Swelling of Paint Films in Water, III[1]

Absorption and Volumetric Swelling of Bound and Free Films From Air of Different Relative Humidities

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This, the third paper in a series, shows that both free and bound films (coatings on glass) absorb moisture from damp air and swell, though the absorption is much less than it is when the films are soaked in water. The measurements in air are complicated by the fact that the films lose weight during the tests from escape of volatile decomposition products steadily formed by oxidation of the paint oils. At low relative humidities such losses overbalance any absorption of moisture.

THE TWO PREVIOUS PAPERS in this series (1, 2)[3] showed that films of house paints, when immersed in water, absorb much of the water and swell in volume. Although bound films (coatings on glass) absorb and swell somewhat less than free films, the imbibition by bound films is still large, particularly if the paint contains pigments that stimulate absorption. The purpose of the experiments reported in this paper was to learn whether bound and free films take up moisture from damp air and, if so, how the extent of the changes varies with the relative humidity of the air.

The experimental technique used to measure absorption, changes in volume, area, and thickness, and loss of soluble and volatile substances during the test period was described in the second paper (2). Five coating materials were selected from those previously tested in water, namely, unpigmented linseed oil and 4 single-pigment paints of 0.30 percent pigment volume made with magnesium silicate, basic carbonate white lead, zinc oxide, and anatase titanium dioxide, respectively. The white lead paint is one of relatively low absorption, the zinc oxide paint is very high in absorption, and the magnesium silicate and titanium dioxide paints are of intermediate absorption.

Bound films were spread on clean glass microscope slides of 1.5 by 3 inches in size. Free films were made from coatings spread on gummed paper. Linseed oil was applied by brushing in three successive coats a day apart. Paints were spread in one application by a doctor blade. The coatings were allowed to dry in a laboratory near a window with northern exposure that was kept closed. Free films were stripped from gummed paper when they had dried for 10 days. They were then cut to 1.5 by 2.5 inches in size and marked in waterproof drawing ink with datum lines for measurement of length and width with a traveling microscope. Each film was equipped with a suitable suspending hook made of copper wire and carefully cut to weight 0.0461 gram in air. The hook supplied a means of suspending the films freely in the air of the humidity rooms and also from the arm of a balance for weighing in air and in water.

Both free films and coatings on glass were dried in a desiccator over calcium chloride before they were weighed initially in air and in distilled water. They were then promptly moved to the humidity room in which they were to be tested. Coatings on glass were supported on shelves of open wire mesh through which air circulated freely. Free films were suspended to expose both faces to the air. Separate samples of each paint were provided for each humidity condition and for each period of exposure. One complete set of films was exposed for 3 days and another complete set for 7 days. In all humidity rooms the air was maintained at 80° F. Five rooms were available in which the relative humidity was held at 97, 90, 80, 65, and 30 percent, respectively. Additional sets of specimens were kept in desiccators over calcium chloride for 3 and for 7 days to provide exposure to nearly complete dryness. The specimens were 14 days' old on entering the 97 and 90 percent humidity rooms, 20 days' old on entering the 80 and 65 percent humidity rooms, and 24 days' old on entering the 30 percent humidity room or the desiccators.

For weighing the specimens in the humidity rooms at the conclusion of the test period a chainomatic balance and a traveling microscope were mounted on a suitable cart to be moved to the room in which measurements were to be made. Thus, the "swollen" weights and dimensions were determined without ambiguity from changes taking place during the time of measurement. Specimens from the desiccators were measured with the equipment standing in the Laboratory, but the results show that moisture changes at low relative humidities are negligible.

The data given in tables 1 and 2 for absorption during immersion in water for 3 days were taken from the previous paper (2). That paper should also be consulted for the methods of calculating results, except for an additional provision described in the fourth paragraph following.

Results

Results with bound films (coatings on glass) are given in table 1, those with free films exposed for 3 days in table 2, and those for free films exposed for 7 days in table 3.

Much less moisture was absorbed from damp air than from contact with water during immersion. Even in 97 percent relative humidity the absorption was never much more than a third, and often it was less than a fifth of the absorption from water. Nevertheless, there was measurable absorption at the higher humidities by all paints except white lead paint in free films and in the bound film of longer exposure. At 30 percent relative humidity no paint took up a measurable amount of moisture.

The absorptions recorded, however, are probably underestimated, particularly so at the intermediate and lower humidities, because there was a steady loss of volatile substances from all of the films throughout the periods of exposure. This loss, except for the more absorptive paints at the higher humidities, is comparable in magnitude to the moisture absorbed. Moreover, it is unlikely that the loss of volatile substances is reliably measured by the losses in weight during test recorded in the tables, for the volatile substances given off arise chiefly from disruptive oxidation of the oil vehicle and

[1] A contributed paper.
[2] Maintained at Madison, Wis., in cooperation with the University of Wisconsin.
[3] Numbers in parentheses refer to references at end of text.

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Table 1.—DATA FOR BOUND FILMS (coatings on glass) OF LINSEED OIL AND OF FOUR PAINTS TESTED BY IMMERSION IN WATER FOR 3 DAYS AND BY EXPOSURE TO AIR OF DIFFERENT RELATIVE HUMIDITIES FOR 3 DAYS AND FOR 7 DAYS—ABSORPTION OF WATER OR OF MOISTURE, VOLUMETRIC SWELLING, SWELLING EFFICIENCY, CHANGES IN VOLUME ON REDRYING, AND LOSS IN WEIGHT DURING TEST

Paint or clear vehicle (density of nonvolatile while liquid)	Whether tested in water or in air of the relative humidity (R.H.) indicated	3-day test period: Before testing: Density	Film thickness T_o	Absorption A/V_o	Swelling in volume ΔV_o	Swelling efficiency $\Delta V_s V_o/A$	Redried change in volume ΔV_r	Loss in weight during test S_2/V_o	7-day test period: Before testing: Density	Film thickness T_o	Absorption A/V_o	Swelling in volume ΔV_o	Swelling efficiency $\Delta V_s V_o/A$	Redried change in volume ΔV_r	Loss in weight during test S_2/V_o
			Mils	Percent	Percent	Percent	Percent	Percent		Mils	Percent	Percent	Percent	Percent	Percent
Raw linseed oil (0.933)	Water	1.15	2.7	17.5	18.3	104	-3.7	4.6	(1)						
	Air, 97% R.H.	1.12	3.8	5.5	6.8	124	-3.2	2.4	1.12	3.0	5.9	5.9	100	-2.3	3.2
	Air, 90% R.H.	1.11	3.3	2.9	4.2	144	-3.1	2.0	1.12	3.5	2.9	2.9	100	-2.2	2.9
	Air, 80% R.H.	1.13	3.7	2.9	2.1	72	-.8	2.0	1.12	3.4	2.4	1.3	54	-.6	2.4
	Air, 65% R.H.	1.14	2.8	2.3	2.0	87	+.3	1.6	1.12	4.2	2.1	2.0	95	-.6	1.5
	Air, 30% R.H.	1.12	3.1	0	0	.....	-1.3	1.7	1.11	4.4	0	0	.....	-.9	1.5
	Air, dry	1.13	3.0	0	0	.....	-.5	.9	1.12	3.3	0	0	.....	-.6	1.3
Magnesium silicate p/nv 0.30 (1.515)	Water	1.70	3.3	40.7	41.9	103	-2.9	3.2	(1)						
	Air, 97% R.H.	1.64	4.6	9.5	10.5	110	-2.5	1.6	1.66	4.1	9.3	9.1	98	-1.7	2.5
	Air, 90% R.H.	1.66	3.8	3.0	4.1	137	-2.7	1.8	1.66	3.9	3.5	3.3	94	-1.7	2.3
	Air, 80% R.H.	1.68	4.1	2.2	1.4	64	-.3	1.6	1.69	3.9	2.4	1.0	42	-.1	2.2
	Air, 65% R.H.	1.69	3.8	1.4	.6	43	+.5	1.1	1.69	3.7	1.5	.3	20	+.7	1.3
	Air, 30% R.H.	1.68	3.8	0	0	.....	-.7	.9	1.68	3.6	0	0	.....	-.5	1.4
	Air, dry	1.68	3.9	0	0	.....	-.7	.7	1.67	3.7	0	0	.....	-.2	.8
Basic carbonate white lead, L, p/nv 0.30 (2.705)	Water	3.00	3.5	8.1	8.7	107	-2.0	3.0	(1)						
	Air, 97% R.H.	2.92	3.5	2.9	4.2	144	-2.8	2.3	2.92	3.4	0	0	.....	-2.1	3.3
	Air, 90% R.H.	2.92	3.3	0	0	.....	-2.8	1.9	2.93	3.3	0	0	.....	-1.5	2.6
	Air, 80% R.H.	2.98	3.3	0	0	.....	+.2	2.1	2.97	3.3	0	0	.....	-.3	2.4
	Air, 65% R.H.	2.98	3.2	0	0	.....	+.6	1.1	2.97	3.3	0	0	.....	+.5	1.2
	Air, 30% R.H.	2.94	3.2	0	0	.....	-.8	.9	2.94	3.5	0	0	.....	-.6	1.1
	Air, dry	2.93	3.6	0	0	.....	-.7	.3	2.95	3.4	0	0	.....	+.2	.6
Zinc oxide, 2, p/nv 0.30 (2.345)	Water	2.51	2.8	62.7	62.0	99	+1.2	2.3	(1)						
	Air, 97% R.H.	2.46	3.3	16.0	16.9	106	-1.5	.4	2.46	3.4	20.0	19.2	96	-.04	.6
	Air, 90% R.H.	2.46	3.0	2.5	3.8	152	-1.5	.2	2.48	3.3	2.4	2.0	83	+.4	.1
	Air, 80% R.H.	2.49	3.4	2.2	.9	41	+.8	.7	2.48	3.3	2.0	.2	10	+1.0	.5
	Air, 65% R.H.	2.50	3.3	1.6	.7	44	+1.3	.3	2.52	3.2	1.5	.5	33	+1.7	.3
	Air, 30% R.H.	2.49	3.4	0	0	.....	-.4	.9	2.47	3.9	0	0	.....	-.2	.9
	Air, dry	2.48	3.5	0	0	.....	-.5	.5	2.47	3.3	0	0	.....	-.3	.8
Titanium dioxide, anatase type, TZ_{20}, p/nv 0.30 (1.820)	Water	2.02	2.6	23.5	24.9	106	-3.0	3.4	(1)						
	Air, 97% R.H.	1.95	4.5	4.0	5.4	135	-2.2	1.0	1.93	3.8	5.0	5.2	104	-1.7	1.9
	Air, 90% R.H.	1.96	3.9	1.9	3.1	163	-2.2	1.1	1.95	4.2	2.1	2.2	105	-1.7	1.6
	Air, 80% R.H.	1.97	4.5	1.7	1.0	59	-.3	1.1	1.98	4.2	2.0	.9	45	-.9	1.7
	Air, 65% R.H.	1.98	4.3	1.2	1.1	92	+.2	.8	1.98	4.3	1.2	.1	8	+.6	.7
	Air, 30% R.H.	1.98	4.0	0	0	.....	-.6	.9	1.98	4.0	0	0	.....	-.9	1.3
	Air, dry	1.96	4.0	0	0	.....	-.8	.7	1.98	4.2	0	0	.....	-.6	.6

(1) Not tested by immersion in water for 7 days.

include the weight of part, though probably not all, of the oxygen taken from the air. To measure the hygroscopicity of paint films precisely, especially when the absorption is small, it would be necessary to exclude oxygen entirely and to expose the films during the test period to an inert gas humidified to the desired extent. For present purposes, however, it is considered sufficient to establish merely the order of magnitude of the effects.

It is probable then that the films absorbed somewhat more moisture than appears in the tables, especially at the lower relative humidities. Where the absorption and swelling are recorded as zero at or above 30 percent relative humidity, there may in fact have been a slight absorption, not greater than the loss in weight during the test period. It should be noted that the absorption and swelling were recorded as zero whenever the measurements after 3 or 7 days' exposure failed to exceed the initial measurements. Usually if no gain in weight, volume, or area was registered during the period of exposure, there was a slight loss which is included in the records of loss in weight and the changes in volume and area after redrying.

Comparison of the 7-day with the 3-day periods of test shows that significant absorption of moisture was nearly always complete within 3 days, but that loss of volatile substances usually continued up to the seventh day. (In fact, films of paint L, p/nv 0.30, and paint TZ_{20}, p/nv 0.30, kept on a desk top in a laboratory in only moderate illumination about 10 feet from a window with northern exposure, were still losing weight progressively after a year and a half.) Better estimates of the absorption of moisture and swelling with less distortion by loss of volatile substances were obtained in the 3-day than in the 7-day test period. Perhaps a 1-day test period would have been still better and might have indicated a small positive absorption at some of the higher humidities in which zero absorption was recorded after 3 days.

Bound Films: The absorption of moisture in 3 days (table 1) exceeded the loss of volatile products at 65 percent and higher relative humidity for raw linseed oil and all paints except white lead paint. For white lead paint there was measurable absorption only at 97 percent relative humidity. White lead paint was also lowest in absorption when soaked in water. Above 65 percent, the absorption increased at each higher step in relative humidity, with the largest increase occurring between 90 and 97 percent, although the increase was by no means so large as that on going from 97 percent relative humidity to soaking in water. None of the paints showed measurable absorption in 30 percent relative humidity, and of course there was none in dry air.

White lead paint absorbed less than linseed oil both in 97 percent relative humidity and in water. Titanium dioxide paint absorbed a little more water but a little less moisture in 97 percent relative humidity than linseed oil did. Magnesium silicate paint had significantly greater absorption than linseed oil both in water and in 97 percent relative humidity, and zinc oxide paint

Table 2.—DATA FOR FREE FILMS OF LINSEED OIL AND OF FOUR PAINTS TESTED BY IMMERSION IN WATER AND BY EXPOSURE TO AIR OF DIFFERENT RELATIVE HUMIDITIES FOR 3 DAYS—ABSORPTION OF WATER OR MOISTURE, SWELLING IN VOLUME, AREA, AND THICKNESS, SWELLING EFFICIENCY, CHANGES IN VOLUME, AREA, AND THICKNESS ON REDRYING, AND LOSS IN WEIGHT DURING TEST

Paint or clear vehicle (density of nonvolatile while liquid)	Whether tested in water or in air of the relative humidity (R. H.) indicated (test period 3 days)	Before testing: Density	Before testing: Film thickness T_o	Absorption A/V_o	Swelling: In volume ΔV_s	Swelling: In area ΔQ_s	Swelling: 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	Loss in weight during test B_o/V_o
			Mils	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent
Raw linseed oil (0.933)	Water	1.11	3.1	21.8	22.0	9.8	10.8	101	-6.0	-4.9	-1.3	5.8
	Air, 97% R.H.	1.12	2.6	5.6	7.9	3.5	4.2	141	-3.0			3.3
	Air, 90% R.H.	1.11	3.1	3.1	4.0	1.9	1.9	129	-2.9	-.7	-1.9	2.5
	Air, 80% R.H.	1.13	3.4	2.3	2.5	2.5	0	109	-2.1	-2.7	+.6	2.7
	Air, 65% R.H.	1.12	3.3	4.7	4.8		1.2	102	-3.8			4.3
	Air, 30% R.H.	1.12	3.0	0	0	0	0		-2.3	-1.8	-.7	1.8
	Air, dry	1.13	3.3	0	0	0	0		-1.3	-.9	-.6	1.1
Magnesium silicate p/nv 0.30 (1.515)	Water	1.68	2.9	56.2	56.1	15.9	31.5	100	-3.8	+2.2	-6.1	4.5
	Air, 97% R.H.	1.63	4.5	9.4	10.1	3.8	6.2	108	-2.4	-.3	-2.2	2.3
	Air, 90% R.H.	1.64	4.3	2.8	3.2	1.3	2.1	114	-2.0	-.3	-2.3	2.1
	Air, 80% R.H.	1.64	4.6	1.9	2.1	1.1	1.1	111	-2.0	-1.1	-1.1	2.3
	Air, 65% R.H.	1.63	4.1	0	0	.9	0		-2.0	-.6	-1.5	2.1
	Air, 30% R.H.	1.65	4.5	0	0	0	0		-1.7	-.8	-1.1	1.4
	Air, dry	1.65	4.2	0	0	0	0		-1.2	-.5	-1.0	1.4
Basic carbonate, white lead, L, p/nv 0.30 (2.705)	Water	2.98	2.8	10.0	9.2	4.7	1.1	92	-3.9	-.2	-3.6	6.1
	Air, 97% R.H.	2.90	3.7	0	0	0	0		-1.8	-.8	-1.1	2.2
	Air, 90% R.H.	2.92	3.7	0	0	0	0		-1.5	-.9	-.5	1.8
	Air, 80% R.H.	2.92	3.4	0	0	0	0		-2.0	-.8	-1.2	2.3
	Air, 65% R.H.	2.92	3.6	0	0	0	0		-1.1	-.7	-.6	1.4
	Air, 30% R.H.	2.94	3.8	0	0	0	0		-.4	-.4	0	.6
	Air, dry	2.93	3.6	0	0	0	0		-.7	-.5	-.3	.9
Zinc oxide, Z, p/nv 0.30 (2.345)	Water	2.46	2.5	96.7	96.5	65.9	16.8	100	-3.5	+24.6	-22.4	6.3
	Air, 97% R.H.	2.45	3.4	15.8	19.7	9.2	9.4	125	-.5	+1.1	-1.8	.6
	Air, 90% R.H.	2.45	3.4	1.5	2.6	.9	1.8	173	-.7	0	-.7	.5
	Air, 80% R.H.	2.46	3.3	1.1	1.8	1.0	.9	164	-1.5	+.1	-1.3	1.7
	Air, 65% R.H.	2.46	3.3	1.4	1.4	1.1	.3	100	-.7	-.4	-.5	1.2
	Air, 30% R.H.	2.47	3.3	0	0	0	0		-.7	-.3	-.6	.5
	Air, dry	2.46	3.4	0	0	0	0		-.6	-.1	-.5	.6
Titanium dioxide, anatase type, T_{420}, p/nv 0.30 (1.820)	Water	2.02	2.7	25.6	25.3	13.5	6.9	99	-4.1	+1.0	-4.7	5.2
	Air, 97% R.H.	1.97	3.8	3.3	4.1	2.3	1.9	125	-1.8	-.8	-1.1	1.5
	Air, 90% R.H.	1.97	3.6	1.8	3.0	1.3	1.7	167	-1.9	-1.3	-.6	1.4
	Air, 80% R.H.	1.98	3.7	0	0	0	0		-2.5	-.8	-1.6	2.4
	Air, 65% R.H.	1.98	3.9	0	0	0	0		-1.9	-1.5	-.3	1.7
	Air, 30% R.H.	1.99	3.8	0	0	0	0		-1.8	-.5	-1.3	1.4
	Air, dry	1.98	3.9	0	0	0	0		-1.9	-.6	-1.3	1.4

had the highest absorptions under both conditions. Zinc oxide paint took up almost as much moisture from 97 percent relative humidity as linseed oil gained when soaked in water; but at 90 percent and lower relative humidities the absorption by zinc oxide paint was not significantly greater than that of the other paints.

At 90 and 97 percent relative humidities the volumetric swelling of all paints exceeded their absorption of moisture. The swelling efficiency ranged from 106 to 163 percent. To be sure, the largest efficiencies occurred where absorption and swelling were not very great and experimental error was therefore relatively large, but the tendency for the efficiency to exceed 100 percent was consistent. When the films were soaked in water, the swelling efficiency likewise usually exceeded 100 percent, but by a margin small enough to be attributed (2) to experimental error due to slight loss of water during the time required to blot up the water clinging to the surfaces of the wet films and weigh them. There were no such losses in 90 and 97 percent relative humidities because the weighings were made while the films were still in the humidity rooms. After the 7-day test period the swelling efficiencies dropped nearly to or even slightly below 100 percent for bound films, but for the free films in table 3 the efficiencies remained above 100 percent. For bound films at 80 percent relative humidity or less, the swelling efficiency was always less, usually far less, than 100 percent; but for free films (tables 2 and 3) the efficiencies exceeded 100 percent, sometimes by a wide margin, even at relative humidity as low as 65 percent.

More study is needed to explain the large swelling efficiencies. Perhaps the marked shrinkage in volume that occurs during the conversion of the liquid coating to a hardened film, which is disclosed by a large increase in density, puts the hardened film in compression. At this stage the linoxyn vehicle consists of a cross-linked network of a "solid phase" that encloses and possibly compresses a large proportion of "liquid phase" (4). When the film is then moved to a moist atmosphere, the moisture absorbed plasticizes the rigid solid phase sufficiently for it to yield under the pressure of the liquid phase. Thus, there may be a springback of volume added to the volume of the absorbed water itself. Plasticization by absorbed moisture markedly affects the mechanical properties of paint films (3).

When redried over calcium chloride after testing in damp air, most bound films shrank to a volume smaller than that when the test began. Such shrinkage was inversely related to the extent of swelling; that is, films tested in 97 percent relative humidity swelled more and then shrank more afterward than films tested in 90 percent relative humidity, and those tested in 90 percent swelled and shrank more than those tested in 80 percent relative humidity. The shrinkage below the initial volume

Table 3.—DATA FOR FREE FILMS OF LINSEED OIL AND OF FOUR PAINTS TESTED BY EXPOSURE TO AIR OF DIFFERENT RELATIVE HUMIDITIES FOR 7 DAYS—ABSORPTION OF MOISTURE, SWELLING IN VOLUME, AREA, AND THICKNESS, SWELLING EFFICIENCY, CHANGES IN VOLUME, AREA, AND THICKNESS ON REDRYING, AND LOSS IN WEIGHT DURING TEST

Paint or clear vehicle (density of nonvolatile while liquid)	Whether tested in water or in air of the relative humidity (R. H.) indicated (test period 7 days)	Before testing: Density	Before testing: Film thickness T_o	Absorption A/V_o	Swelling: In volume ΔV_s	Swelling: In area ΔQ_s	Swelling: 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	Loss in weight during test S_2/V_o
			Mils	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent
Raw linseed oil (0.933)	Air, 97% R.H.	1.12	2.7	0	0		0		-4.4	-2.6	-4.4	5.9
	Air, 90% R.H.	1.12	2.7	0	0	0.9	2.6		-2.8		-3.0	4.2
	Air, 80% R.H.	1.12	3.0	0	0	0	0		-3.4	-3.0	-3.0	3.6
	Air, 65% R.H.	1.13	3.0	2.8	3.4	0	.7	121	-2.6	-1.4	-2.7	2.4
	Air, 30% R.H.	1.11	2.6	0	0	0			-3.6	-2.3	-3.4	2.8
	Air, dry											
Magnesium silicate p/nv 0.30 (1.515)	Air, 97% R.H.	1.63	4.3	6.9	7.4	2.5	4.4	107	-3.1	-.6	-3.0	2.8
	Air, 90% R.H.	1.62	4.1	3.2	3.8	1.1	1.0	119	-2.8	-.4	-3.0	3.1
	Air, 80% R.H.	1.64	4.6	0	0	0	0		-2.7	-1.1	-2.4	2.9
	Air, 65% R.H.	1.65	4.3	0	0	0	0		-1.9	-1.0	-1.6	1.7
	Air, 30% R.H.	1.65	4.4	0	0	0	0		-2.5	-.8	-2.5	1.8
	Air, dry	1.65	4.5	0	0	0	0		-1.6	-.5	-1.6	1.3
Basic carbonate, white lead, L, p/nv 0.30 (2.705)	Air, 97% R.H.	2.92	3.7	0	0	0	0		-.2	-.6	-.3	2.9
	Air, 90% R.H.	2.91	3.6	0	0	0	0		-2.3	-.6	-2.5	2.3
	Air, 80% R.H.	2.92	3.6	0	0	0	0		-1.9	-1.0	-1.7	2.0
	Air, 65% R.H.	2.92	3.7	0	0	0	0		-1.8	-.5	-1.9	1.7
	Air, 30% R.H.	2.92	3.6	0	0	0	0		-2.0	-.5	-1.7	1.4
	Air, dry	2.92	3.9	0	0	0	0		-1.8	-.5	-1.8	1.0
Zinc oxide, Z, p/nv 0.30 (2.345)	Air, 97% R.H.	2.44	3.5	13.4	19.6	6.2	18.3	146	-1.5	+3.5	-1.8	1.2
	Air, 90% R.H.	2.46	3.3	1.4	1.8	.5	1.2	129	-.6	-.4	-.3	.7
	Air, 80% R.H.	2.46	3.7	1.0	1.6	.6	.3	160	-1.2	-.6	-1.3	1.3
	Air, 65% R.H.	2.45	3.5	1.4	1.5	.2	.3	107	-1.1	-.6	-1.1	1.0
	Air, 30% R.H.	2.43	3.3	0	0	0	0		-2.8	-.4	-3.0	2.5
	Air, dry	2.47	3.6	0	0	0	0		-1.1	-.3	-.8	1.0
Titanium dioxide, anatase type, T_{420}, p/nv 0.30 (1.820)	Air, 97% R.H.	1.97	3.6	2.9	7.3	1.0	4.5	251	-3.2	-.4	-3.1	2.7
	Air, 90% R.H.	1.96	3.9	2.0	2.5	0	0	125	-2.4	-1.7	-2.5	2.1
	Air, 80% R.H.	1.98	3.6	0	0	0	0		-2.7	-1.7	-2.8	2.8
	Air, 65% R.H.	1.98	3.6	0	0	0	0		-1.6	-1.4	-1.4	1.6
	Air, 30% R.H.	2.00	3.6	0	0	0	0		-2.5	-1.3	-2.2	1.7
	Air, dry	1.99	3.6	0	0	0	0		-2.5	-.7	-2.5	2.1

was due partly, perhaps entirely, to loss of volatile substances during testing and redrying. But all bound films tested for 3 days in 65 percent relative humidity and the films of white lead paint and of zinc oxide paint tested for 3 days in 80 percent relative humidity remained slightly swollen after redrying over calcium chloride. Perhaps the degree of plasticization at these moderate relative humidities was insufficient to permit full shrinkage on redrying when all change in volume was confined to one dimension, thickness. The corresponding free films (tables 2 and 3), which could change in 3 dimensions, did shrink on redrying to less than the volume before testing. All films tested in 30 percent relative humidity or kept continuously in dry air, none of which experienced any swelling, came to a final volume smaller than their initial volume because of their loss of volatile substances.

Losses in weight during testing and redrying were greater when tests were made in 80 percent or higher relative humidity than when the tests were made in lower humidity. Apparently disruptive oxidation with formation of volatile substances goes on more rapidly in moist than in dry air. When films were soaked in water, however, the losses in weight were significantly greater than any of the losses in air. Water evidently extracts substances of low volatility that are probably present in the films before immersion in the water and that can be recovered by evaporation of the soaking water and drying the residue at 105° C.

Free Films: Although all of the free films absorbed more water than bound films when soaked in water, the absorption of moisture from damp air was not much greater, and usually was somewhat less, than that of corresponding bound films. Failure to find larger absorption by free than by bound films in air may be due in part to the relatively small absorption from air, which makes the difference between free and bound films still smaller. But in large part, the failure may be attributed to larger loss of volatile substances by the free films, both faces of which were exposed to oxidation, whereas only one face of the bound films was similarly exposed.

Absorption by free films paralleled that by bound films in that, except for anomalies with linseed oil and zinc oxide paint in 65 percent relative humidity, it was greater in 97 than in 90 percent and greater in 90 than in 80 percent relative humidity, and was less than the loss of volatile substances in 30 percent relative humidity and in dry air. Further, white lead paint absorbed less water than any other; in fact, none at all from air. Titanium dioxide paint absorbed less from air but a little more from water than linseed oil did; and magnesium silicate paint and zinc oxide paint absorbed more than linseed oil did, with the zinc oxide paint absorbing most of all.

With free films the volumetric swelling exceeded the absorption of moisture not only at 90 and 97 percent relative humidity but at 65 and 80 percent, provided that there was measurable absorption. If the excess swelling above the volume of moisture absorbed is due to springback from release of compression acquired during the original hardening of the coatings, it is perhaps not surprising for it to be more marked for free than for bound films.

Part of the volumetric swelling of free films expressed itself in swelling

in area and the balance in swelling in thickness. Although a real swelling usually increased with any marked increase in volumetric swelling, there were no fixed relations between them even for one kind of paint in different conditions of humidity.

On redrying after testing, all free films shrank to less than the volume before test. Usually they shrank also in area and thickness to less than the initial dimensions before test. However, zinc oxide paint in water and in 97 percent relative humidity and in 80 percent relative humidity for the 3-day period remained greater in area after redrying than it was initially, as did also the titanium dioxide paint and the magnesium silicate paint when soaked in water and redried.

Conclusions

Both free and bound films of linseed oil and of oil paints pigmented with magnesium silicate, white lead, zinc oxide, and titanium dioxide, respectively, absorbed moisture and swelled measurably when hung in damp air for 3 days, but the absorption and swelling were much less than when the films were soaked in distilled water. From damp air, the higher the relative humidity, the greater were the absorption and swelling; but at 30 percent relative humidity or lower, and at even higher relative humidity for the least absorptive paints, any absorption that may have occurred was overbalanced by loss in weight from evolution of volatile oxidation products. Pure white lead paint was less absorptive than any of the others. Titanium dioxide paint absorbed a little less from air but a little more from water than linseed oil did. Magnesium silicate paint and zinc oxide paint absorbed much more than linseed oil did, with zinc oxide paint absorbing most. Volumetric swelling often exceeded the volume of moisture absorbed. This may indicate a springback in volume from release of compression in a "liquid phase" of linoxyn acquired during the original hardening of the paint, brought about when the rigid "solid phase" is plasticized by absorbed moisture. Although free films absorbed and swelled more than bound films when soaked in water, when hung in damp air the free films absorbed little more, and usually less, than bound films. The free films with 2 faces exposed to the air lost more volatile substances than the bound films, only 1 face of which was exposed to air. When redried after testing, free films always shrank to less than their volume before test. Bound films shrank to less than the initial volume after test at high relative humidity, and also at low relative humidity where loss of volatile predominated over absorption; but after testing at intermediate relative humidities, bound films failed to shrink back as far as their initial volume. This may be further evidence of a rigid "solid phase" of linoxyn preventing free movement when insufficiently plasticized by absorbed moisture.

References

1. Browne, F. L. 1953. The Absorption of Water, Swelling, and Solubility of Free Films of Paint. J. Forest Products Research Society 3 (No. 5):108–124.
2. ————. Swelling of Paint Films in Water, II. Absorption and Volumetric Swelling of Bound and Free Films Before and After Weathering. (For publication in J. Forest Products Research Society.)
3. Elm, Adolf C. 1953. Some Mechanical Properties of Paint Films, Official Digest, Paint and Varnish Production Clubs, No. 346:751–74.
4. Long, J. S., Rheineck, A. E., and Ball, G. L. 1933. Studies in the Drying Oils, XVII. Influence of Several Factors on the Mechanism of Drying of Oil Films. Ind. Eng. Chem. 25:1086–91.