Swelling of Paint Films in Water
VII. Latex Vehicles[1]

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Discusses the effect of four water emulsion vehicles on the behavior of free films of paints when soaked in distilled water for three days and then redried, when soaked again for three days and redried, and when weathered before soaking for three days and redried. Measured were changes in density, absorption of water, swelling during absorption, shrinkage on redrying, loss in weight while soaking, and loss in weight while weathering.

THE BEHAVIOR OF FREE FILMS of different oil and oleoresinous vehicles with and without pigments when soaked in distilled water for 3 days and then redried was reported in the sixth paper of this series (3).[3] This seventh paper describes similar tests of unpigmented and pigmented films in latex (water emulsion) vehicles.

Vehicles and Paints Tested

Three commercial latex vehicles were chosen: an acrylic-resin emulsion, a polyvinyl acetate emulsion, and a styrene-butadiene emulsions. The emulsions contained necessary plasticizers, the nature of which was not disclosed by the makers. It should be recognized, of course, that different brands of any one of the three kinds of latex may vary considerably in their properties, particularly in absorption and swelling. For the present purpose, however, the interest is not primarily in comparison of one kind of latex with another, but rather in comparing latexes as a group with the oil and oleoresinous vehicles previously studied and in learning whether pigments exert similar effects in latex and in oleoresinous vehicles.

The pigments were basic carbonate white lead, rutile titanium dioxide, zinc oxide, and magnesium silicate of the same brands and grades used in the previous work with oil and oleoresinous vehicles. Pigmented films were made with single-pigment paints only, and always at 30 per cent pigment volume. It was not found possible, however, to make a white lead paint with the polyvinyl acetate latex, because white lead apparently broke the emulsion and a granular product resulted.

The latex paints were strictly experimental. The desire was to study films composed as nearly as possible of polymer and pigment without the complications of the several additives necessary to make practical paints. Other investigators (2, 4, to 7) indicate that additives, especially those soluble or partly soluble in water, often greatly increase the absorption of water and swelling of latex paints. Accordingly, no wetting agent, dispersing agent, antifoaming agent, bodying agent, or preservative was added except as described later in the report.

The experimental paints were made in laboratory batches of less than 1 pint, with such precautions to avoid foaming as it was possible to take without the use of additives. Most of the paints held some foam, and films made from some of them, especially those containing white lead or zinc oxide, retained some air bubbles. Nevertheless, all films proved impermeable to dry air under one-third atmosphere pressure except those of zinc oxide in acrylic resin and in polyvinyl acetate latex and titanium dioxide in styrene-butadiene latex. Paints containing one additive, methyl cellulose in the proportion of 4.5 per cent based on the nonvolatile content of the latex, were made with each of the four pigments in styrene-butadiene latex.

For comparison with the experimental paints, one commercial latex paint was tested. It was made with rutile titanium dioxide and magnesium silicate at 35.5 per cent pigment volume in a polyvinyl acetate latex with methyl cellulose and other customary additives.

Preparation of Free Films and Tests

Free films of latex vehicles and paints could not be prepared by spreading on gummed paper because the water in the latex softened the dextrine gum and the coatings usually cracked in an alligator pattern as they dried. Accordingly, all films were spread on tinplate and, after curing or curing followed by artificial weathering, were stripped by amalgamating the tinplate.

All coatings were allowed to stand 30 days after spreading to allow them to cure thoroughly. Those to be weathered were then exposed to ultra-violet

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

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light from a flaming carbon arc enclosed in Corex D glass (1,200 kilowatt-hours of electric input) and sprayed with distilled water three times each hour for a period of 15 days.

Unweathered films of each vehicle and paint were subjected to two successive cycles of soaking in distilled water for three days followed by redrying over calcium chloride. This was done because it was observed that some films of latex paint absorb much less water and swell less in the second soaking than in the first, presumably because the first soaking removes soluble ingredients that stimulate absorption and swelling. Weathered films of each vehicle and paint, which were always well leached during the weathering process, were subjected to one cycle only of soaking for three days and redrying.

Dry films of latex paints usually begin to absorb water and swell much more rapidly than oil or oleoresinous paint films. For that reason great care was taken to make the weighings of dry latex films as quickly as possible after immersion.

Wet films of latex paints, when blotted to remove free water, were found to lose weight more rapidly by evaporation while being weighed than was the case with films of oil or oleoresinous paints. The wet films of latex paint were therefore placed in tared weighing bottles immediately after blotting.

In all other respects the methods of testing were the same as those previously described for the oil and oleoresinous paints.

Results with Experimental Paints

The results with the experimental vehicles and paints are reported in Table 1.

Density: The relatively large increase in density that was characteristic of oil paints during their initial drying period (3) was conspicuously lacking among the latex vehicles and paints. In fact, only 5 of the 18 latex vehicles and paints gained at all in density during drying and curing, and for 4 of the 5, the gain was no greater than 3 per cent. The clear film of acrylic latex was 6.4 per cent denser than the nonvolatile part of the liquid latex, but the films of clear polyvinyl acetate and styrene-butadiene dried and cured without change in density.

On the other hand, 11 of the 15 latex paints made films of lower density than the nonvolatile part of the liquid paint. Decrease in density during initial drying and curing probably indicates the formation of porous films that enclose voids. This interpretation is consistent with the finding that all latex paints exhibited less than 100 per cent swelling efficiency, and the swelling efficiency usually was particularly low when the decrease in density on drying and curing was more than 4 per cent.

The densities of the nonvolatile portions of the liquid latexes and paints were as follows: acrylic latex, 1.09; polyvinyl acetate latex, 1.16; styrene-butadiene latex, 1.02; acrylic paints pigmented with white lead, zinc oxide, titanium dioxide, and magnesium silicate, respectively, 2.80, 2.44, 2.02, and 1.62; polyvinyl acetate paints pigmented with zinc oxide, titanium dioxide, and magesium silicate, respectively, 2.19, 1.95, and 1.67; styrene-butadiene paints pigmented with white lead, zinc oxide, titanium dioxide, and magnesium silicate, respectively, 2.76, 2.39, 1.97, and 1.57; and styrene-butadiene with methyl cellulose pigmented with white lead, zinc oxide, titanium dioxide, and magnesium silicate, respectively, 2.77, 2.33, 1.98, and 1.58.

When soaked in water for the first time, all films decreased in density by an amount roughly proportional to the absorption of water except the films of titanium dioxide and of zinc oxide in polyvinyl acetate, both of which gained in density despite large absorptions of water. The two exceptions were the paints whose films decreased most markedly in density during drying and curing. Hence the gain in density when soaked in water may indicate a reduction in volume of voids brought about by release of internal stresses in the films when they are plasticized by absorbed water.

When redried after the first soaking, all but four films regained or, more often, exceeded their density before soaking. Increase in density and decrease in volume are to be expected as a result of loss of water-soluble ingredients of low density to the soaking water. Of the four films that failed to regain the density before soaking, two fell short by less than 2 per cent and contained either no pigment or the light pigment magnesium silicate. The other two, zinc oxide in styrene-butadiene with and without methyl cellulose, fell short by 5.7 and 4.8 per cent, respectively, and also were larger in volume after redrying than before soaking.

When soaked in water a second time, the density of most films decreased, again roughly proportionally to the absorption of water. The exceptions were films that had originally dried with a density less than that of the nonvolatile in the liquid paint and had not yet regained that density after the first soaking and redrying. When redried after the second soaking, all but three films regained or only very slightly exceeded their density before the second soaking. The three exceptions, titanium dioxide in styrene-butadiene, zinc oxide in acrylic resin, and magnesium silicate in styrene-butadiene, were films that remained larger in volume after redrying than before the second soaking.

Weathering increased the density of all films except those of zinc oxide in acrylic resin, in styrene-butadiene, and in styrene-butadiene with methyl cellulose. These films decreased substantially in density. The three exceptions were notable also for very low swelling efficiencies after weathering, 32, 29, and 40 per cent, respectively, which indicates that weathering increased the volume of voids within the films.

When soaked in water, all but five weathered films decreased in density. All five of the films that failed to decrease in density were films that, unlike the others, were still below the density of the non-volatile in the liquid paints even after weathering. Four of the five were paints whose unweathered films had failed to decrease in density during one or both of the soaking periods, and four of the five had, as unweathered films, increased in volume after redrying following one of the soaking periods. These five films, then, were porous films that tended to become less porous when soaked in water. When the weathered films were redried after soaking, they all regained or very nearly regained their density before soaking except one, zinc oxide in polyvinyl acetate, which retained 2.9 per cent greater volume after soaking.

The observations of density changes indicate that the latex vehicles and paints, although subject to less changes during film formation and weathering from oxidation, contraction, and decomposition of the vehicle constituents themselves than are the oil and oleoresinous paints, nevertheless are subject to a greater extent than the oil paints to changes in film structure, particularly to formation of voids within the films and alteration in the volume of voids.

Absorption of Water: Clear films of acrylic resin in both the first and second soakings of unweathered and weathered film were remarkably high in absorption, more than twice as high as the films of unbodied linseed oil previously reported (3). Polyvinyl acetate film before weathering absorbed less than unbodied linseed oil and about as much as films of bodied linseed oil or of alkyd resin. After weathering, however, polyvinyl acetate film, unlike the oil and oleoresinous films, became very highly absorptive.

Unweathered styrene-butadiene film in the first soaking was about equal

GLD38023

to unweathered polyvinyl acetate, but in the second soaking the absorption by styrene-butadiene film was very low. Failure of the styrene-butadiene film on weathering precluded measurement of its absorption after weathering, which may indicate that weathering greatly increased its absorption as it did that of clear acrylic resin and polyvinyl acetate. Weathering, then, seems to increase the absorption of water by clear latex films.

Pigmentation altered the absorption of all latex vehicles, usually significantly. In acrylic latex, the clear film of which was very absorptive, all pigments except zinc oxide greatly reduced absorption. Zinc oxide increased the absorption if allowance is made for the fact that only 70 per cent of the pigmented film was acrylic resin. Unweathered pigmented films of polyvinyl acetate or styrene-butadiene were always higher in absorption than the clear films of the same latex, and among them, the films with zinc oxide were highest in absorption. Thus zinc oxide seems to have the same effect of stimulating high absorption in latex paints that it has in oil and oleoresinous paints.

White lead, however, behaved differently in the latex paints than it did in oil paints. In acrylic latex, white lead did not reduce absorption nearly as much as titanium dioxide did,

Table 1.—DATA FOR FREE FILMS OF DIFFERENT KINDS OF LATEX VEHICLES WITH AND WITHOUT PIGMENTS WHEN SOAKED IN WATER FOR THREE DAYS AND REDRIED, WHEN SOAKED AGAIN FOR THREE DAYS AND REDRIED, AND WHEN WEATHERED BEFORE SOAKING FOR THREE DAYS AND REDRIED—CHANGES IN DENSITY; ABSORPTION OF WATER AND SWELLING IN VOLUME, AREA, AND THICKNESS; SWELLING EFFICIENCY, SHRINKING IN VOLUME, AREA, AND THICKNESS WHEN REDRIED; LOSS IN WEIGHT WHILE SOAKING; AND LOSS IN WEIGHT WHILE WEATHERING

Kind of latex vehicle	Stage in cycle of testing	Weight loss while weathering S_1/V_o	Density of film: Dry	Swollen in water	Redried	Initial thickness of film T_o	Absorption of water A/V_o	Swelling: In volume ΔV_s	In area ΔQ_s	In thickness ΔT_s	Swelling efficiency $\frac{\Delta V_s V_o}{A}$	Redried: Volume ΔV_r	Area ΔQ_r	Thickness ΔT_r	Loss in weight soaking S_2/V_o
		Percent				Mils	Percent	Per-cent	Percent	Percent	Percent	Per-cent	Percent	Percent	Gr. per 100 cc.
CLEAR VEHICLES CONTAINING NO PIGMENT															
Acrylic	First soak		1.16	1.10	1.16	3.9	57.9	57.5	42.7	9.7	99	-0.5	-2.2	+1.5	1.2
	Second soak		1.16	1.10	1.16	4.0	52.0	51.7	35.1	11.8	99	-.5	0	-.5	.3
	Weathered	5.3	1.17	1.09	1.16	3.6	68.7	68.2	34.9	24.7	99	0	+3.8	-3.9	.5
Polyvinyl acetate	First soak		1.16	1.15	1.16	3.8	8.2	8.1	5.9	-5.5	99	-8.2	-6.3	-2.1	9.3
	Second soak		1.16	1.16	1.16	3.7	8.1	7.8	4.0	3.2	96	-.3	+1.1	-1.6	.3
	Weathered	9.1	1.17	1.12	1.17	3.7	48.9	48.9	28.0	15.6	100	-1.2	+5.9	-6.7	9.1
Styrene-butadiene[1]	First soak		1.02	1.00	1.00	4.4	8.7	8.6	9.2	-6.8	99	-6.7	-2.0	-8.6	7.8
	Second soak		1.00	1.00	1.00	4.2	3.3	3.1	2.7	0	94	-.2	-.6	-3.6	1
BASIC CARBONATE WHITE LEAD, SINGLE-PIGMENT PAINTS, PIGMENT VOLUME 0.30															
Acrylic	First soak		2.78	2.56	2.82	5.2	22.7	18.7	5.7	10.5	82	-1.8	0	-1.9	2.0
	Second soak		2.82	2.64	2.82	5.1	16.9	13.2	3.7	8.7	78	-.2	-.3	0	.4
	Weathered	4.5	2.89	2.33	2.89	4.4	47.2	44.2	5.6	36.3	94	-.3	+.6	-1.1	1.0
Styrene-butadiene	First soak		2.74	2.61	2.78	4.9	11.9	11.0	3.4	3.7	92	-3.6	-.9	-2.8	5.5
	Second soak		2.78	2.65	2.79	4.8	9.2	8.9	1.5	6.3	97	-.5	-.4	-.6	.5
	Weathered	8.9	2.82	2.58	2.82	4.4	16.7	16.1	8	14.6	96	-.7	-.1	-.5	2.0
Styrene-butadiene plus methyl cellulose	First soak		2.65	2.17	2.72	3.9	51.5	47.4	3.1	12.1	92	-5.6	0	-5.4	9.4
	Second soak		2.72	2.33	2.73	3.7	35.7	32.7	1.7	29.1	92	-1.2	-1.0	-.3	1.1
	Weathered	11.1	2.75	2.58	2.75	3.7	15.0	12.7	1.3	9.5	85	-1.5	-.6	-1.1	4.0
RUTILE TITANIUM DIOXIDE, SINGLE-PIGMENT PAINTS, PIGMENT VOLUME 0.30															
Acrylic	First soak		2.08	2.03	2.08	4.9	7.0	6.4	6.2	-1.4	91	-1.6	-3.1	+1.4	2.8
	Second soak		2.08	2.03	2.09	5.0	7.3	6.7	4.2	1.8	92	-.7	-.2	-.4	.8
	Weathered	3.0	2.09	2.04	2.11	5.3	6.5	6.4	2.8	1.9	99	-1.2	-.8	-.2	1.1
Polyvinyl acetate	First soak		1.71	1.89	1.77	4.8	23.0	6.3	6.0	5.0	27	-5.7	-5.2	-.6	3.6
	Second soak		1.77	1.91	1.78	4.8	21.6	4.2	5.2	-1.7	19	-.5	-.1	-.4	.2
	Weathered	4.2	1.80	1.98	1.82	3.8	15.0	13.9	.4	11.9	93	-1.8	-2.1	+.5	.6
Styrene-butadiene	First soak		1.95	1.88	1.96	5.1	10.9	9.9	6.9	.2	91	-3.0	-2.8	-.2	4.6
	Second soak		1.96	1.93	1.95	5.1	6.2	4.3	3.2	1.6	69	+.6	-.3	+.8	.3
	Weathered	1.5	2.00	1.89	1.99	4.8	15.2	13.7	1.1	12.6	90	0	0	+.4	.4
Styrene-butadiene plus methyl cellulose	First soak		1.93	1.84	1.96	3.7	15.3	14.8	10.1	-1.1	97	-6.2	-4.9	-1.4	7.8
	Second soak		1.96	1.87	1.97	3.6	12.5	12.0	6.2	5.2	96	-.2	+.3	-.5	.2
	Weathered	1.8	2.01	1.98	2.02	3.7	5.9	5.0	1.4	2.7	85	-1.4	-.8	-.5	2.1
ZINC OXIDE, SINGLE-PIGMENT PAINTS, PIGMENT VOLUME 0.30															
Acrylic	First soak		2.48	2.06	2.49	2.8	50.5	45.2	2.9	39.4	90	-1.8	-1.5	-.4	3.9
	Second soak		2.49	2.08	2.42	2.8	47.8	40.0	2.0	39.4	84	+2.2	-.9	+2.9	1.1
	Weathered	14.3	1.99	2.14	2.00	3.6	42.5	13.7	.6	12.1	32	-.9	-.6	-.3	1.2
Polyvinyl acetate	First soak		1.81	1.95	2.40	3.5	49.7	42.6	5.8	11.0	86	-25.0	-6.2	-20.0	3.7
	Second soak		2.40	1.95	2.40	2.8	64.2	55.2	1.9	52.0	86	-2.2	+2.9	-3.6	2.1
	Weathered	22.5	2.67	2.11	2.58	2.8	61.7	54.3	.9	54.1	88	+2.9	-.6	+4.3	2.1
Styrene-butadiene	First soak		2.31	2.17	2.19	5.0	20.4	10.5	4.0	9.4	52	+3.3	-3.0	+6.2	4.9
	Second soak		2.19	2.19	2.20	5.3	17.1	8.1	2.9	-4.3	47	-.8	-.8	+.4	4
	Weathered	.7	2.13	2.19	2.12	6.0	18.7	5.4	.5	4.9	29	+.4	-.2	+.7	7
Styrene-butadiene plus methyl cellulose	First soak		2.10	1.97	2.00	4.5	27.7	15.6	4.7	19.6	57	+1.4	-2.4	-4.0	7.0
	Second soak		2.00	2.01	2.00	4.7	23.4	11.5	3.2	7.9	49	-.4	-.5	+.2	.6
	Weathered	6.9	1.97	2.06	2.01	4.6	23.7	9.5	.9	5.6	40	-3.3	-.4	+2.8	2.7
MAGNESIUM SILICATE, SINGLE-PIGMENT PAINTS, PIGMENT VOLUME 0.30															
Acrylic	First soak		1.57	1.45	1.57	4.2	30.2	29.5	15.0	12.0	98	-1.3	0	-1.0	2.2
	Second soak		1.57	1.47	1.58	4.2	23.5	23.0	12.2	8.9	98	-.9	-.2	-4.3	.9
	Weathered	18.3	1.80	1.36	1.81	4.6	119	120	20.6	81.4	101	-1.4	+14.0	-13.4	1.6
Polyvinyl acetate	First soak		1.67	1.65	1.71	4.6	8.9	8.4	4.3	-2.6	94	-6.8	-4.2	-1.7	8.0
	Second soak		1.71	1.66	1.71	4.5	8.9	8.5	2.9	5.1	96	-.4	0	-.4	.3
	Weathered	7.7	1.72	1.61	1.73	4.4	18.2	18.2	5.1	6.5	100	-1.8	-.8	-5.0	1.9
Styrene-butadiene	First soak		1.44	1.41	1.43	4.7	13.3	10.6	3.4	3.6	80	-3.4	-.8	-2.5	5.8
	Second soak		1.43	1.43	1.42	4.6	8.3	5.0	1.3	3.9	60	+.1	-.2	0	.4
	Weathered	1.0	1.51	1.51	1.50	5.8	10.6	6.8	.7	4.7	64	-1.1	-.6	-.5	2.1
Styrene-butadiene plus methyl cellulose	First soak		1.58	1.49	1.60	3.7	20.6	20.4	7.0	6.0	99	-7.2	-3.0	-4.4	9.2
	Second soak		1.60	1.53	1.60	3.5	15.5	15.1	4.6	9.7	98	-.6	-.3	-.3	.8
	Weathered	8.9	1.66	1.62	1.68	3.5	8.1	8.6	.6	4.8	106	-2.9	-.8	-2.0	3 0

[1] This paint cracked and scaled too badly during weathering to permit further study.

whereas in styrene-butadiene, white lead increased absorption more than titanium dioxide did, and in styrene-butadiene containing methyl cellulose, white lead increased absorption much more than even zinc oxide did.

Titanium dioxide produced the lowest absorption of any pigment in all latex vehicles except polyvinyl acetate in which still lower absorption was produced by magnesium silicate. Addition of methyl cellulose to pigmented films of styrene-butadiene always increased the absorption of the unweathered films.

Absorption during the second soaking of unweathered films was usually less than during the first soaking. The chief exception was zinc oxide in polyvinyl acetate, for which absorption was distinctly higher in the second than in the first soaking. Absorption by titanium dioxide in acrylic latex was very slightly higher and absorption by magnesium silicate in polyvinyl acetate was the same in the second as in the first soaking.

Weathering decreased the absorption by 9 and increased the absorption by 6 of the 15 pigmented films. The increase on weathering was very great for magnesium silicate in acrylic latex and in polyvinyl acetate, and for white lead in acrylic latex. The decrease was very great for white lead, titanium dioxide, and magnesium silicate in styrene-butadiene containing methyl cellulose. No explanation for these differences in the effect of weathering can be offered at present.

Swelling: In general, films of latex paints differed from the oil and oleoresinous paints previously reported (3) in that the unweathered latex films never swelled in volume quite so much as their absorption of water during the 3-day soaking periods would indicate. That is, the swelling efficiency was always less than 100 per cent and usually was considerably less. Moreover, the swelling efficiency for the second soaking period was usually less than that for the first soaking period. Low swelling efficiency is considered indicative of porosity, or voids within the film in which free water can be held and cause no swelling. Published electron photomicrographs (1) of latex films reveal such porosity due to incomplete fusion of the latex droplets and gathering of pigment in the interfaces between droplets. Some of the water-soluble substances leached by the first soaking may likewise come from these interfaces and increase the void volume for the next soaking.

Unpigmented latex films gave less evidence of porosity than pigmented films. For the unpigmented films, the swelling efficiency in the first soaking was 99 per cent. In the second soaking of acrylic latex, which lost little soluble material in the first soaking, the swelling efficiency remained at 99 per cent, but for films of polyvinyl acetate and of styrene-butadiene, which had higher solubility in the first soaking, the efficiency dropped to 96 and 94 per cent, respectively. For weathered polyvinyl acetate film, however, the swelling efficiency was 100 per cent.

Among unweathered pigmented films, only three attained 97 to 99 per cent swelling efficiency in the first soaking: magnesium silicate in acrylic resin and in styrene-butadiene with methyl cellulose, and titanium dioxide in styrene-butadiene with methyl cellulose. For titanium dioxide in polyvinyl acetate, the efficiency was only 27 per cent. For zinc oxide in acrylic resin, polyvinyl acetate, styrene-butadiene, and styrene-butadiene with methyl cellulose, the swelling efficiency was 90, 86, 52, and 57 per cent, respectively. In the second soaking period, the swelling efficiency for pigmented films was usually less than in the first soaking, sometimes much less. For three films, however, the two efficiencies were equal and for three the efficiency was somewhat higher in the second than in the first soaking.

After weathering, the swelling efficiency of films pigmented with zinc oxide was usually lower, and that of films with other pigments was sometimes lower and sometimes higher, than the swelling efficiency of the corresponding unweathered films. There seems to be no clear evidence of correlation with other properties of the films except perhaps that a relatively large decrease in swelling efficiency after weathering seems to be associated with a significant decrease in film density. Apparently, weathering may either increase or decrease the volume of voids in pigmented latex films.

All latex films swelled in area during the 3-day soaking periods, but the areal swelling showed even greater lack of proportionality to volumetric swelling than was previously observed with oil and oleoresinous paints (3). Areal swelling ranged from 7 per cent to 107 per cent of volumetric swelling for unweathered films soaked for the first time, from 5 per cent to 87 per cent for unweathered films soaked for the second time, and from 2 per cent to 57 per cent for weathered films. In the second soaking of unweathered films, the areal swelling was usually a lower percentage of the volumetric swelling than in the first soaking, and for weathered films, the areal swelling was usually a still lower percentage of the volumetric swelling.

The discrepancy in proportionality of areal to volumetric swelling was compensated by reciprocal variation in the proportionality of swelling in thickness to swelling in volume. In seven extreme cases, the thickness of unweathered films actually decreased during the soaking period.

Shrinkage on Redrying: On redrying after the first soaking of unweathered latex films, all but two shrank to a volume less than that before soaking. Such shrinkage is attributable chiefly to the fact that all films lost appreciable amounts of soluble substances to the soaking water. The films of zinc oxide in styrene-butadiene and in styrene-butadiene with methyl cellulose remained larger in volume and also lower in density after redrying than before soaking, which indicates an increase in volume of voids within the films. On redrying after the second soaking, most films shrank still further, though less markedly than after the first soaking, which indicates smaller losses of soluble substances. Films of titanium dioxide and of magnesium silicate in styrene-butadiene and of zinc oxide in acrylic resin, however, gained slightly in volume and lost in density.

Redried weathered films likewise exhibited a slight loss in volume, except for clear acrylic resin and titanium dioxide in styrene-butadiene, which exhibited no change in volume but a slight loss in density and in soluble substances, and zinc oxide in polyvinyl acetate and in styrene-butadiene, which gained in volume and lost in density.

Shrinkage in area during redrying was not at all proportional to shrinkage in volume. Most films shrank proportionately less in area and correspondingly more in thickness than they did in volume whereas many others shrank proportionately more in area and less in thickness. In this respect, even films of the same paint often behaved differently on redrying after the first and second soakings of the unweathered film and after soaking of the weathered film.

Loss in Weight While Soaking: During the first soaking of unweathered films, from 1.2 to 9.4 grams of soluble substances per 100 cubic centimeters of film were lost to the soaking water. The loss was less than 3 grams per 100 cubic centimeters for only 4 of 18 films. During the second soaking the losses were less and ranged from 0.1 to 2.1 grams per 100 cubic centimeters, with only 3 losses over 1 gram per 100 cubic centimeters. Thus most of the soluble material seems to be in the latex films before the first soaking.

Whether the loss during the second soaking is due to incomplete leaching the first time or to further formation of soluble substances by hydrolysis while the film is in water is as yet uncertain. The loss from weathered films was always less than that from unweathered films when soaked for the first time but greater than that from unweathered films soaked the second time. Styrene-butadiene films containing methyl cellulose always lost more soluble material than similarly pigmented films of styrene-butadiene without methyl cellulose at the same stage of the testing program.

Pigmentation always increased the solubility of acrylic-resin films but usually decreased the solubility of polyvinyl acetate or styrene-butadiene films.

Loss in Weight While Weathering: All films lost weight during weathering, usually substantially. The losses are attributed mainly to leaching of water-soluble substances by the water spraying in the weathering cycle.

Pigmentation greatly altered the weathering losses. Titanium dioxide caused low weight losses in all latexes. Zinc oxide caused remarkably low loss in styrene-butadiene, larger loss in styrene-butadiene with methyl cellulose, and very high loss in acrylic resin and in polyvinyl acetate. Magnesium silicate caused very low loss in styrene-butadiene, fairly high losses in styrene-butadiene with methyl cellulose and in polyvinyl acetate, and very high loss in acrylic resin. With white lead, the loss was moderate in acrylic resin, fairly high in styrene-butadiene, and still higher when the styrene-butadiene contained methyl cellulose.

Weathering losses in films of styrene-butadiene were always higher when the films also contained methyl cellulose.

Results with a Commercial Paint

Table 2 shows the results of tests on films made with a commercial latex paint intended for exterior use.

The density of films prepared with the commercial paint was less than the density of the nonvolatile in the liquid paint, and the swelling efficiency of the unweathered film was less than 100 per cent. The film was therefore somewhat porous, as were some of the experimental paints. The commercial paint was free from foam and made smooth films that contained no observable air bubbles. After weathering, the film density was no greater and perhaps a trifle less than before weathering. When soaked in water, the density of both unweathered and weathered films decreased roughly in proportion to the quantity of water absorbed. On redrying, the unweathered film regained the density before soaking but no more, whereas the weathered film increased nearly to the density of the nonvolatile in the liquid paint and its swelling efficiency reached 100 per cent.

The unweathered film absorbed 75.9 per cent of water by volume when soaked for three days. Among the experimental paints, the highest absorption for an unweathered film was 64.2 per cent (zinc oxide in polyvinyl acetate). Titanium dioxide in polyvinyl acetate absorbed 23.0 per cent, and magnesium silicate in polyvinyl acetate absorbed 8.9 per cent. Although the polyvinyl acetate latexes were not the same in the commercial and experimental paints, it is reasonable to conclude that the additives necessary in commercial latex paints materially increase the absorption of water by their films. In agreement with that conclusion, the solubility of the unweathered film of commercial paint was relatively high. Weathering reduced the solubility and absorption of the film of commercial paint to about the same levels as those of the weathered films of experimental polyvinyl acetate paints pigmented with titanium dioxide or magnesium silicate.

The remaining data of Table 2 confirm the essential similarity in behavior of the commercial and experimental paints when due allowance is made for the effect of the additives in the commercial paint. No measurements were made when the unweathered film of commercial paint was subjected to a second soaking and redrying, but it was observed that absorption and swelling were much less in a second soaking than in the first.

Conclusions

During film formation and curing, latex vehicles and paints undergo little or no shrinkage in volume or increase in density from the oxidation, contraction, and loss of decomposition products that characterize oil and oleoresinous paints. Instead, the latex vehicles and paints tend to form porous films that contain voids, as indicated often by a density less than that of the nonvolatile ingredients of the liquid paint and by a swelling efficiency in water of less than 100 per cent. The volume of voids may change when the films absorb water and dry again or when the films are weathered artificially. There may be a reduction in void volume, perhaps by release of internal stresses when water plasticizes the film, or an increase in void volume, which seems to be particularly likely to occur when the film contains zinc oxide.

Latex films absorb water on soaking and give it up again on redrying much more rapidly than oil or oleoresinous paints. Latex films, like oil and oleoresinous films, vary greatly in the quantity of water they will absorb in three days of soaking, and the absorption is greatly affected by pigmentation. Some pigments increase and others decrease the absorption. Among the pigments, zinc oxide greatly increases absorption of latex films just as it does that of oil and oleoresinous films. White lead, which minimizes absorption by oil films, stands midway among the pigments in its effect in latex films. Titanium dioxide greatly reduced absorption in acrylic latex but was less effective in polyvinyl acetate and styrene-butadiene films.

Absorption is greater in styrene-butadiene films when they also contain methyl cellulose than when they are free from that water-soluble substance. Likewise, absorption is less for all latex films during a second soaking than it was in the first, presumably because the first soaking removes much water-soluble material. Artificial weathering seems to increase the absorption of some latex films and to reduce that of others; perhaps there is a balance between production of water-soluble decomposition products and their removal by leaching.

Table 2.—DATA FOR FREE FILMS OF A COMMERCIAL POLYVINYL ACETATE LATEX PAINT BEFORE AND AFTER WEATHERING

Item	Unweathered film	Weathered film
Density of nonvolatile in liquid paint, 2.18		
Density of dry film	2.08	2.07
Density of film when soaked in water	1.62	2.02
Density of redried film	2.08	2.15
Initial thickness of film, mils	3.3	3.2
Absorption of water, per cent by volume	75.9	12.5
Swelling in volume, per cent	78.8	12.5
Swelling in area	36.2	5.1
Swelling in thickness, per cent	25.0	3.1
Swelling efficiency, per cent	97	100
Change in volume on redrying, per cent	—3.8	—4.7
Change in area on redrying, per cent	+4.3	—0.6
Change in thickness on redrying, per cent	—7.3	—4.3
Loss in weight during weathering, grams per 100 cubic centimeters	——	9.4
Loss in weight during soaking, grams per 100 cubic centimeters	7.6	1.6

The volumetric *swelling* of *latex films, especially pigmented films,* is usually slightly to considerably less than the volume of absorbed water, probably because some absorbed water is held in voids within the film, where it causes no swelling. The void volume is often increased by leaching the first time the film is soaked and redried, so that the swelling efficiency becomes still lower in a second soaking. On weathering, some latex films become more porous and others less so, as indicated by the swelling efficiency. Zinc oxide, however, usually increases the porosity.

When latex films are redried after soaking, the volume tends to be less than before soaking in accordance with the loss of soluble substance to the soaking water. Sometimes, however, especially if the film contains zinc oxide, such shrinkage may be more than offset by increase in void volume so that the redried volume exceeds the volume before soaking. With latex films, as with oil and oleoresinous films, swelling and shrinking in area may be proportionately larger or smaller than swelling and shrinking in volume, with compensating variation in the changes in film thickness.

Much more soluble matter is leached *from latex films during the first soak*ing in water than during the second soaking, though the fact that there was always some further loss in the second soaking suggests that there may be slow formation of soluble substances by hydrolysis while the film is in water. The solubility and loss of weight of weathered films show that decomposition goes on during weathering and is materially affected by the presence and nature of pigments. Titanium dioxide seems to reduce the loss of weight during weathering. Zinc oxide and magnesium silicate seem to increase the weight loss from acrylic and polyvinyl acetate films but reduce the loss from styrene-butadiene films.

The absorption and swelling of the experimental paints used in this study were probably much less than is to be considered normal for practical latex paints because of the exclusion of water-soluble or water-absorptive additives from the experimental paints, except for the methyl cellulose in some of the styrene-butadiene paints. The inclusion of methyl cellulose increased absorption and swelling, and the one commercial latex paint tested, which contained methyl cellulose and other customary additives, was much higher in absorption and swelling than the experimental paints.

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