Swelling of Paint Films in Water

V. Effects of Different Pigments[1]

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Describes measurements of absorption, swelling, and related data for free films of single-pigment paints tested by soaking in distilled water for three days both before and after artificial weathering for 15 days. Forty-four pigments tested and classified.

TO DETERMINE THE EFFECTS of different pigments on the behavior of free films of paint when soaked in water, 44 single-pigment paints of 0.30 pigment volume in linseed oil were made and tested before and after artificial weathering for 15 days.

Changes in density during drying and weathering gave evidence of a varying effect of pigments on oxidation of linseed oil. Losses in weight during weathering were due, first, to leaching of soluble organic and inorganic materials and, later on, to mechanical losses by chalking.

Some pigments reduced the absorption of water and swelling of free films below the absorption and swelling of unpigmented linseed oil, whereas others increased absorption and swelling, sometimes greatly. The effects of the pigments on absorption of water seem to be connected with their effects on the oxidation of linseed oil.

Weathering tends to make some films porous so that part of the water they take up is free water in pores that causes no swelling. Measurements were made of swelling in volume, area, and thickness, and of shrinkage in volume, area, and thickness, from which further indications of the film structure and effect of weathering were obtained.

Soluble substances derived from decomposition of linseed oil and sometimes from the pigments, were extracted from paint films during the 3-day period of soaking in water.

Previous papers in this series described the technique of preparing free films of weathered and unweathered house paints and of measuring their absorption of water and swelling when soaked in distilled water for 3 days, together with the changes in density, the shrinkage on redrying after soaking, the loss of soluble substances to the soaking water, and the losses in weight during artificial weathering in a Weatherometer (5).[3] The effects on absorption and swelling of such factors as time of soaking in water, temperature and pH of soaking water, age of films before soaking, thickness of films, pigment volume of the paints, and both artificial and natural weathering were reported.

Data were given for some unpigmented paint vehicles and for laboratory-made and commercial paints of widely differeing compositions (4, 7). Absorption and swelling of free films of vehicles and paints when exposed to air of different relative humidities were measured (6).

Dunn (10) has reported measurements of the absorption of water, swelling in area, and solubility of free films

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[3] Numbers in parentheses refer to literature cited.

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of single-pigment linseed oil paints made with white lead, zinc oxide, titanium dioxide, and magnesium silicate, of multiple-pigment paints, and of unpigmented linseed oil and various resinous vehicles. His findings are similar to those described in this series of papers.

In house paints made with linseed oil, the most important factor determining the absorption and swelling in water proves to be the kind of pigments with which the paint is made.

Pigments and Paints Tested

All pigments except mica and aluminum, which are "leafing" pigments, were tested in linseed-oil paints of pigment volume 0.30 made according to the following general formula:

Pigment	0.261 gallon
Raw linseed oil	.609 gallon
Lead-manganese naphthenate liquid drier	.020 gallon
Mineral spirits	.110 gallon
Total	1.000 gallon

The aluminum paint consisted of 2 pounds of commercial aluminum paste (75 per cent aluminum powder, 25 per cent mineral spirits) in 1 gallon of bodied-linseed-oil vehicle (66.5 per cent bodied linseed oil, 33.5 per cent mineral spirits and lead-manganese drier, viscosity B). The mica paint consisted of 2 pounds of a commercial surface-treated mica in 1 gallon of the bodied-linseed-oil vehicle.

In commercial practice, basic carbonate white lead is commonly used for house painting as a single-pigment paint, of which the paint tested is representative. The aluminum paint was also a commercially practicable paint. All of the other pigments, however, are used in house paints only as admixtures with other pigments in making mixed-pigment paints. For the present study, however, the purpose was to learn the effect of each pigment by itself on the absorption and swelling of paint films.

Although all of the pigments tested are purchasable under the names by which they are designated, they are not all single chemical compounds. The following are either "composite" pigments or naturally occurring mixtures.

Leaded zinc oxides are mixtures of basic lead sulfate and zinc oxide; those tested were cofumed products, that is, mixtures condensed together from the gas phase in the process of manufacture. Basic silicate white lead is a composite of basic lead sulfate and silica said to consist of granules of silica firmly coated with the basic lead sulfate. Lithopone is a mixture of zinc sulfide and calcium sulfate precipitated together from aqueous solution in manufacture. Titanium-calcium pigment is a mixture of rutile titanium dioxide precipitated in a slurry of calcium sulfate. Venetian red is a mixture of ferric oxide and calcium sulfate made by calcining together ferrous sulfate and calcium carbonate.

The manufactured and natural iron-oxide reds contain siliceous minerals present in the ore from which the pigments are made. Some of the titanium dioxides contain small additions of other substances deliberately incorporated to control the chalking properties of paints made with the pigments. Other pigments may contain small proportions of extraneous substances classifiable as impurities.

Other comments about the pigments tested are the following: Antimony oxide is an opaque white pigment used for house paints more widely in Europe than in the United States. Lead titanate is a slightly yellowish opaque white pigment formerly used in house paints but no longer available in the American market. Dibasic lead phosphite is an opaque white pigment recently developed primarily for use in vinyl resins and chloriated hydrocarbons but with properties that might well prove useful in house paints.

Basic carbonate white lead Nos. 1 and 2 were products of the same manufacturer. No. 1 was higher in ratio of lead hydroxide to lead carbonate than No. 2.

Of the two leaded zinc oxides tested, one is a pigment that has long been in use in house paints; the other, 18 per cent leaded zinc oxide, is a recent development in which an unusually high proportion of the lead component is said to be in a form available for reaction with acids formed in the paint vehicle.

Four of the five lead-free zinc oxides tested were chosen to represent the range in reactivity of the zinc oxide pigments made in the United States. Ten widely used brands were tested for their rate of reaction with meso-tartaric acid in aqueous medium. Zinc oxide No. 1 was the brand found slowest in reaction, zinc oxide No. 4 was the fastest in reaction, and Nos. 2 and 3 were intermediate. Relative rates of reaction were expressible by the figures 1.65, 3.70, 5.15, and 7.10 for zinc oxides Nos. 1, 2, 3, and 4 respectively.

Zinc oxide No. 1 was of large and No. 4 was of fine particle size. Zinc oxide No. 5 was an experimental product made in accordance with a suggestion by a manufacturer of silicone in the following manner: commercial zinc oxide No. 2 was slurried in a 1 per cent aqueous solution of vinylsilane containing 0.02 per cent of sodium hydroxide and was then filtered and dried at 105° C. The treatment was said to make zinc oxide water repellent.

Titanium dioxide Nos. 1, 3, and 4 were products of one manufacturer, and Nos. 2 and 5 of another manufacturer. Nos. 1 and 2 were of the anatase crystal structure; 3, 4, and 5 of the rutile crystal structure. Nos. 1, 2, and 3 were said to contain no modifying agents, but Nos. 4 and 5 contained not more than a total of 6 per cent of alumina, silica, and zinc oxide incorporated in manufacture to give maximum resistance to chalking.

Lead chromate and zinc chromate are bright yellow pigments. Basic lead chromate is bright orange in color. The ferric oxide pigments and Venetian red are red in color. Ferric oxide Nos. 1 and 2 were manufactured pigments from 2 different makers, and No. 3 was a naturally occurring iron ore known as Spanish oxide. Ferric hydroxide yellow was a manufactured pigment of dull yellow color. Zinc dust is dark gray in color without metallic luster, but aluminum pigments are light gray with high luster.

Magnesium silicate Nos. 1 and 2 came from different producers. Calcium carbonate Nos. 1 and 2 were surface-treated pigments from different makers. Calcium carbonate Nos. 3 and 4 were naturally occurring products of which No. 3 was of relatively coarse particle size and remarkably low oil absorption, and No. 4 was typical of the pigments called whiting.

Diatomaceous silica is a porous pigment consisting of the skeletons of diatoms found in what were ocean beds in former geologic times. The treated bentonite was dimethyloctadecyl ammonium bentonite made by cation exchange between the organic base and the naturally occurring montmorillonite (clay) known as bentonite; it is a recent development used as a gelling agent in paints. Magnesium silicate, calcium carbonate, barium sulfate, calcium sulfate, silica, diatomaceous silica, treated bentonite, and mica are all pigments of low opacity that make transparent or nearly transparent coatings when made into paints with linseed-oil vehicle.

Preparation of Free Films and Tests

To prepare unweathered films, the paints were spread on gummed paper by doctor blade and suction plate at a thickness designed to make coatings approximately 4 mils thick when dry. Actually 36 of the 44 films reported in Table 1 were within 0.5 mil of the desired thickness. The films were stripped from the gummed paper when they were 7 or 8 days old, and the soaking tests were started when they were 10 days old.

To prepare weathered films, the paints were spread on tared tinplate by doctor blade and suction plate to make coatings approximately 4 mils thick. When 10 days old, the coated tinplate specimens were weighed to find the weight of coating and were then sub-

jected to artificial weathering for 15 days in a Weatherometer. Distilled water was supplied to the Weatherometer sprays. After weathering, the specimens were weighed to determine the loss in weight of the coatings during weathering. The films were then stripped from the tinplate by amalgamation and promptly submitted to soaking tests.

For details of the testing technique and methods of expressing results, reference should be made to a previous paper (5).

Unweathered Films

The results obtained with unweathered films are reported in Table 1.

Density Changes: All paints increased significantly in density when the liquid paint hardened to a dry coating. The increase in density, however, was always less than that calculated from the increase in density and in weight of the linseed oil in the paint, assuming that the changes in the oil of the paints are the same as for unpigmented linseed oil.

Data of Carrick and Permoda (8) indicate that 10-day-old linseed-oil films have a density of 1.12 and are 4.45 per cent heavier than the original, undried oil. Data in the second paper of this series (5) agree about the density of 1.12.

If the oil in the antimony oxide paint of Table 1 had reached the same condition 10 days after spreading, the density of the film would have been 2.64, which exceeds the density of 2.54 actually found by 0.10. Similar calculations for all of the other paints of Table 1 reveal differences in the density, as calculated and as determined, that range from 0.01 to 0.26.

Rhodes and coworkers (15, 16) showed that some pigments greatly alter the absorption of oxygen and evolution of volatile matter from paint films over a length of time that included the 10-day period, whereas other pigments exert much less effect. Silica, iron oxide, and Venetian red were pigments that had little effect. For all of them the discrepancy between the calculated and determined density in Table 1 was less than 0.10.

On the other hand, Rhodes found large effects for basic carbonate and basic sulfate white lead, lithopone, titanium-barium pigment, barium sulfate, leaded zinc oxide, and zinc oxide. For all of them the discrepancy between calculated and determined density in Table 1 was 0.10 or greater. It is, therefore, reasonable to attribute the differences between calculated density and density actually found to the effect of pigments on the oxidation of linseed oil.

The pigments in Table 1 for which the difference between calculated and determined density of paint films was less than 0.10 were: basic silicate white lead, dibasic lead phosphite, 18 per cent leaded zinc oxide, zinc sulfide, zinc chromate, titanium dioxide Nos. 1, 2, and 3, titanium-calcium, all iron oxide and iron hydroxide pigments including Venetian red, both magnesium silicates, all calcium carbonates, calcium sulfate, silica, and treated bentonite. The aluminum and mica paints cannot be considered in this connection because they were made with bodied linseed oil and have a different paint structure. For paints made with all the other pigments, the differences between the calculated and determined densities were 0.10 or more.

It is of interest that the 2 paints made with titanium dioxide Nos. 4 and 5, both of which contained small amounts of zinc oxide, exhibited higher density difference than the other titanium dioxides.

The density of all paint films decreased when they absorbed water during the 3-day soaking period. After redrying, the density usually returned to a value slightly greater than that just before soaking. By that time, of course, the paints were 4 or 5 days older. Paints made with calcium sulfate, titanium-calcium, and Venetian red, which contained calcium sulfate, lost part of the calcium sulfate by leaching while soaking, and on redrying they failed to attain a density greater than that before soaking.

Zinc oxide No. 5, which was treated with vinyl silane, and zinc chromate, ferric oxide No. 1, and calcium carbonate Nos. 1 and 2 all made paints that lost much of the soluble pigment ingredients during soaking. After redrying, they remained lower, or at least no higher, in density than they were before soaking. The paints made with 35 per cent leaded zinc oxide and with treated bentonite were anomalous in that the density after redrying was no higher than before soaking, although the leaching losses were only moderate.

Absorption of Water: In the second paper of this series (5) the absorption of water by unpigmented raw linseed oil on soaking for 3 days was reported as approximately 20 per cent. Since the paint films reported here contained 70 per cent linseed oil by volume, they would be expected to absorb 14 per cent of water if the pigment present had no effect beyond reducing the volume of oil in 1 cubic centimeter of film.

Table 1 shows that paints made with the following pigments were significantly less absorptive than unpigmented linseed oil: antimony oxide, lead titanate, the white leads including the basic carbonates, basic sulfate, and basic silicate white lead, dibasic lead phosphite, lead chromate (but not basic lead chromate), barium sulfate, silica, mica, and aluminum.

In addition, paints with the following pigments were either slightly less, or only slightly more, absorptive than unpigmented linseed oil: basic lead chromate, titanium dioxide Nos. 1, 2, and 3, which contained no zinc oxide, ferric oxide No. 2 (but not Nos. 1 or 3), ferric hydroxide, and coarse particle-size calcium carbonate No. 3 (but not calcium carbonate Nos. 1, 2, and 4).

All other pigments made paints of greater absorptiveness than unpigmented linseed oil. Zinc oxides, leaded zinc oxides, and zinc chromate made paints of very high absorption, from 74.5 to 117 per cent. Other pigments that made highly absorptive paints were ferric oxide No. 1, Venetian red, and calcium carbonate Nos. 1, 2, and 4.

Zinc sulfide, lithopone, and zinc dust made paints that absorbed 39.9 to 45.5 per cent of water—significantly more than unpigmented linseed oil but only about half as much as zinc oxide paints. Among the titanium dioxide pigments the 2 (Nos. 4 and 5) in which small quantities of zinc oxide were incorporated by the maker to reduce chalking made paints of distinctly higher absorptiveness than the 3 in which there were no such additives.

Calcium sulfate and the pigments that contained calcium sulfate, titanium-calcium, and Venetian red, made paints of moderately high (about 35 per cent) or very high (87.5 per cent) absorptiveness. Magnesium silicate paint films absorbed 56.2 to 69.6 per cent of water.

The extreme variation in absorptiveness among the 3 ferric oxide pigments, 22.4, 31.4, and 110 per cent, respectively, is as yet unaccountable, as are the differences among the 4 calcium carbonates, from 24.5 to 117 per cent absorption. Diatomaceous silica made paint of slightly higher absorption than unpigmented linseed oil, whereas ordinary silica gave low absorption.

It is not yet possible to relate the effect of pigments on the absorption of water by paint films to other physical or chemical properties of the pigments. Chemical reactivity in the sense of soap formation between basic pigments and free acids or acid decomposition products of the oil is not a determining factor because unreactive silica or barium sulfate, as well as reactive white leads, reduce absorption below that of unpigmented linseed oil; whereas unreactive magnesium silicates and titanium dioxides, as well as reactive zinc oxides, increase absorption.

Furthermore, the great variation in chemical reactivity of the 4 untreated zinc oxides was not paralleled by similar variation in absorption. In fact, the

Table 1.—DATA FOR FREE FILMS OF SINGLE-PIGMENT PAINTS BEFORE WEATHERING—CHANGES IN DENSITY, ABSORPTION OF WATER AND SWELLING IN VOLUME, AREA, AND THICKNESS WHEN SOAKED IN WATER FOR THREE DAYS; SWELLING EFFICIENCY; SHRINKING IN VOLUME, AREA, AND THICKNESS WHEN REDRIED; AND LOSS IN WEIGHT BY LEACHING DURING THE SOAKING PERIOD

Paint	Density of nonvolatile in liquid paint	Density of film: Dry	Swollen in water	Redried	Initial thickness T_o	Absorption of water A/T_o	Swelling: In volume ΔV_s	In area ΔQ_s	In thickness ΔT_s	Swelling efficiency $\frac{\Delta V_s T_o}{T}$	Redried: Volume ΔV_r	Area ΔQ_r	Thickness ΔT_r	Loss in weight in soaking L_s/T_o
					Mils	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent
Antimony oxide	2.38	2.54	2.52	2.61	3.4	5.3	5.8	2.9	0.3	109	-4.3	-1.4	-2.9	4.7
Lead titanate	2.84	2.98	2.89	3.04	4.0	7.8	7.5	3.7	.7	96	-2.9	-.5	-2.0	3.8
Basic carbonate white lead No. 1	2.67	2.84	2.71	2.90	3.9	10.7	10.8	6.0	1.6	101	-3.3	+1.0	-3.6	4.8
Basic carbonate white lead No. 2	2.70	2.87	2.74	2.90	3.8	8.9	9.3	5.1	1.3	104	-2.5	+.1	-2.1	3.8
Basic sulfate white lead	2.57	2.74	2.59	2.78	4.2	9.7	11.6	7.4	1.7	120	-3.2	-.7	-2.4	3.8
Basic silicate white lead	1.86	2.01	1.92	2.03	4.2	10.1	10.5	5.9	2.2	105	-3.0	+1.4	-4.3	4.1
Dibasic lead phosphite	2.74	2.97	2.78	3.01	3.6	11.7	12.1	3.8	6.7	103	-1.5	+.3	-2.8	1.3
Lead chromate	2.80	2.98	2.84	2.61	4.1	11.4	11.5	6.3	2.4	101	-2.9	-.2	-2.7	3.6
Basic lead chromate	2.72	2.78	2.45	2.79	4.1	24.0	23.3	13.7	7.2	97	-1.8	+2.5	-3.1	3.1
35 percent leaded zinc oxide	2.45	2.58	1.76	2.42	4.1	111	108	61.3	29.0	97	+4.8	+25.2	-16.2	4.3
18 percent leaded zinc oxide (reactive)	2.38	2.55	1.89	2.59	3.4	74.5	74.5	47.0	16.4	100	-3.4	+18.1	-18.1	5.4
Zinc oxide No. 1	2.34	2.48	1.86	2.53	3.7	78.6	78.6	42.7	20.0	100	-3.9	+9.4	-12.0	5.6
Zinc oxide No. 2	2.33	2.44	1.80	2.47	3.7	83.3	81.6	28.4	39.2	98	-3.6	+5.0	-8.0	5.9
Zinc oxide No. 3	2.34	2.47	1.72	2.48	4.1	106	105	70.8	19.2	99	-2.0	+32.5	-26.1	4.2
Zinc oxide No. 4	2.34	2.47	1.75	2.48	4.1	82.0	87.3	22.9	54.4	106	-2.9	-3.3	+.5	6.4
Zinc oxide (treated) No. 5	2.33	2.40	1.66	2.17	3.3	117	112	50.5	41.0	96	+7.2	+20.5	-10.9	7.4
Zinc sulfide	1.86	2.00	1.73	2.02	3.8	39.9	40.3	24.0	11.2	101	-2.7	+3.8	-6.0	2.7
Lithopone	1.94	2.07	1.74	2.10	3.7	45.5	45.9	27.1	12.9	101	-2.5	+5.7	-7.3	2.9
Zinc chromate	1.69	1.83	1.43	1.82	3.9	88.5	87.4	45.1	26.4	99	-4.7	+15.4	-17.5	9.9
Zinc dust	2.76	3.64	2.86	3.70	3.4	43.2	43.3	25.9	12.4	100	-2.5	+2.3	-4.7	3.6
Titanium dioxide (anatase) No. 1	1.82	1.95	1.83	1.99	3.7	17.3	17.9	9.2	4.0	103	-3.7	+.5	-4.5	3.7
Titanium dioxide (anatase) No. 2	1.82	1.98	1.79	2.02	3.5	26.6	27.2	13.5	8.2	102	-4.9	+1.4	-6.2	5.3
Titanium dioxide (rutile) No. 3	1.92	2.06	1.92	2.08	4.0	16.5	17.2	9.8	4.5	104	-2.8	0	-4.5	2.8
Titanium dioxide (rutile) No. 4	1.92	2.03	1.87	2.06	4.0	30.3	30.7	16.5	10.4	101	-2.7	+1.6	-4.0	2.2
Titanium dioxide (rutile) No. 5	1.91	2.06	1.80	2.13	3.5	34.9	35.5	17.1	12.4	102	-4.2	+3.3	-7.1	4.1
Titanium-Calcium	1.63	1.75	1.54	1.75	3.9	35.4	35.6	17.8	10.7	101	-5.3	+2.7	-7.4	9.9
Ferric oxide red (manufactured) No. 1	2.06	2.23	1.99	2.22	3.8	110	108	58.4	29.6	98	-2.5	+12.3	-13.5	7.5
Ferric oxide red (manufactured) No. 2	2.16	2.32	2.11	2.38	3.7	22.4	22.9	9.5	9.1	102	-4.1	-.2	-3.5	4.2
Ferric oxide red (natural) No. 3	1.99	2.14	1.84	2.16	3.9	31.4	36.5	17.8	13.5	116	-3.1	+2.8	-5.6	4.2
Venetian red	1.82	1.99	1.49	1.83	4.6	87.5	81.0	48.3	22.2	93	0	+9.8	-9.1	15.9
Ferric hydroxide yellow	1.87	2.00	1.88	2.04	3.3	16.4	16.4	7.1	5.7	100	-3.4	-.8	-2.4	4.4
Magnesium silicate No. 1	1.51	1.68	1.44	1.70	2.9	56.2	56.1	13.7	37.3	100	-3.8	+2.2	-5.8	4.5
Magnesium silicate No. 2	1.51	1.62	1.37	1.63	3.7	69.6	69.3	20.4	39.2	99	-2.2	+4.3	-6.2	3.0
Calcium carbonate No. 1	1.46	1.58	1.33	1.51	3.8	71.8	66.5	46.9	11.9	93	-2.9	+17.6	-17.3	11.6
Calcium carbonate No. 2	1.46	1.58	1.28	1.58	4.1	104	103	57.9	26.4	99	-4.0	+14.9	-16.2	5.8
Calcium carbonate No. 3	1.47	1.60	1.49	1.62	4.5	84.5	84.7	12.7	7.5	101	-3.4	+.5	-3.8	4.1
Calcium carbonate No. 4	1.46	1.54	1.26	1.55	3.6	117	107	64.5	23.1	92	-4.6	+18.2	-19.2	6.3
Barium sulfate	1.97	2.06	1.98	2.09	4.7	11.4	11.1	8.6	0	97	-2.7	+.9	-3.4	2.2
Calcium sulfate	1.36	1.47	1.19	1.23	3.8	36.8	33.4	10.7	6.3	91	-20.4	-4.7	-16.2	50.5
Silica	1.45	1.56	1.52	1.57	4.8	9.3	9.7	5.5	1.9	104	-2.6	-.5	-2.1	2.1
Diatomaceous silica	1.25	1.31	1.29	1.33	4.7	28.7	25.1	10.0	10.7	87	-3.2	+.2	-3.4	3.0
Treated bentonite	1.19	1.26	1.20	1.26	3.3	30.9	30.9	17.2	9.2	100	-2.9	+3.2	-5.8	3.6
Mica in bodied oil	1.18	1.30	1.27	1.32	3.0	11.6	12.4	.9	7.0	107	-4.6	+.1	-5.4	4.0
Aluminum in bodied oil	1.11	1.21	1.20	1.23	2.7	9.3	10.1	1.8	1.5	109	-7.2	-.4	-6.9	6.8

most rapidly reactive zinc oxide, No. 4, made paint little more absorptive than the least reactive zinc oxide, No. 1, and less absorptive than No. 2, which was about half as rapidly reactive.

On the other hand, basic carbonate white lead No. 1 contained a higher proportion of reactive lead hydroxide and made paint slightly more absorptive than basic carbonate white lead No. 2, and basic lead chromate made more absorptive paint than neutral lead chromate.

Solubility of pigments or pigment ingredients may be a minor factor that increases absorption, as in the cases of calcium sulfate, Venetian red, calcium carbonate, and zinc chromate, but such nearly insoluble pigments as the titanium dioxides increase absorption at least moderately.

The dominant effect of pigments, including nonreactive and insoluble pigments, indicates that the interface between pigment and oil is the seat of the unknown mechanism by which absorption is chiefly governed. But the area of interface, which increases greatly as the size of the pigment particles diminishes, seems to be of secondary importance. Zinc oxide No. 4, which was of exceedingly fine particle size (about 0.12 micron), made paint less absorptive than zinc oxide No. 2, which was much coarser, and little more absorptive than the zinc oxide No. 1, which was of relatively coarse particle size (about 1 micron).

The titanium dioxides, though finer in particle size than zinc oxide No. 1, made much less absorptive paints. The white lead pigments were comparable in particle size to zinc oxide No. 1, but made paint of much lower absorption. Among the calcium carbonate pigments, the one of coarsest particle size, No. 3, made the least absorptive paint, but it was higher in absorption than such paints as those made with the white leads and lead titanate with much finer particle size.

Likewise, particle shape seems to be unimportant because the paint made with markedly acicular zinc oxide No. 2 fell between the paints made with distinctly nodular zinc oxide Nos. 3 and 4, and the paints with acicular magnesium silicates fell within the range of absorptiveness of the calcium carbonate paints with nodular pigments.

It is reasonable to suppose that water absorbed by pigmented paints in excess of that taken up by unpigmented linseed oil is held chiefly at the interface between pigment and oil, at least when the pigments do not react to form oil-soluble products diffused through the vehicle. If so, a relation might well be expected between absorption of water by films and adsorptive properties of pigments, or between absorption of water by films and the interfacial tensions between pigment and water and pigment and oil. Gardner (11) published data on the adsorption of methylene blue from aqueous solution by pigments; and Gardner (12) and MacGregor (14) reported tests of the distribution of pigments between water and organic liquids, including linseed oil, but no significant parallels can be found between either of these pigment properties and the absorption of water by paint films in the present tests.

Bartell and coworkers (1, 2) studied the interfacial tensions between pigments and liquids in great detail, but again there seems to be no clear relation between their findings and the effects

of pigments on the absorption of water by paint films.

The lack of agreement between the surface properties of pigments and the absorptiveness of paints made from them may be due to the change in chemical nature of liquid linseed oil as it is transformed into the linoxyn gel of dried paint films (3) and to the effect of pigments on that change.

The work of Rhodes and coworkers (15, 16), which has already been shown to be related to the increase in density during the drying of paints observed in these experiments, also proves roughly indicative of the absorption of water by the paint films. Basic carbonate white lead, basic sulfate white lead, and barium sulfate increased the consumption of oxygen and evolution of volatile matter in Rhodes' experiments, and they caused a reduction of the absorption of water by films in the present tests. Zinc oxide and leaded zinc oxide markedly reduced the consumption of oxygen and evolution of volatile matter and greatly stimulated absorption of water by films.

Lithopone and titanium-barium pigment moderately reduced the consumption of oxygen and evolution of volatile matter, and lithopone and titanium dioxide paint films exhibited moderate increase over unpigmented linseed oil in amount of water absorbed. Silica, which had little effect in Rhodes' experiments, made paint films of low absorption. There were variations among iron oxide pigments in both Rhodes' experiments and these. Venetian red reduced consumption of oxygen and evolution of volatile matter only slightly, but it made highly absorptive films. Iron oxides increased consumption of oxygen and evolution of volatile matter slightly to moderately, but they made moderately to highly absorptive paints.

But with the exception of the variable iron oxide pigments, the most anomalous one of which was not available at the time of Rhodes' work, there is a reasonably close parallel between the effect of pigments on the oxidation of linseed oil and the absorption of water by the films they produce. High absorption of water apparently comes from use of pigments that markedly reduce the consumption of oxygen and evolution of volatile matter when the paint has dried.

Swelling: For most of the unweathered films, the volumetric swelling during 3 days' soaking in water was nearly equal to the absorption of water. The swelling efficiency was therefore close to 100 per cent, a little greater than 100 per cent more often than less. The high efficiencies for paints made with antimony oxide, basic sulfate white lead, and aluminum in bodied oil could result from slight underestimation of the absorptions, which were small, from loss of moisture while weighing the wet films in air.

The film of paint made with iron oxide No. 3 gave high swelling efficiency with moderately high absorption, which suggests more serious experimental error. Low swelling efficiencies, less than 96 per cent, were found for films containing Venetian red, calcium carbonate Nos. 1 and 4, and calcium sulfate, all of which lost substantial proportions of pigment by solution in the soaking water, and diatomaceous silica, which has a highly porous pigment structure (7).

Swelling in area was always less than swelling in volume. All films, therefore, swelled also in thickness. The ratio of swelling in area to swelling in thickness, however, varied from 3.7 for zinc oxide No. 3 to 0.4 for zinc oxide No. 4, if only those pigments are considered for which the swelling was large enough to give confidence in the significance of the ratio. The swelling in area exceeded the swelling in thickness for 36 of the 48 pigments tested. There seems to be no recognizable connection between the ratio of areal to thickness swelling and other properties of the pigments.

In the first paper of this series (4), it was shown that most paints swell more across the grain of the paint than along the grain, especially when the paint contains markedly acicular pigments. The grain of the paint is determined by the direction of last flow of the liquid paint before it sets and begins to harden. The ratio of swelling in width (across the grain) to swelling in length, $\Delta B/\Delta L$, was greater than 2 for the following pigments in Table 1: dibasic lead phosphite, zinc oxide No. 2, ferric hydroxide yellow, magnesium silicate Nos. 1 and 2, and calcium sulfate, all of which have decidedly needle-shaped crystals.

Among the zinc oxides, No. 2, with acicular particles, gave a ratio $\Delta B/\Delta L$ of 4.0, but for zinc oxide Nos. 1, 3, and 4, with nodular particles, the ratios were 1.2, 1.0, and 1.0, respectively. But when acicular zinc oxide No. 2 was treated with vinyl silane, making zinc oxide No. 5, the ratio $\Delta B/\Delta L$ fell to 1.1. The treatment could not have altered the shape of the particles, but it probably resulted in clumping of the acicular crystals into larger aggregates of effectively spherical shape that were not dispersed by grinding into paint. In conformity with that view, the oil absorption of the pigment was very greatly increased by the treatment.

Pigments for which the ratio $\Delta B/\Delta L$ was greater than 1.2 but less than 2 were: antimony oxide (1.3), titanium–calcium (1.4), diatomaceous silica (1.5), and aluminum (1.8). For all other pigments in Table 1, the ratio was 1.0 to 1.2, except for titanium dioxide No. 2 and treated bentonite, for which the ratio was 0.9.

Shrinkage on Redrying: All films except those of the paints made with 35 per cent leaded zinc oxide, treated zinc oxide No. 5, and Venetian red shrank to less than their initial volume when they were redried after soaking in water. The 3 exceptions were films for which the swelling efficiency was less than 100 per cent, indicating the development of some degree of porosity, but not all films of low swelling efficiency remained swollen or failed to shrink on redrying.

Shrinkage to less than the initial volume on redrying may be attributed primarily to loss of soluble ingredients to the soaking water. The film of calcium sulfate paint, which lost 50.5 grams of soluable material per 100 cubic centimeters, chiefly calcium sulfate, shrank 20.4 per cent in volume when redried. For the other paints the volumetric shrinkage was 1.5 to 7.2 per cent.

In area, 33 of the 44 films remained larger after redrying than they were before soaking. In thickness, all films shrank after redrying, sometimes considerably, except that of zinc oxide No. 4. Its 0.5 per cent increase was small enough to be within experimental error. In general, therefore, unweathered free films after swelling seem to be able to shrink in thickness more readily than in area. That appears to be particularly true of films for which the swelling in water is large.

Loss in Weight While Soaking: All films lost weight during the 3 days of soaking in water. Unpigmented films of linseed oil lose 5 to 6 grams per 100 cubic centimeters of film (5), much but not all of which can be recovered by evaporating the soaking water to dryness. Volatile organic solutes, of course, are lost during evaporation and drying at 105° C.

Films of most of the paints in Table 1 lost 1.3 to 5.3 grams per 100 cubic centimeters of film. When the films contained insoluble, nonreactive pigments such as silica, magnesium silicate, barium sulfate, titanium dioxide, and lead titanate, the soluble ingredients consisted entirely of organic matter from the linseed-oil vehicle.

Likewise, the leachings from films containing any of the white leads or basic lead chromate contained organic matter with no more than a trace of soluble lead compounds. Any salts of lead formed by reaction with acids from decomposition of the linseed oil must, therefore, be nearly insoluble in water.

The films of paint made with calcium sulfate lost 50.5 grams per 100 cubic

Table 2.—DATA FOR FREE FILMS OF SINGLE-PIGMENT PAINTS AFTER ARTIFICIAL WEATHERING FOR 15 DAYS—LOSS IN WEIGHT WHILE WEATHERING; CHANGES IN DENSITY; ABSORPTION OF WATER AND SWELLING IN VOLUME, AREA, AND THICKNESS WHEN SOAKED IN WATER FOR THREE DAYS; SWELLING EFFICIENCY; SHRINKING IN VOLUME, AREA, AND THICKNESS WHEN REDRIED; AND LOSS IN WEIGHT BY LEACHING DURING THE SOAKING PERIOD

Paint	Weight loss: weathering	Density			Initial thickness	Absorption of water	Swelling			Swelling efficiency	Redried			Loss in weight soaking
	B_1/V_0	Dry	Swollen in water	Redried	T_0	A/V_0	In volume ΔV_0	In area ΔS_0	In thickness ΔT_0	$\frac{\Delta V_0 V_0}{A}$	Volume ΔV_r	Area ΔS_r	Thickness ΔT_r	B_2/V_0
	Percent				Mils	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent
Antimony oxide	34.4	2.94	2.97	2.97	2.9	2.5	2.3	2.3	-0.7	92	-1.5	-0.8	-0.3	1.5
Lead titanate	12.8	3.23	3.24	3.24	5.9	3.8	.9	1.3	.2	24	-.4	-.7	+.5	.3
Basic carbonate white lead No. 1	21.7	3.11	3.11	3.16	5.9	7.4	3.9	2.2	1.0	53	-2.4	-1.1	-.6	2.0
Basic carbonate white lead No. 2	21.0	3.26	3.06	3.11	2.8	9.9	8.7	.7	8.8	88	+2.3	-.7	+8.1	2.9
Basic sulfate white lead	36.3	3.37	3.27	3.38	3.6	7.5	4.9	2.0	3.6	65	-1.1	-.7	+.3	2.5
Basic silicate white lead	28.9	2.27	2.24	2.28	5.0	4.5	2.8	1.7	.8	62	-.8	-.5	-1.0	.6
Dibasic lead phosphite	11.1	3.27	3.21	3.27	3.1	4.4	3.3	1.4	1.3	75	-.8	-.2	-.3	2.7
Lead chromate	10.1	2.78	2.73	2.79	5.2	3.2	3.2	1.8	2.5	100	-.7	-1.3	-.4	.7
Basic lead chromate	16.3	3.12	2.99	3.14	3.2	7.2	7.5	4.2	6.6	104	-.7	-.9	-.9	.5
35 percent leaded zinc oxide	10.1	2.60	2.53	2.76	5.2	16.0	14.7	8.0	8.8	92	-5.7	+1.5	-6.1	.1
18 percent leaded zinc oxide (reactive)	16.1	2.80	2.53	2.80	2.9	20.0	18.5	10.3	6.8	93	-.3	+1.7	-2.0	.9
Zinc oxide No. 1	12.1	2.67	2.32	2.67	3.8	29.6	27.5	13.4	12.2	93	-.1	+4.1	-4.2	.6
Zinc oxide No. 2	11.7	2.61	2.30	2.61	3.8	28.2	26.0	7.4	26.0	92	0	+1.4	-.3	.8
Zinc oxide No. 3	19.6	2.71	2.17	2.65	3.9	25.5	27.3	11.6	22.3	107	+2.3	+3.3	+2.0	.7
Zinc oxide No. 4	40.8	2.89	2.44	2.82	3.1	32.0	30.8	.....	.....	96	+1.7	.....	.....	2.3
Zinc oxide (treated) No. 5	10.8	2.68	1.74	2.27	2.6	132	121	17.3	89.0	92	+10.8	+7.0	+3.9	5.4
Zinc sulfide	26.0	2.20	1.98	2.20	3.3	26.0	23.5	14.9	22.3	90	-2.0	+2.1	-2.1	6.6
Lithopone	27.2	2.27	2.19	2.36	3.1	16.1	15.3	7.2	8.7	95	-6.8	+.5	-6.7	6.1
Zinc chromate	9.2	1.94	1.88	1.93	4.4	8.5	8.5	4.3	7.7	100	-.9	-.6	-.7	1.1
Zinc dust	7.6	3.90	3.85	3.89	3.2	33.2	29.3	12.5	29.4	88	+7.7	+5.1	+2.5	3.7
Titanium dioxide (anatase) No. 1	55.1	2.36	2.36	2.34	2.7	9.6	3.2	2.2	2.2	33	-.8	-1.4	-.7	3.4
Titanium dioxide (anatase) No. 2	53.8	2.38	2.36	2.40	2.9	5.2	2.2	2.7	1.0	81	-1.9	-1.1	-.3	1.8
Titanium dioxide (rutile) No. 3	32.1	2.39	2.36	2.38	3.0	2.8	2.3	2.2	2.6	82	+.4	-.9	+.7	.4
Titanium dioxide (rutile) No. 4	19.0	2.28	2.24	2.30	3.5	4.6	4.3	4.3	3.5	93	-1.1	-1.4	-.9	.8
Titanium dioxide (rutile) No. 5	24.1	2.34	2.32	2.37	3.1	8.3	5.7	3.6	3.9	69	-1.8	-1.3	0	1.0
Titanium-Calcium	31.5	1.87	1.95	1.97	3.5	6.1	-4.9	2.9	-7.5	.....	-6.8	-.7	-8.7	7.8
Ferric oxide red (manufactured) No. 1	22.4	2.52	2.22	2.52	2.9	86.8	85.5	12.6	10.3	97	-1.3	+.4	-1.4	2.6
Ferric oxide red (manufactured) No. 2	28.0	2.66	2.57	2.67	2.8	6.1	6.0	2.9	2.8	99	-.9	-.5	0	1.3
Ferric oxide red (natural) No. 3	16.1	2.36	2.30	2.37	4.0	4.6	4.9	1.7	4.3	107	-.7	-.9	-.5	.5
Venetian red	18.5	2.20	2.00	2.00	3.1	12.7	6.2	4.3	4.2	49	-2.1	-.8	-2.3	15.3
Ferric hydroxide yellow	19.9	2.21	2.17	2.25	3.0	6.0	6.0	2.9	3.4	100	-1.7	-1.4	0	1.1
Magnesium silicate No. 1	.....	1.89	1.81	1.89	2.6	7.5	9.8	5.0	6.7	130	-2.1	-3.4	+.4	2.6
Magnesium silicate No. 2	19.0	1.77	1.72	1.78	3.5	7.6	7.5	2.1	6.0	99	-1.5	0	-1.7	8.1
Calcium carbonate No. 1	26.5	1.73	1.64	1.75	3.2	19.7	18.5	10.8	14.5	94	-4.2	-1.9	-4.0	7.9
Calcium carbonate No. 2	42.3	1.63	1.74	1.69	2.5	15.0	14.7	6.3	11.1	98	-3.6	-1.9	-3.6	5.4
Calcium carbonate No. 3	51.8	1.90	1.75	1.89	2.7	19.0	19.3	3.9	19.5	101	0	-1.9	+.4	.9
Calcium carbonate No. 4	44.3	1.77	1.68	1.79	2.7	15.2	14.9	6.6	4.4	98	-4.4	-.5	-4.0	6.1
Barium sulfate	61.4	2.71	2.67	2.69	2.7	7.8	4.0	3.2	4.1	51	+.2	-.1	0	1.2
Calcium sulfate	53.2	1.68	1.12	1.38	2.5	80.2	-3.9	-.6	-2.8	.....	-35.7	-9.4	-29.2	85.5
Silica	51.5	1.78	1.81	1.78	2.7	8.7	3.7	1.7	2.8	43	-1.7	-.5	-1.5	2.3
Diatomaceous silica	51.8	1.88	1.40	1.18	3.3	48.5	22.8	1.6	22.7	47	+4.8	-.6	+4.8	4.9
Treated bentonite	45.8	1.43	1.37	1.43	2.6	13.8	14.1	5.5	5.5	102	-3.2	-.5	-2.6	2.2
Mica in boiled oil	34.1	1.40	1.39	1.37	1.9	19.5	19.9	1.1	17.3	102	-2.6	-.7	-2.6	1.9
Aluminum in boiled oil	20.1	1.30	1.29	1.32	2.1	9.7	9.4	1.8	6.0	97	-1.1	-.4	-1.4	.2

centimeters of films. Upon evaporation of the soaking water and drying, 39.6 grams of calcium sulfate crystals and 0.9 gram of organic matter were recovered. Likewise, calcium sulfate was found in the soaking water from the films containing titanium-calcium and Venetian red, for which the solubility losses were 9.9 and 15.9 grams per 100 cubic centimeters, respectively.

Films of zinc chromate paint lost 9.9 grams per 100 cubic centimeters to the soaking water and colored the water strongly with dissolved zinc chromate. But the water from the films of lead chromate paint, with a loss of 3.6 grams, remained colorless. Leaching from films of all paints containing ferric oxide were colorless and gave no test for soluble compounds of iron. The high loss in soaking of the film with ferric oxide No. 1 may be due to soluble ingredients in the pigment that were not identified.

Leachings from all paints containing zinc oxide, leaded zinc oxide, zinc sulfide, or zinc chromate contained substantial proportions of soluble zinc salts from which zinc sulfide could be readily precipitated by hydrogen sulfide. Presumably, zinc oxide and zinc sulfide reacted with organic acids from the linseed oil to form soluble zinc soaps.

Similarly, all calcium carbonate paint films yielded leachings from which the soluble calcium was precipitated as calcium oxalate in amounts that were proportional to the losses during soaking.

Weathered Films

The results obtained with films that were subjected to artificial weathering for 15 days before testing are reported in Table 2.

Weight Loss During Weathering: All paints lost weight during weathering. The losses ranged from 7.6 grams per 100 cubic centimeters of weathered film for zinc-dust paint to 61.4 grams for barium sulfate.

Zinc pigments generally exhibited low losses, from 7.6 to 27.2 grams per 100 cubic centimeters, except that zinc oxide No. 4, with very fine particle size, lost 40.8 grams. Zinc sulfide and lithopone lost more than any other zinc pigments except zinc oxide No. 4. Dibasic lead phosphite, lead titanate, the lead chromates, and leaded zinc oxides had low losses of the same order as zinc oxide Nos. 1, 2, 3, and 5, but the white leads lost somewhat more—about as much as zinc sulfide.

Losses by the titanium dioxide paints ranged from 19.0 to 55.1 grams per 100 cubic centimeters. The freely chalking anatase pigments lost more than 50 grams, much of which may have been in the form of chalk mechanically eroded from the surface of the films. Pure rutile titanium dioxide No. 3 lost 32.1 grams, and the zinc-containing, highly chalk-resistant titanium dioxide Nos. 4 and 5 lost only 19.0 and 24.1 grams, nearly all of which was probably in the form of water-soluble leachings. Titanium-calcium lost no more than titanium dioxide No. 3 despite its content of calcium sulfate.

The iron oxide pigments, including Venetian red, aluminum, and magnesium silicate, exhibited losses of about the same order of magnitude as the lead and zinc pigments. But barium sulfate, calcium sulfate, silica, mica, and treated bentonite gave high losses. Losses by calcium carbonates varied from 26.5 to 51.8 grams per 100 cubic centimeters.

It is not yet possible to explain satisfactorily the variation in weathering losses by paints of differing pigmentation. Probably several factors are involved. It has already been shown (4) that much of the loss occurs early in the weather exposure before chalking sets in.

Leaching of water-soluble ingredients presumably accounts for the first portion of the loss on weathering. It is, in turn, regulated in amount by the effect of the pigments on the disruptive oxidation of the oil vehicle and by the solubility of any soaps formed by reaction between chemically active pigments and acid decomposition products of the oil vehicle. Later on there may be additional mechanical loss by chalking from the surface if a condition of free chalking sets in.

Density Changes: Weathering increased the density of all paint films except those of paints made with diatomaceous silica, for which the density dropped from 1.31 before weathering to 1.28 afterward. The anomalous behavior of the diatomaceous silica paint may be connected with the porosity of the film due to the porous nature of the pigment itself.

The swelling efficiency of the 10-day old films was 87 per cent and that of the weathered films 47 per cent. Perhaps the increased porosity on weathering was sufficient to diminish the density. For all other paints the increase in density during weathering was in accord with the contraction in volume normally expected in linseed-oil paints (9).

The density of the weathered films usually decreased when they were swollen in water, just as was always the case with unweathered films But with weathered films there were seven exceptions to the general rule. Films of the paints with basic carbonate white lead No. 1 and titanium dioxide No. 1 were not changed measurably in density. Films of antimony oxide, lead titanate, and silica paints increased slightly in density when swollen in water. These were all films of low absorption of water, low volumetric swelling, and low swelling efficiency after they had been weathered.

Where most of the water absorbed is held in pores and little water enters the vehicle to cause swelling, the density when wet should exceed the density when dry. The film of diatomaceous silica paint, which was decidedly porous even before weathering, showed this effect even though it absorbed a relatively large amount of swelling water in addition to the free water in pores.

The increased density of the films of titanium-calcium paint after soaking corresponded to an actual loss in volume of 4.9 per cent during the soaking period. This loss was caused by leaching of the calcium sulfate in the pigment, which left a higher proportion of the heavier titanium dioxide in the leached film. This effect did not appear in the unweathered films because it was overbalanced by the much greater absorption of swelling water.

On redrying after soaking, the density usually returned to the density before soaking or to a slightly higher density unless the film remained swollen in volume, as with basic carbonate white lead No. 2, zinc oxide Nos. 3, 4, and 5, zinc dust, titanium dioxide No. 3, barium sulfate, and diatomaceous silica, or unless there was a large loss of soluble ingredients during the soaking period as with calcium sulfate and Venetian red.

Absorption of Water: Weathered films of all but five of the paints absorbed less water than the unweathered films. The five exceptions can be explained in part on the basis of difference in film thickness because the weathered films were all thinner than the unweathered films.

With the diatomaceous silica paint, and perhaps to a less extent with the paints made with basic carbonate white lead No. 2 and treated zinc oxide No. 5, the increased porosity of the weathered films was a contributing factor by permitting the weathered films to take up more free water in pores. The other two exceptions were the mica and the aluminum paints, both of which contained much less pigment than the other paints, and in both of which the pigments concentrated largely at the surface of the film, leaving nearly a pure vehicle in the underlying parts of the film.

A previous paper (5) reported that bodied linseed oil absorbs more water after weathering than before. Thus, the mica and aluminum paints seem to act much like unpigmented oil. If so, the smaller increase in absorption by aluminum than by mica paint is due to the high opacity of aluminum and the transparency of mica to visible and ultraviolet light.

Weathering reduced the absorption of water by films of paint containing zinc oxides and leaded zinc oxides from the level of 75 to 110 per cent to the order of 16 to 32 per cent. But the zinc oxide treated with vinyl silane absorbed even more water after than before weathering.

Zinc sulfide, lithopone, and zinc-dust paints still absorbed from 16 to 33 per cent of water after the films were weathered. Films containing titanium dioxides after weathering fell in the low-absorption class with 2.8 to 9.6 per cent absorption. Weathered iron oxide films, with the exception of ferric oxide No. 1, and magnesium silicate films also were low in absorption.

Swelling: Weathering reduced volumetic swelling as much or more than it did the absorption of water. Films for which the swelling efficiency remained 96 per cent or higher were those made with the lead chromates, zinc oxide Nos. 3 and 4 (but not Nos. 1, 2, or 5), zinc chromate, ferric oxide Nos. 1, 2, and 3, ferric hydroxide, magnesium silicate, calcium carbonate Nos. 2, 3, and 4 (but not No. 1), treated bentonite, mica, and aluminum. For all other films the swelling efficiency after weathering was less than 96 per cent, indicating the development of porosity.

Films for which the swelling efficiency after weathering became less than 80 per cent were: lead titanate, all white leads except basic carbonate No. 2, dibasic lead phosphite, titanium dioxide Nos. 1 and 5, Venetian red, barium sulfate, silica, and diatomaceous silica.

Swelling of weathered films in area was less than the swelling in volume except for films containing antimony oxide, lead titanate, and titanium dioxide No. 4, for which the swelling was small enough for experimental error to account for the anomaly; and for calcium sulfate and titanium-calcium, for which the leaching of calcium sulfate caused abnormalities.

Weathered films, in contrast to the unweathered films, showed a strong tendency to swell more in thickness than in area. For 22 of the 40 weathered films for which the data are available, the swelling in thickness exceeded the swelling in area, whereas the proportion for unweathered films was 8 of 44. The ratio of swelling in area to swelling in thickness ranged from 0.02 to 2.3 for weathered films compared with 0.4 to 3.7 for unweathered films, if 1 or 2 films with swelling too small for accurate measurement are excluded from each set.

Evidently the denser, harder, more brittle films produced by weathering find it easier to change in thickness than in area. Calcium sulfate and titanium-calcium paint films shrank in thickness during the soaking period, but they lost much of their calcium sulfate by leaching.

Shrinking on Redrying: On redrying after soaking, most weathered films shrank to a smaller volume than they had before soaking, but such residual shrinkage was usually less for the weathered than for the unweathered films. The decrease in residual shrinkage after weathering was due largely to a concomitant decrease in the leaching loss during soaking.

Films of lithopone, Venetian red, and calcium sulfate paint shrank more and lost more by leaching after weathering than before. But films of titanium-

calcium, calcium carbonate No. 1, and treated bentonite paint shrank slightly more despite slightly lower leaching loss after than before weathering; and weathered films of 35 per cent leaded zinc oxide paint shrank much more despite much lower leaching loss than the unweathered films.

The weathered films showed less tendency to shrink more readily in thickness than in area than was the case for unweathered films. Thus, only 10 weathered films, compared with 33 unweathered films, retained larger area after redrying than before soaking; and 10 weathered films, compared with only 1 unweathered film, were thicker after redrying than before soaking.

Embrittlement by weathering apparently renders the films less capable of accomplishing their volumetric shrinkage more by change in thickness than by change in area. No doubt this property is closely connected with the fact that paints seldom develop checks or cracks from their own internal stresses until they have become embrittled by weathering.

Loss in Weight While Soaking: Weathered films of all but eight paints lost less in weight during soaking than the corresponding unweathered films. The unweathered films probably contain water-soluble decomposition products of linseed oil that are leached out during weathering. In addition, it may be that weathered linoxyn is less subject to hydrolysis during soaking than is unweathered linoxyn.

The eight paints that lost more in weight during soaking after than before they were weathered were: the paints made with dibasic lead phosphite, zinc sulfide, lithopone, zinc dust, Venetian red, calcium sulfate, silica, The leaching losses by films of dibasic lead phosphite paint and the silica paint were so small both before and after weathering that the differences may be of no significance.

The losses by the films of zinc-dust paint were slightly larger but the difference between the weathered and unweathered films was small enough to be of doubtful significance. The increase in porosity of the diatomaceous silica paint after weathering may have allowed the soaking water to have had longer access to the inner portions of the films than before weathering. The other anomalous paints are ones for which the leachings include much soluble material derived from the pigment, and for which the increased porosity on weathering may well render the pigment more accessible to the soaking water.

The calcium sulfate paint and the Venetian red paint yielded much calcium sulfate to the soaking water. The titanium-calcium paint, which also contained calcium sulfate, had high leaching loss after weathering, even though the loss was slightly less than before weathering.

In the films of zinc sulfide and lithopone paints, the soluble zinc salts probably are formed by reaction between zinc sulfide and organic acids from decomposition of the oil. Apparently such reactions go on in weathered films more readily with zinc sulfide than with zinc oxide, either because zinc sulfide reacts with weaker acids than zinc oxide does or because the pigments have different effects on the formation of the organic acids from linoxyn.

Conclusions

1. Linseed-oil paints containing pigments increased in density when the liquid paint hardened to a dried coating. But the increase in density was less than that calculated on the assumption that the oil in the paints gains as much in weight and density as unpigmented linseed oil does in the same length of time (10 days). The discrepancy between calculated and observed density differed for different pigments and seemed to be related to the effect of the pigments on the absorption of oxygen and loss of volatile material by linseed oil as reported in the literature. There was a further increase in density of films during artificial weathering except for diatomaceous silica paint, which contained a structurally porous pigment, and which may have increased in pore volume during weathering.

2. Unweathered films always decreased in density as they absorbed water and, on redrying, returned to a density at least as high as that before soaking, unless the soaking water leached out soluble material derived from the pigment to cause a lowering of the density. Most weathered films behave similarly, but if weathering made the film sufficiently porous to hold enough free water, which caused no swelling, the density when soaked sometimes exceeded the density when dry.

3. All paints lost in weight during weathering, but the weight loss varied widely with different pigments. Part of the loss occurred early in the weathering period and was probably water-soluble material extracted by rain, the amount of which may be governed by the effect of pigments on the disruptive oxidation of linseed oil. Later in the weathering period, paints that chalked freely lost substance by mechanical erosion from the surface.

4. Some pigments reduced the absorption of water by free films below the absorptiveness of unpigmented linseed oil. In this class were the white leads and other lead pigments, antimony oxide, barium sulfate, silica, mica, and aluminum. Little effect on absorption was exerted by zinc-free titanium dioxides, some iron oxides, and calcium carbonate of coarse particle size.

Zinc oxides, leaded zinc oxides, zinc chromate, one iron oxide, Venetian red, and most calcium carbonates made paint films highly absorptive. Other pigments such as zinc sulfide, lithopone, zinc-treated titanium dioxides, and magnesium silicates made paint films of greater absorptiveness than unpigmented linseed oil but less than zinc oxide paints.

Efforts to relate the effect of pigments on the absorption of water to such surface properties as the relative wetting by water and organic liquids or the interfacial tension between pigments and liquids were fruitless. But there does seem to be a relation to the effect of pigments on the absorption of oxygen and evolution of volatile substances from linseed oil while drying.

5. Weathering reduced the absorption of water by paint films materially, unless it greatly increased the porosity of the films or unless the pigments were of the leafing type (mica and aluminum), so that most of the underlying portions of the oil film contained little or no pigment and acted like unpigmented linseed oil.

6. The volumetric swelling of unweathered free films was nearly equal to the absorption of water; that is, the swelling efficiency was close to 100 per cent, unless the films contained pigments from which the water extracted much soluble matter.

Weathering diminished the volumetric swelling proportionately to the absorption, leaving the swelling efficiency near 100 per cent, for films of paint made with the lead chromates, zinc chromate, some zinc oxides, some iron oxides; ferric hydroxide, magnesium silicate, some calcium carbonates, treated bentonite, mica, and aluminum. Films containing any other pigments decreased in swelling efficiency and presumably became porous on weathering.

7. Unweathered films always swelled less in area than in volume and usually swelled still less in thickness. Weathered films, in contrast, tended strongly to swell more in thickness than in area.

8. Films of paints made with acicular pigments swelled more, sometimes 4 to 5 times as much, across the grain than along the grain of the paint. The grain is determined by the direction of last flow of the liquid paint before the coating hardens.

9. Unweathered films, on redrying after soaking, shrank to a volume slightly smaller than that before soaking unless the swelling efficiency indicated that the film was somewhat porous. The residual shrinkage was due chiefly to extraction of soluble substances by the soaking water. Often the

area remained enlarged after drying, but the thickness was always diminished. Thus, unweathered films seem to shrink in thickness more readily than they do in area.

10. For weathered films redried after soaking, the residual shrinkage in volume was usually less, but so was the loss of soluble matter, than that of unweathered films. Weathered films proved much less likely to shrink proportionately more in thickness than in area than was the case for unweathered films.

11. Films of all paints lost weight from extraction of soluble matter when soaked in water. When the pigments were insoluble and nonreactive, the material dissolved consisted entirely of organic matter derived from the linseed-oil vehicle, much of which could be recovered by evaporating the leaching water to dryness.

When the pigments contained water-soluble ingredients or formed soluble salts by reaction with organic acids from decomposition of the oil, the losses were larger and the leachings contained the inorganic constituents from the pigments in addition to organic matter from the oil. Weathering reduced the amount of soluble organic matter leached from the films, but it sometimes increased the amount of inorganic extract.

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