94	2.85	2.94	3.5	4.9	4.6	94	0	.4	-3.8	-4.1
	10	.....	2.92	2.82	2.94	3.6	4.6	5.3	115	-1.0	.4		
	15	.....	2.94	2.85	2.94	3.5	4.2	4.6	109	-.3	.3		
Antimony oxide (2.38)	1	.....	2.52	2.50	2.53	3.8	2.7	2.1	78	-1.5	2.3		
	2	.....	2.53	2.50	2.57	3.7	2.6	3.5	135	-1.7	1.0		
	5	.....	2.57	2.53	2.57	3.7	2.1	1.8	86	+.1	.4	-6.1	-7.4
	10	.....	2.55	2.53	2.58	3.7	2.6	3.2	123	-1.8	.6		
	15	.....	2.59	2.55	2.61	3.6	3.0	3.3	110	-.8	.6		
Rutile titanium dioxide (1.91)	1	.....	2.07	1.90	2.09	3.9	20.7	20.3	98	-2.9	3.5		
	2	.....	2.09	1.92	2.12	3.8	20.7	21.2	102	-2.2	1.1		
	5	.....	2.14	2.00	2.14	3.6	14.4	13.8	96	-.1	.7	-10.4	-11.1
	10	.....	2.15	2.01	2.17	3.6	14.3	15.2	106	-1.4	.7		
	15	.....	2.18	2.04	2.18	3.5	12.7	12.9	101	-.6	.6		
Zinc oxide (2.33)	1	.....	2.45	1.96	2.49	3.8	37.8	35.6	96	-3.2	4.8		
	2	.....	2.49	2.18	2.50	3.7	28.8	27.0	94	-.6	.5		
	5	.....	2.47	2.19	2.45	3.7	28.8	25.4	88	+.6	.5	-1.6	-10.8
	10	.....	2.38	2.15	2.41	3.8	29.8	25.8	87	-1.1	.4		
	15	.....	2.36	2.18	2.39	3.8	29.6	28.9	77	-1.3	.6		
Magnesium silicate (1.51)	1	.....	1.67	1.52	1.68	3.7	29.6	29.3	99	-4.3	3.8		
	2	.....	1.68	1.53	1.70	3.6	27.5	28.6	104	-1.8	1.0		
	5	.....	1.70	1.55	1.70	3.5	27.7	27.3	99	-.7	2.0	-10.3	-12.1
	10	.....	1.70	1.54	1.72	3.4	31.3	31.8	102	-1.4	.7		
	15	.....	1.73	1.56	1.73	3.3	30.6	31.0	101	-.9	.7		
COATINGS AFTER WEATHERING													
Basic carbonate white lead (2.70)	1	11.4	3.10	2.98	3.03	3.3	5.5	6.0	109	+2.4	.6		
	2	.....	3.03	2.98	3.04	3.4	6.0	6.1	98	-.4	.7		
	5	.....	3.04	2.97	3.02	3.4	5.8	6.2	72	+.6	.6	+.1	-5.5
	10	.....	3.05	2.96	3.04	3.3	7.0	6.3	86	+.9	.5		
	15	.....	3.04	3.01	3.06	3.3	4.6	8.9	63	-.4	.8		
Antimony oxide (2.38)	1	31.2	2.98	2.92	2.97	2.9	3.7	3.6	97	0	1.2		
	2	.....	2.97	2.91	2.99	2.9	3.9	4.0	102	-1.1	.9		
	5	.....	2.98	2.91	2.96	2.9	4.0	3.3	82	+.2	1.0	-3.2	-7.1
	10	.....	2.99	2.90	3.00	2.9	4.7	4.9	104	-.7	.6		
	15	.....	2.98	2.95	3.01	2.9	5.5	8.9	83	-1.0	.1		
Rutile titanium dioxide (1.91)	1	22.3	2.34	2.22	2.34	3.1	9.7	10.2	105	-.4	1.1		
	2	.....	2.34	2.20	2.34	3.1	10.8	11.7	108	-.5	.3		
	5	.....	2.33	2.18	2.31	3.1	11.5	11.4	99	+.2	.8	-1.4	-2.6
	10	.....	2.33	2.18	2.33	3.1	11.7	12.4	106	+.1	.1		
	15	.....	2.32	2.21	2.34	3.1	11.2	11.0	99	-.8	0		
Zinc oxide (2.33)	1	13.2	2.69	2.33	2.67	3.3	17.4	17.7	102	+.6	.1		
	2	.....	2.67	2.32	2.63	3.4	19.7	19.6	99	+1.3	.1		
	5	.....	2.64	2.28	2.62	3.4	20.2	19.0	95	+.5	.7	-.9	-5.0
	10	.....	2.61	2.27	2.63	3.4	20.0	19.7	98	+.6	.2		
	15	.....	2.56	2.33	2.56	3.5	19.4	18.2	94	-.3	.3		
Magnesium silicate (1.51)	1	27.8	1.87	1.76	1.87	2.9	12.1	12.9	106	-.7	1.4		
	2	.....	1.87	1.76	1.87	2.9	13.4	14.3	107	-.3	.6		
	5	.....	1.86	1.75	1.84	2.9	13.0	13.0	100	+.4	.6	-1.1	-3.4
	10	.....	1.85	1.76	1.85	2.8	14.8	15.2	103	0	.4		
	15	.....	1.85	1.77	1.86	2.9	12.9	11.8	92	-.4	.1		

the glass and free from blisters throughout the 15 cycles of testing. Half of these coatings had already withstood the preliminary weathering. Unweathered coatings of zinc oxide developed a few small blisters in the first soaking test, when the solubility was 4.8 grams per 100 cubic centimeters. The blisters disappeared when the coatings were redried and did not appear in subsequent soakings, when the solubility never exceeded 0.7 gram. Weathered zinc oxide coatings developed no blisters at any time.

Both weathered and unweathered coatings of magnesium silicate became blistered in the tenth cycle. The blisters disappeared when the films were redried but they appeared again in each subsequent cycle. The blisters were somewhat larger on the weathered than on the unweathered test specimens. Unweathered coatings of zinc oxide and of magnesium silicate began to come loose along the edges of the test specimens by the end of the fifth cycle. The loosened area increased during subsequent cycles but had not progressed beyond 5 to 10 per cent of the total area of contact between coating and glass at the end of the fifteenth cycle. The defects of blistering and loosening of coatings were confined to the paints with the greatest degree of swelling.

Conclusions

Most paint films, both before and after weathering, absorb more water and swell more when soaked in warm water (119° F.) and absorb and swell less when soaked in cold water (33° F.) than when soaked in water at 70° F. Films of antimony oxide paint are exceptions to the rule because they take up a little more water and swell a little more at 119° than at the lower temperatures.

The quantity of soluble material extracted from films of any one kind of paint is nearly proportional to the temperature of the soaking water, at least for the unweathered films. The temperature coefficient of solubility for unweathered films ranges from 0.051 to 0.087 gram per cubic centimeter of film for each degree of temperature Fahrenheit. Moreover, when films that give no evidence of porosity are redried, the volumetric shrinkage beyond the volume before soaking is almost directly proportional to the solubility at the different temperatures.

The slope of the graph relating loss in volume to solubility seems to be nearly the same for unweathered films of chemically inert pigments (antimony oxide and magnesium silicate) but is slightly less for unweathered white lead films. At 70° F., the ratio of solubility to loss in volume indicates that the soluble material from white lead films has a density of 1.2 and the soluble material from antimony oxide or magnesium silicate film has a density of 1.1.

The temperature prevailing during the formation of paint coatings (first three days after spreading) greatly affects the absorption of water and swelling of free films cut from the unweathered coatings of most paints. The most striking effect is that of high temperature of formation (160° F.) on paints that are high in absorption and swelling when formed at 70° to 80° F.

None of the paints tested absorbs more than 10.2 per cent of water when the coating is formed at 160° F. For the highly absorptive zinc oxide, magnesium silicate, and titanium dioxide paints, this is less than one-sixth of their absorption when formed at 70° to 80° F. Formation at 160° F. reduces absorption and swelling of titanium dioxide and megnesium silicate as much as does 15 days of artificial weathering, and reduces the absorption and swelling of zinc oxide paint considerably more than does weathering.

Although temperature as high as 160° F. may be attained at times on parts of houses exposed to full sunshine during hot days within a month or so of the summer solstice, practical painting can hardly be confined to such times and places even in the southern part of the United States. Nevertheless discovery of the marked improvement in highly absorptive paints by high temperature during hardening suggests that other and more practicable means might be found to accomplish the purpose.

Antimony oxide paint is not significantly improved by formation at high temperature, but its absorption and swelling are very low at all temperatures.

Formation of coatings at low temperatures (36° F.) increases the absorption and swelling of unweathered films markedly for zinc oxide and magnesium silicate paints, and slightly for titanium dioxide, white lead, and perhaps for antimony oxide paint. After weathering, however, the effect of low temperature during formation is no longer observable.

Data for repeated soaking and redrying of unweathered and weathered coatings of zinc oxide paint on glass give evidence of a disruption of the internal structure and development of porosity from the stresses involved in swelling and shrinking while two of the three dimensions of the coating remain fixed by its attachment to the glass. A loosening of the coatings from the glass along edges of the test specimens after a few cycles of test with unweathered zinc oxide gives further evidence of stress.

Unweathered coatings of white lead, antimony oxide, titanium dioxide, and magnesium silicate paints on glass withstand 15 cycles of soaking and redrying without evidence of serious impairment of structure, but weathered coatings begin to show disruption of structure and porosity if the cycles are repeated often enough. Unweathered coatings of magnesium silicate paint begin to loosen from the glass at edges of the test specimens after a few cycles, and both unweathered and weathered coatings of magnesium silicate paint become blistered during each of the later soaking periods.

Although unweathered coatings yield more soluble material in the first cycle than in later cycles, the solubility remains nearly constant after a few cycles and is appreciable for at least 15 cycles. Solubilization apparently goes on continually either from aging or from hydrolysis because of contact with water. Weathered coatings contain less soluble matter at the outset than unweathered coatings. Solubilization continues for many cycles but may ultimately cease after 15 cycles or more.

From the ratio of the cumulative loss in weight to loss in volume during 15 cycles for unweathered coatings that seem to retain unimpaired internal structure, the density of the soluble material lies between 1.1 and 1.2.