

Swelling of Paint Films In Water

IV. Effect of Thickness of Film and Pigment Volume of Paint

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Presents systematic data on how absorption of water, swelling, and solubility of free films in water vary with the thickness of films. Discusses how pigment volume affects absorption and swelling.

THE ABSORPTION OF WATER, swelling, and solubility of free films of house paints vary with the thickness of the films. The relations were studied for 5 paints, each in 6 thicknesses between 2 and 7 or 8 mils. The thicker films gave lower values than the thinner films. Absorption and swelling vary also with the pigment volume of the paint. Results are reported for 3 paints, each at pigment volumes ranging from 20 to 60 per cent at intervals of 5 per cent.

Absorption and swelling were minimum near a critical pigment volume characteristic of the pigment. Unweathered films of paints of pigment volume less than the critical point swelled 1 cubic centimeter in volume for each gram of water absorbed. Above the critical point, swelling was less than 1 cubic centimeter per gram of water absorbed, presumably because the films contained voids that could hold water that did not cause swelling. Weathering had the effect of shifting the critical point to lower pigment volume.

The second paper in this series (3)¹ described a method of measuring the volumetric swelling of free and bound films of house paint when soaked in distilled water for 3 days together with determinations of the absorption of water, the swelling of free films in area, the changes in dimensions on redrying after soaking, and the weight of soluble ingredients leached from the films by the soaking water.

The first paper in the series (2) showed that absorption, swelling, and solubility are greater for thin than for thick films and suggested that the pigment volume of the paint may affect the

absorption and swelling of its films in water. This paper presents more systematic data on the effects of film thickness and of pigment volume. The methods and paints used, and the calculation and expression of results were described in detail in the second paper.

Effect of Film Thickness

For the study of film thickness 5 paints were chosen, pure white lead paint, L, p/nv 0.30; pure zinc oxide paint, Z, p/nv 0.30; pure magnesium silicate paint, p/nv 0.30; and 2 titanium-zinc paints differing in pigment volume, paints TZ₃₀, p/nv 0.30 and TZ₄₀, p/nv 0.40. Films of 6 different thicknesses were spread on gummed paper with each paint by use of a Bird doctor blade and suction plate together with suitable shims. Films approximately 2, 3, and 4 mils thick were spread in 1 coat; films of approximately 5, 6 and 7 mils thickness were spread in 2 coats with a day between for the first coat to dry. Films were stripped from the gummed paper when they were 6 days old, and the soaking tests were started when the films were 9 days old.

Table 1 gives the data for free films of the different thicknesses.

During the initial drying or hardening of the coatings after spreading the liquid paints, the density increased by about 8 per cent. For any one paint the density reached a somewhat higher value the thinner the coating. Thinner films perhaps became more thoroughly oxidized during the 9-day drying period than thicker films.

After soaking the free films in water for 3 days, the density of the swollen films was always materially decreased; but on redrying afterward the density returned to the value just before soaking or to a slightly higher value. Leaching of soluble organic material by the soaking water would be expected to raise the density because the pigments are much heavier than the organic vehicle.

Some paints not included in this series on film thickness lose greater pro-

portions of pigment by leaching or become somewhat porous after redrying and therefore fail to return quite to the density they had immediately before soaking (3).

For any one paint the absorption of water during the 3-day soaking period decreased significantly as the thickness of film increased. There were discrepancies in the data but the trends were clear. The 5-mil films of paints L and Z were somewhat too high in absorption; and there were irregularities for magnesium silicate paint and for paint TZ₃₀, p/nv 0.40, but not for paint TZ₄₀, p/nv 0.30.

Some of the discrepancies were greater than the experimental errors; they suggest that there are minor factors affecting the absorption of water that have not yet been discovered and controlled. Nevertheless, the general trend of diminishing absorption with increasing film thickness is clearly revealed in Table 1.

Films 7 to 8 mils thick absorbed only 50 to 65 per cent of the water taken up by films of the same paint that were 2 mils thick, except for the magnesium silicate paint for which the variation with thickness was less than for the other paints.

The volumetric swelling for all paints was nearly equal to the absorption of water and therefore showed similar variation with film thickness. Swelling efficiencies ranged between 99 and 106 per cent. Swelling in area and in thickness followed much the same pattern. On redrying, the trend was for the thinner films to shrink in volume somewhat more than the thicker films, but the shrinking in area appeared to be nearly independent of film thickness.

The weight loss by leaching during the 3-day soaking period was greatest for the thinnest films of any one paint and decreased as the film thickness increased.

The effect of film thickness on absorption, swelling, shrinking, and solubility is important enough to be kept constantly in mind when comparing the behavior of different paints in soaking tests. But it is not yet possible to calculate precise relations between thickness and absorption, swelling, and solu-

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

² Numbers in parentheses refer to literature cited.

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Table 1.—EFFECT OF THICKNESS OF FILM ON CHANGES IN DENSITY, ABSORPTION OF WATER AND SWELLING DURING SOAKING FOR 3 DAYS IN DISTILLED WATER, SHRINKING ON REDRYING, AND LOSS OF SOLUBLE SUBSTANCES BY LEACHING FOR FREE FILMS OF FIVE PAINTS OF DIFFERENT COMPOSITION

Paint (density of nonvolatile white liquid)	Density			Film thickness: T_0	Absorption: A/V_0	Swelling		Shrinking		Redried change			Weight loss while soaking: ΔT_0	
	Dry	Swollen: in water	Redried			In volume: ΔV_1	In area: ΔQ_1	In thickness: ΔT_1	Efficiency: $\Delta V_2/V_0$	In area: ΔV_3	In thickness: ΔQ_3	In area: ΔV_4		In thickness: ΔQ_4
				Mils	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent		
Basic carbonate white lead, L, p/nv 0.30 (2.705)	2.92	2.74	2.98	1.9	12.8	12.6	8.6	1.0	99	-3.6	-0.3	-3.1	5.3	
	2.91	2.74	2.95	2.7	11.7	11.7	7.3	1.9	100	-3.1	-0.6	-2.2	4.4	
	2.89	2.75	2.92	3.5	9.4	9.3	5.6	2.3	99	-2.5	-0.7	-1.1	4.0	
	2.88	2.73	2.91	4.9	10.4	10.8	6.2	2.7	104	-2.5	-0.9	-1.4	3.6	
	2.87	2.76	2.90	6.1	8.1	8.1	4.7	2.0	100	-2.1	-0.7	-1.1	3.0	
	2.85	2.75	2.88	8.4	7.2	7.4	4.4	1.9	103	-2.1	-0.7	-1.1	2.7	
Zinc oxide, Z, p/nv 0.30 (2.345)	2.54	1.84	2.59	1.8	85.5	85.6	38.2	31.5	100	-5.0	+5.6	-9.8	8.6	
	2.49	1.84	2.53	2.8	78.4	78.2	31.9	32.2	100	-4.2	+7.4	-10.9	7.5	
	2.48	1.89	2.51	3.3	70.0	69.1	26.1	35.0	99	-3.9	+5.9	-9.0	6.8	
	2.50	1.77	2.51	4.8	96.5	96.2	30.4	48.1	100	-2.9	+7.7	-9.8	5.0	
	2.46	1.91	2.48	7.2	61.0	60.6	20.9	31.0	99	-2.4	+6.1	-8.0	3.7	
	2.45	1.95	2.47	8.0	55.4	55.0	9.0	40.4	99	-1.9	+4.8	-6.1	2.9	
Magnesium silicate, p/nv 0.30 (1.515)	1.67	1.42	1.68	2.1	57.2	57.3	15.1	32.5	100	-5.0	+1.3	-6.5	7.6	
	1.66	1.45	1.68	2.8	45.7	45.8	14.9	23.6	100	-4.5	+2.3	-6.5	6.0	
	1.65	1.44	1.67	3.4	47.4	47.5	15.7	23.7	100	-4.0	+3.3	-7.4	5.0	
	1.64	1.42	1.65	5.2	54.7	54.8	16.1	31.1	100	-3.2	+3.5	-6.1	3.9	
	1.63	1.44	1.64	7.8	43.5	44.2	13.1	25.8	101	-2.2	+2.6	-4.2	1.9	
	1.62	1.43	1.64	8.3	45.5	46.0	14.0	26.0	101	-2.2	+2.7	-4.2	1.7	
Titanium-sinc, Ti_{20} , p/nv 0.30 (1.728)	1.86	1.31	1.89	2.1	168	167	68.7	55.0	99	-6.2	+20.4	-24.2	9.4	
	1.86	1.32	1.87	2.9	153	155	65.4	51.6	101	-3.7			6.3	
	1.86	1.35	1.86	3.4	145	146	56.0	56.3	101	-1.9			3.4	
	1.85	1.41	1.87	5.0	109	109	58.8	49.0	100	-4.3	+21.7	-21.3	6.1	
	1.85	1.45	1.86	6.0	89.2	88.6	42.5	30.2	99	-2.6			4.3	
	1.85	1.48	1.86	6.8	80.9	80.3	39.0	27.7	99	-2.8	+14.4	-15.0	4.3	
Titanium-sinc, Ti_{20} , p/nv 0.40 (1.975)	2.14	1.54	2.16	1.7	92.2	97.9	50.2	28.2	106	-5.1	+8.8	-12.8	8.5	
	2.14	1.55	2.16	2.2	105	104	47.8	35.7	99	-4.1	+9.6	-11.6	6.9	
	2.13	1.53	2.15	2.7	111	110	43.6	44.2	99	-4.6	+5.4	-9.1	7.2	
	2.13	1.61	2.14	4.4	86.5	85.8	45.3	26.7	99	-2.2	+10.8	-11.3	4.3	
	2.11	1.70	2.12	6.4	60.3	59.7	27.2	24.0	99	-1.7	+6.5	-7.5	2.8	
	2.10	1.70	2.11	6.8	59.5	58.8	26.4	24.6	99	-1.7	+8.3	-9.3	3.0	

bility because the data are not reproducible closely enough for that purpose. However, the variations with film thickness, and the limitations of reproducibility are small in comparison with the differences among paints. In comparing different kinds of paints, uncertainties can arise only if the paints are similar enough in absorptive properties to make distinction between them of little consequence or if the films differ greatly in thickness.

Effect of Pigment Volume

For the study of the effect of pigment volume of paint on the absorption and swelling of free films, three kinds of single-pigment paints were chosen, made respectively with basic carbonate white lead, zinc oxide, and anatase titanium dioxide. The first was a kind of paint that is very low in absorption and swelling, the second very high, and the third intermediate.

For each kind of pigmentation a series of 9 paints, varying in pigment volume from 0.20 to 0.60 in steps of 0.05 were made. Each paint was spread by doctor blade, suction plate, and suitable shims at a wet-film thickness that was intended to make a coating approximately 4½ mils thick when dry. The thicknesses actually pro-

duced, however, varied from the intent somewhat more than might be desired, but not sufficiently to obscure the general trend in the relations between pigment volume and absorption.

Each paint was spread on gummed paper to provide samples of free films for test before weathering. Each paint was spread also on previously weighed tinplate to furnish samples for exposure in artificial weathering for 15 days in a Weatherometer. Unweathered films were 17 days old when submitted to the soaking test. Coatings on tinplate were 17 days old when exposure began in the Weatherometer. Hard water was used in the Weatherometer sprays.

Results with unweathered films are reported in Table 2 and those with weathered films in Table 3.

Coatings of white lead paints dried with the degree of gloss typical of house paints at all pigment volumes below 0.60. At p/nv 0.60 white lead paint dried flat, that is, without gloss. Zinc oxide paints dried glossy at p/nv of 0.45 and less, with low gloss at p/nv 0.50, and without gloss at p/nv 0.55 and 0.60. Titanium dioxide paints dried glossy at p/nv of 0.40 and less, with low gloss at p/nv 0.45, and without gloss at higher pigment volume.

Asbeck and Van Loo (1) showed that the pigment volume at which transition from the glossy to the glossless condition occurs is a critical point at which marked changes occur in other properties of the paint such as sensitivity to moisture blistering, permeability to moisture, and protective power against rusting of metal. They therefore called the point the critical pigment volume. Presumably it is the point at which the film contains just enough vehicle to cover the surfaces of the particles of pigment and to fill the voids between them.

Thus in these tests the critical pigment volume was between 0.55 and 0.60 for white lead paint, between 0.45 and 0.50 for zinc oxide paint and between 0.40 and 0.45 for anatase-titanium-dioxide paint.

The results of the tests of absorption and swelling indicate that absorption and swelling may now be added to the paint properties that are known to change sharply at the critical pigment volume.

Films Before Weathering

Unweathered films of all 3 kinds of paint (Table 2) exhibited a minimum absorption at or just below the pigment

Table 2—UNWEATHERED PAINTS—EFFECT OF PIGMENT VOLUME OF PAINT ON THE ABSORPTION OF WATER AND SWELLING DURING SOAKING FOR 3 DAYS IN DISTILLED WATER, SHRINKING ON REDRYING, AND LOSS OF SOLUBLE SUBSTANCES BY LEACHING FOR FREE FILMS OF PAINTS MADE WITH THREE DIFFERENT KINDS OF PIGMENTS

Paint	Pigment		Initial: Absorp-		Swelling			Swelling:		Redried			Weight loss	
	volume	thick-	tion		In	In	area	thick-	effi-	In	In	In	while	ing
	of	ness	A/V ₀		volume	area	thick-	ness	ciency	volume	area	thick-	soak-	g
	p/nv	T ₀			ΔV _s	ΔQ _s	ΔV _s /A	ΔT _s		ΔV _r	ΔQ _r	ΔT _r	ΔV _l	ΔT _l
		Mils	Percent	Percent	Per-	Per-	Percent		Per-	Per-	Per-	Percent		Percent
			cent	cent	cent	cent			cent	cent	cent			
Basic carbonate white lead, L, p/nv 0.30	0.60	5.8	12.2	6.7	3.0	3.4	55	0	-0.5	+0.5		2.8		
	0.55	6.1	5.2	3.7	2.2	1.3	71	-1.5	-0.5	-1.0		2.4		
	0.50	6.2	4.7	4.5	2.4	2.0	96	-1.5	-0.6	-0.9		1.9		
	0.45	5.2	4.7	4.9	2.9	2.1	104	-1.8	-0.4	-1.4		2.0		
	0.40	4.6	5.6	5.8	3.5	2.2	103	-2.7	-0.4	-2.3		2.8		
	0.35	5.8	5.5	5.6	3.1	2.3	102	-2.3	0	-2.3		2.6		
	0.30	4.1	6.4	6.5	4.4	2.0	102	-3.3	-0.4	-2.9		3.7		
	0.25	3.9	6.9	7.3	4.6	2.6	106	-3.8	-0.3	-3.5		4.2		
Zinc oxide, Z, p/nv 0.30	0.60	4.1	6.8	6.9	5.2	1.4	102	-3.6	-0.6	-3.0		3.9		
	0.55	6.1	33.5	25.9	6.6	18.0	77	+5.4	+1.9	+3.5		3.4		
	0.50	5.9	32.6	22.3	9.3	12.0	68	+2.1	+1.5	+4.6		6.0		
	0.45	5.7	34.7	33.1	15.1	15.5	95	-0.9	+1.3	-2.0		1.8		
	0.40	3.7	65.5	63.3	33.2	22.5	97	-1.0	+4.5	-5.3		4.8		
	0.35	4.3	71.6	70.1	35.4	25.6	98	-0.6	+6.2	-6.5		2.7		
	0.30	4.7	76.3	75.5	39.9	25.5	99	-1.5	+8.4	-9.2		2.9		
	0.25	4.3	71.6	71.4	33.1	28.7	100	-2.5	+18.8	-15.0		4.1		
Anatase titanium dioxide, T ₄₂₀ , p/nv 0.30	0.60	5.4	26.6	21.0	2	20.8	79	+1.7	-0.1	+1.8		3.7		
	0.55	4.9	16.5	13.0	4	12.3	79	-1.4	-0.2	-1.2		4.1		
	0.50	5.4	17.1	14.1	3.0	11.1	82	-0.6	-0.3	-0.3		3.0		
	0.45	4.2	11.3	11.2	6.1	4.8	99	-4.0	-1.0	-3.0		4.5		
	0.40	4.0	13.1	13.1	8.1	4.5	100	-3.1	-0.8	-2.3		3.3		
	0.35	4.5	15.2	15.1	9.4	5.2	99	-2.5	-0.7	-1.8		3.0		
	0.30	4.0	16.1	16.3	9.0	6.7	101	-3.2	0	-3.2		3.6		
	0.25	3.9	16.2	16.4	9.6	6.2	101	-3.2	+0.1	-3.3		3.9		
	0.20	3.7	18.4	18.8	9.3	8.6	102	-3.7	-0.1	-3.6		4.3		

¹These paints dried without any gloss.

²These paints dried with low gloss.

volume of transition from gloss to flat. The volumetric swelling reached a minimum at the same or the next step in pigment volume above that of minimum absorption.

The swelling efficiency was always close to 100 per cent (between 97 and 106 per cent) at pigment volumes from 0.20 to the critical pigment volume and was always less than 97 per cent, sometimes as low as 55 per cent, at higher pigment volumes. This is strong confirmation of the interpretation of low swelling efficiencies made in a previous paper (3), namely, that an efficiency less than 100 per cent by more than reasonable experimental error indicates that the film contains voids capable of holding absorbed water that does not cause swelling.

Films of paint of pigment volume higher than critical necessarily contain such voids because there is insufficient vehicle to fill all spaces between particles of pigment. Experimental evidence of porosity above the critical pigment volume and absence of pores below that point was published by Eckhaus, Wolock, and Harris (4) on the basis of measurements of permeability to moisture and surface roughness of free films of paint made with titanium dioxide and with magnesium silicate pigments.

Swelling in area was approximately parallel to the volumetric swelling, except that, on passing from the critical to higher pigment volume, swelling in volume increased from the minimum, but swelling in area either continued to decrease or increased very little.

On redrying, white lead paint of p/nv 0.60 shrank to its initial volume before soaking. All other white lead paints shrank to less than the initial volume, increasingly so the lower the pigment volume. Thus there was no evidence of a change in shrinking at a critical point.

With zinc oxide paints the films of paints of p/nv 0.60 and 0.55 failed to return on redrying to the initial volume, whereas films of paints of lower p/nv shrank below the initial volume, increasingly so as p/nv decreased further. Films of titanium dioxide of p/nv 0.60 after redrying remained somewhat above their initial volume, but those of p/nv 0.55 or less shrank to less than the initial volume. On the whole, the relation between shrinking on redrying after soaking and pigment volume is much less sharply defined than the relation between swelling and pigment volume.

The loss in weight from leaching of soluble substances during soaking seems to be nearly independent of pigment volume.

Weathered Films

Use of hard water in the Weatherometer sprays may be responsible for irregularities in the data for loss of weight during weathering, particularly with the zinc oxide paints (3). Nevertheless, there was clearly a trend to higher losses at low than at high pigment volume, but no evidence of a minimum at a critical pigment volume.

The absorption of water on soaking was minimum at the critical pigment volume for the weathered just as it was for the unweathered films of white lead paints and zinc oxide paints. But for the weathered films of titanium dioxide paints the minimum of absorption was at p/nv 0.35, much below the pigment volume of minimum absorption for the unweathered films. All titanium dioxide paints were chalking very freely by the end of the 15-day weathering period, but those of p/nv 0.35 and higher were chalking much more seriously than those of lower pigment volume.

The volumetric swelling of weathered films was minimum for all three kinds of paint at the same pigment volume at which absorption was minimum. At pigment volumes above that of the minimum the swelling increased less than the absorption did.

Table 3.—WEATHERED PAINTS—EFFECT OF PIGMENT VOLUME OF PAINT ON THE LOSS OF WEIGHT WHILE WEATHERING, ABSORPTION OF WATER AND SWELLING DURING SOAKING FOR 3 DAYS IN DISTILLED WATER, SHRINKING ON REDRYING, AND LOSS OF SOLUBLE SUBSTANCES BY LEACHING FOR FREE FILMS OF PAINTS MADE WITH THREE DIFFERENT KINDS OF PIGMENTS

Paint	Pigment volume of paint p/nv	Weight loss weather- ing S_1/V_0	Initial thick- ness T_0	Absorp- tion A/V_0	Swelling			Swelling effi- ciency $\Delta V_0/V_0$	Redried			Weight loss while soak- ing S_2/V_0
					In volume ΔV_a	In area ΔQ_a	In thick- ness ΔT_a		In volume ΔV_r	In area ΔQ_r	In thick- ness ΔT_r	
		Percent	Mils	Percent	Per- cent	Per- cent	Per- cent	Percent	Per- cent	Per- cent	Per- cent	Percent
Basic carbonate white lead, L, p/nv, 0.30	1.60	9.2	7.2	15.8	6.3	3.9	2.3	40	+2.9	+1.2	+1.7	2.0
	.55	5.1	7.3	8.8	6.1	2.1	4.0	69	-.5	-.7	+.2	1.2
	.50	6.6	8.4	8.9	7.8	2.5	5.1	88	0	-.6	+.7	1.0
	.45	12.2	4.5	24.0	22.9	3.6	18.6	95	+2.2	-1.0	+3.2	1.1
	.40	17.7	3.9	36.5	35.0	3.1	31.0	96	+.6	-1.2	+1.8	1.6
	.35	12.8	7.7	11.5	11.0	2.1	8.7	96	-.9	-.3	-.6	1.7
	.30	27.0	4.3	16.7	16.7	3.3	13.0	100	-2.1	-1.1	-1.0	2.6
	.25	39.8	2.8	52.5	56.7	3.1	51.8	108	-2.1	-2.0	-.1	4.0
	.20	21.7	4.8	18.2	17.8	3.4	14.0	98	-1.8	-.7	-.1	2.5
Zinc oxide, Z, p/nv 0.30	1.60	(2)										
	.55	11.5	5.9	40.6	24.6	6.1	17.1	60	-6.5	+1.3	-7.7	12.2
	.50	5.8	5.6	25.0	21.6	8.8	11.8	86	-1.6	+.5	-2.1	2.1
	.45	8.1	4.8	37.6	33.4	16.2	11.9	85	-3.3	+2.7	-5.9	6.6
	.40	11.3	4.4	43.1	40.6	21.1	16.0	94	-1.6	+5.2	-6.5	3.9
	.35	9.9	4.7	44.4	40.5	22.4	14.8	92	+.2	+6.9	-6.1	3.5
	.30	14.0	3.3	75.2	69.1	21.6	39.2	92	+1.3	+6.4	-4.8	6.0
	.25	9.7	5.0	46.7	45.0	23.8	17.1	96	+.8			1.8
	.20	14.5	3.6	67.0	63.4	31.8	24.0	95	-2.2			7.3
Anatase titanium dioxide, T_{420} , p/nv 0.30	1.60	(4)										
	.55	(5)										
	.50	24.9	4.4	23.8	12.7	1.5	11.0	53	-2.5	-.5	-2.0	4.8
	.45	31.9	2.9	22.2	8.5	1.5	12.6	58	+1.6	0	+1.6	3.7
	.40	27.6	3.7	18.4	6.9	1.3	10.9	57	+.7	-.7	0	3.2
	.35	26.0	3.7	6.2	4.0	3.4	.5	65	+1.8	-2.2	+4.0	6.0
	.30	38.3	2.8	12.6	9.8	5.1	4.2	78	-1.3	-1.6	+.3	4.4
	.25	44.2	2.9	13.1	11.5	5.4	5.8	88	-2.6	-1.1	-1.5	4.5
	.20	51.0	3.1	17.2	13.2	5.9	7.0	77	+1.2	-1.3	+2.5	4.6

¹These paints dried without any gloss.

²Film too brittle to be stripped from tinplate after weathering.

³These paints dried with low gloss.

⁴Films cracked and scaled from tinplate during weathering.

For all weathered films of zinc oxide paints and titanium dioxide paints and for white lead paints of p/nv 0.35 or higher, the swelling efficiency was less than 97 per cent. Moreover, the trend was from higher swelling efficiency at low to lower efficiency at high pigment volume. Weathering, then, seems to reduce swelling efficiency and to reduce it more rapidly at high than at low pigment volume.

Weathering markedly increased the absorption and volumetric swelling (but not the swelling in area) of the white lead paints at or below the critical pigment volume. Similar results were reported for artificial weathering but not for natural weathering in a previous paper (3). A subsequent paper will show that artificial weathering reduces rather than increases the absorption and swelling of white lead paint when distilled water is used instead of hard water for the Weatherometer sprays. Weathering decreased the absorption and swelling of the zinc oxide and the titanium dioxide paints at or below the critical pigment volume.

Swelling in area of the weathered films paralleled the volumetric swelling fairly closely, except that swelling in

area increased little if any at pigment volumes above the critical.

Shrinking on redrying weathered films after soaking seemed to follow no consistent pattern. With all three kinds of paint, some films failed to shrink back to the initial volume before soaking and others shrank to slightly smaller volume.

Loss in weight from leaching during soaking was independent of pigment volume and was about the same for weathered as for unweathered films.

Conclusions

1. Film thickness at which paint coatings are spread has the following effects: Density increases slightly less during initial drying of wet paint the thicker the film. Absorption of water and volumetric swelling of free films during 3 days' soaking in distilled water decrease as film thickness increases; but unweathered films, regardless of thickness, usually swell about 1 cubic centimeter for each gram of water absorbed. On redrying after soaking, thin films shrink in volume more than thick films, but the shrinking in area is independent of thickness. Weight losses

by leaching of soluble substances are greater for thin than for thick films.

2. Although the effect of film thickness on absorption and swelling must be kept in mind when comparing different paints, it is not so great as to obscure differences between paints unless the film thicknesses are far apart or the paints are too nearly alike in absorption and swelling for difference between them to have much significance.

3. Absorption of water and swelling of free films of unweathered paints are minimum at a critical pigment volume that is characteristic of the kind of pigment and vehicle in the paint. The critical pigment volume is well above the pigment volume at which house paints are usually made.

4. At and below the critical pigment volume unweathered films swell 1 cubic centimeter for each gram of water absorbed, but above the critical point they swell less than 1 cubic centimeter per gram of water. Since the films of higher than critical pigment volume contain less than enough vehicle to completely fill the spaces between particles of pigment, a conclusion previously drawn, that less than a cubic centimeter of swelling for a gram of absorbed water

indicates the presence of voids in the film, is confirmed.

5. Loss of weight of paint coatings during artificial weathering is greater at low than at high pigment volumes, but there is no evidence of a minimum of loss at a critical pigment volume.

6. For weathered films there are minima of absorption and swelling at an intermediate pigment volume, but the

minima occur at lower pigment volumes in weathered than in unweathered films. Perhaps it may fairly be concluded that weathering lowers the critical pigment volume of paints.

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