Swelling of Paint Films in Water

VI. Effects of Different Oil or Oleoresinous Vehicles[1]

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Discusses the effect of four oil or varnish vehicles on the behavior of free films of paints when soaked in distilled water for three days and then redried. The films were tested when 10 days old and after 15 days of artificial weathering. Measured were changes of density, absorption of water, swelling during absorption, shrinkage on redrying, loss in weight while soaking, and loss in weight while weathering.

THE FIFTH PAPER in this series (3 to 7)[3] described the effect of 44 different pigments on the behavior of free films of single-pigment paints made with linseed oil when the films were soaked in distilled water for 3 days and then redried. The films were tested when 10 days old and also after an additional 15 days of artificial weathering.

This sixth paper describes similar studies of the effects of different oil and oleoresinous vehicles. Unpigmented films of bodied linseed oil, an alkyd-resin vehicle recommended for making house paints, and a phenolic-resin varnish were tested both before and after artificial weathering. The results were compared with previous data for films of unbodied linseed oil. Single-pigment and multiple-pigment paints were made with each of the vehicles, and films with these pigments were tested before and after weathering. The tests included measurements: (1) of changes in density during formation of films, (2) on free films after they were soaked in distilled water for three days, (3) on the redried films, (4) on the absorption of water during soaking, (5) of the swelling in volume, area, and thickness when water was absorbed, (6) of the contraction in volume, area, and thickness when the films were redried, (7) of the loss of soluble matter from the films while they were soaking, and (8) of the loss in weight while the films were artificially weathered.

In the meantime, a number of publications on the swelling of films by other investigators have appeared (1, 9 to 11, 16 to 22).

Vehicles and Paints Tested

Three paint vehicles were chosen: a heat-bodied linseed oil of viscosity Z-6; a commercial long-oil, pure alkyd-resin vehicle sold for use in "stain- and blister-resistant" house paints; and a pure phenolic-resin varnish of 33-gallon length in linseed and tung oils. A fourth vehicle, refined but unbodied linseed oil, had already been tested extensively, as reported in previous papers (4, 7). Driers in the unbodied and bodied linseed oils were lead and manganese naphthenates; in the alkyd-resin vehicle, they were cobalt and calcium naphthenates; and in the phenolic-resin varnish, they were cobalt and lead naphthenates.

Unpigmented films of the alkyd-resin vehicle and the phenolic-resin varnish were tested, and data for unpigmented films of unbodied and bodied linseed oil were available from a previous paper (4).

All experimental paints were made at 30 per cent pigment volume (symbol p/nv 0.30). Each kind of pigment was of the same make and grade in all experimental paints reported in this paper.

With each of the vehicles, there were single-pigment paints made with basic carbonate white lead (symbol L), antimony oxide (symbol A), rutile titanium dioxide (symbol T), zinc oxide (symbol Z), and magnesium silicate (symbol X). There were also three mixed-pigment paints as follows: (a) a lead-zinc paint LZ_{25} (the subscript represents the percentage of the pigment symbolized in the total pigment by volume), (a) an antimony-zinc paint, AZ_{25}, and (c) a titanium-zinc paint, TZ_{25}. In the alkyd-resin vehicle, the titanium-zinc paint also contained magnesium silicate, $TZ_{25}X_{57}$. A fourth mixed-pigment paint, $TA_{25}X_{57}$, was also used with the alkyd-resin vehicle.

The five pigments for the single-pigment paints were chosen on the basis of the absorption and swelling properties previously found for unbodied linseed oil paints (7). Two were chosen for unusually low, one for very high, and two for moderately high absorption and swelling. The mixed-pigment paints represented two combinations of low- and high-swelling pigments and two combinations of moderately high- and high-swelling pigments.

Preparation of Free Films and Tests

Clear vehicles and paints to be tested before weathering were spread on gummed paper by doctor blade and suction plate, and allowed to dry for 10 days. The free films were then stripped from the paper by immersion in cold water for about 15 minutes until the paper backing became wet and the dextrine gum softened. Vehicles and paints to be weathered before testing were spread on tinplate, and

[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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allowed to dry for 10 days. They were then sprayed with distilled water three times an hour in a Weatherometer for 15 days, and simultaneously exposed to ultraviolet light from a flaming carbon arc enclosed in Corex D glass (1,200 kilowatt-hours of input of electric current). The tinplate specimens were weighed before coating, after the coatings had dried and cured, and after the period of artificial weathering, to determine the loss in weight of the coatings while weathering. Free films were then stripped for testing by amalgamation of the tinplate.

Procedures for measuring absorption, swelling, and solubility were essentially those described previously (4). Test films were cut 1½ by 2½ inches in size, scribed with reference marks for measuring changes in length and width with a traveling microscope, and dried in a desiccator over calcium chloride. The films were then measured for length and width, and weighed in air and under water to determine the initial weight and volume. Each film was submerged in a crystallizing dish under 250 cubic centimeters of distilled water and a weighted pad of glass cloth to prevent undue curling of high-swelling films. The films were soaked for 3 days at 70° F., and weighed under water. They were then sandwiched between microscope cover glasses for measurement of length and width, removed from the cover glasses and quickly blotted with paper towels to remove free water, and weighed in air. Finally, the films were redried for 3 days in a desiccator, and then measured for length and width and weighed in air and under water.

At each of the three test stages, before and after soaking and after redrying, the data yielded the weight in air, W, the volume, V, and the length and width between reference marks. The reasonable assumption that the whole film swelled or shrank in the same proportion as the part between reference marks made it possible to compute the swollen and redried lengths, L, and widths, B, of the entire film from the known initial dimensions. The following relations then apply at each stage of test:

Area	$Q = L \times B$
Thickness	$T = V/Q$
Density	$D = W/V$

Indicating the initial, swollen, and redried stages by the subscripts o, s, and r, respectively, changes in the film usually can be calculated from the relations:

- Absorption of water, A, in per cent by volume $= 100\,(W_s - W_r)/V_o$
- Increase in volume, ΔV_s, in per cent $= 100\,(V_s - V_r)/V_o$
- Increase in area, ΔQ_s, in per cent $= 100\,(Q_s - Q_r)/Q_o$
- Increase in thickness, ΔT_s, in per cent $= 100\,(V_s/Q_s - V_o/Q_o)$
- Swelling efficiency, in per cent $= 100\,\Delta V_s V_o/A$
- Decrease in volume, ΔV_r, in per cent $= 100\,(V_o - V_r)/V_o$
- Decrease in area, ΔQ_r, in per cent $= 100\,(Q_o - Q_r)/Q_o$
- Decrease in thickness, ΔT_r, in per cent $= 100\,(V_r/Q_r - V_o/Q_o)$
- Solubility, S_2, the loss in weight while soaking, in grams per 100 cubic centimeters $= 100\,(W_o - W_r)V_o$
- Solubility, S_1, the loss in weight while weathering, is similarly calculated in per cent as 100 times the weight loss divided by V_o.

In the literature on swelling of paint films, the absorption of water has often been reported in percentage by weight for convenience, but the great variation in density of paints impairs even the relative significance of such measurements. Swelling is by nature a volumetric process. There is, therefore, a growing practice of reporting absorption volumetrically (2, 8, 10). Expression of solubility in percentage by weight is similarly questionable. As long as the density of the soluble ingredients remains unknown, the most useful method of reporting solubility for the present purpose seems to be the weight of dissolved matter per 100 cubic centimeters of film.

Occasionally the volume and often the area of a redried film remain greater than they were before soaking, despite loss of soluble substances to the soaking water. If the increase is beyond the limits of experimental error, either there has been a disproportionally large shrinking in thickness or a decrease in film density on redrying after soaking. In such cases, the volumetric swelling was taken as $\Delta V_s = V_s - V_o$ and the areal swelling as $\Delta Q_s = Q_s - Q_o$.

Unweathered Films

The effects of soaking on unweathered films are reported in Table 1.

Density: All four clear vehicles became more dense after they had dried for 10 days. Although the density of the liquid vehicle varied from 0.93 for unbodied linseed oil to 1.02 for the phenolic-resin varnish (nonvolatile only), the 10-day-old films all reached the same density, 1.11. The increase in density was 19.4, 14.4, 11.0, and 8.8 per cent of the density of the liquid unbodied linseed oil, bodied linseed oil, alkyd-resin vehicle, and phenolic-resin varnish, respectively.

The density of all paints made with the four vehicles similarly increased during the 10-day drying period. For paints made with unbodied linseed oil, the percentage increases ranged from 4.7 to 11.3 per cent; for paints made with bodied linseed oil, from 1.3 to 6.5 per cent; for paints made with alkyd-resin vehicle, from 2.9 to 8.6 per cent; and for paints made with phenolic-resin varnish, from 0.8 to 3.2 per cent.

It was shown previously (7) for unbodied linseed oil paints that the increase in density is always less than that calculated on the assumption that the oil in a paint undergoes the same changes in weight, volume, and density that occur in the oil when no pigments are present. Thus pigments alter the course of the drying process in unbodied linseed oil to an extent that varies for different pigments. It now appears that pigments similarly alter the drying of bodied linseed oil, alkyd-resin vehicle, and phenolic-resin varnish. The increase in density during drying was always less than that calculated from the changes in the unpigmented vehicle by an amount that ranged from 0.01 to 0.21. The shortage was usually greatest for white lead, antimony oxide, and zinc oxide, and least for titanium dioxide and magnesium silicate. Also, the shortage was usually greater in bodied linseed oil and phenolic-resin vehicles than in raw linseed oil and alkyd-resin vehicles.

When soaked in water for 3 days, all films, clear or pigmented, decreased in density to an extent roughly proportional to the quantity of water absorbed unless the absorption was less than 1 per cent. Exact proptionality is not to be expected because there was a loss of soluble substances from the films during soaking.

On redrying after soaking, the lost density was regained or exceeded by all films except two—antimony-zinc and titanium-zinc in alkyd-resin vehicle. Higher density after redrying could come from further aging of the paint during the soaking and drying periods, or from loss of soluble ingredients of low density. The two paints that failed to regain their lost density were also the two with the lowest swelling efficiency, which may indicate that they acquired some internal voids from the soaking and redrying treatment.

Absorption of Water: When the clear vehicles were soaked for 3 days, the amount of water they absorbed decreased in the following order: unbodied linseed oil, 21.8 per cent; bodied linseed oil, 9.0 per cent; alkyd resin, 7.7 per cent; phenolic resin, 1.5 per cent. Since the film of alkyd resin was thicker than the others, the absorption by alkyd-resin vehicle may be as great or even somewhat greater than by bodied linseed oil vehicle. If all sorption to be expected if the vehicle absorbed proportionately as much water as it did without pigment. Thus in unbodied oil, where 15.3 per cent absorption might be expected, the antimony oxide paint absorbed only 5.3 per cent. Basic carbonate white lead likewise reduced the absorption in unbodied and bodied linseed oil, but failed to reduce or perhaps slightly increased the absorption in alkyd-resin and phenolic-resin vehicles, although the absorption still remained relatively low.

All other pigments greatly increased the absorption of water above that expected for the proportion of clear vehicle in the paint. Among the single-pigment paints, zinc oxide and magnesium silicate caused the highest absorptions. Zinc oxide was highest in unbodied and bodied linseed oil and in alkyd resin, but magnesium silicate exceeded zinc oxide in phenolic-resin vehicle. In zinc oxide, the absorption reached 83.3 per cent in unbodied linseed oil and 61.8 per cent in alkyd-resin vehicle. Magnesium silicate in phenolic-resin vehicle absorbed 15.3 per cent. Absorptions by titanium dioxide paints were 34.9, 6.8, 16.6, and 2.5 per cent in unbodied oil, bodied oil, alkyd resin, and phenolic resin, respectively.

Absorptions by mixed-pigment paints, all of which contained at least one high-swelling pigment, were relatively high. Presence of a low-swelling pigment in the mixture moderated the absorption appreciably in bodied linseed oil or phenolic-resin vehicle, as was previously found in unbodied linseed oil (4), but in alkyd-resin vehicle, mixtures of low- and high-swelling pigments usually showed higher absorption than the zinc oxide alkyd-resin paint. Apparently, high-swelling pigments tend to dominate low-swelling pigments in all vehicles.

Swelling: The volumetric swelling of films was usually equal to or a trifle greater than the volume of absorbed water. The swelling efficiency was therefore usually 100 per cent or a little over, which means that each cubic centimeter of water absorbed increased the volume of the film by a like amount or a little more. The slight excess of swelling over absorption may be due to the experimental difficulty of weighing the soaked films in air without significant loss of absorbed water by evaporation. If some films really did swell by more than the volume of water absorbed, it may be that the films, after their initial formation and hardening (1, 14), acquired internal compression stresses from further absorption of oxygen, and that the stresses were released to add an increment of volume as soon as absorbed water plasticized and softened the films. The data show no evidence of the compression of swelling liquid reported by Weinmann (22). A swelling efficiency greater than 104 per cent appears in Table 1 only when the absorption was less than 8 per cent and the excess of swelling over absorption less than 1.3 percent; that is, when the measured values were small enough to make the experimental errors relatively large. Nevertheless, the relatively large swelling efficiency of the clear film of alkyd-resin vehicle, for example, appeared again when the corresponding weathered film was tested. Similarly, a swelling efficiency of less than 97 per cent was recorded only for antimony oxide in bodied oil, for which the absorption was only 0.8 and the volumetric swelling 0.7 per cent. The two measurements of 97 per cent swelling efficiency, however, may be accepted as true deficiency in swelling because the film density was less after redrying than before soaking, which indicates that soaking developed void spaces capable of holding free water, the evaporation of which caused no shrinking of the swollen films.

All films swelled in area when soaked in water, but areal swelling was not proportional, in general, to volumetric swelling. Usually, areal swelling was much less than volumetric swelling, but sometimes the two were nearly or even fully equal, especially when the absorption was relatively low. Of course, when areal swelling was large in relation to volumetric swelling, swelling in thickness was correspondingly small, and for seven of the films it was even negative. That is, the films became thinner on swelling.

It was shown previously (3, 7) that the ratio of length to width in areal swelling of linseed oil paints may vary greatly among paints of different pigmentation, and may vary greatly for any one paint according to the tool used and methods followed in application, particularly if the paint contains acicular pigments that may become preferentially oriented when the paint is spread and dried. Similar variations were observed among paints in the vehicles of the present study, but these variations need not be presented in detail. It is sufficient to point out that volumetric swelling is independent of a number of considerations that markedly affect the distribution of swelling among length, width, and thickness (11). Volumetric swelling is therefore more readily reproducible and, in general, more reliable than areal or linear swelling.

Shrinkage on Redrying: On redrying, all swollen films shrank to a volume less than that before soaking, except the film of antimony-zinc paint in alkyd resin, which shrank only to its volume before soaking. Such loss in volume is due primarily to loss of soluble substances during soaking. Since the nature, and therefore the density, of the dissolved substances has not yet been determined, it is not possible to compare the volume lost by the film with that of the substances dissolved.

However, another factor must also be considered, namely, the change in density of the film before soaking and after redrying due to aging of the film or to development of voids within the film. The antimony-zinc paint in alkyd resin, which had the same volume after redrying as before soaking, despite a solubility of 3.3 per cent, exhibited such formation of voids by decreased density and low swelling efficiency. Similarly, titanium-zinc paint in alkyd resin, which showed a loss in density and low swelling efficiency, experienced only 2.5 per cent loss in volume despite 7.3 per cent solubility.

After redrying, 27 of the 34 films remained larger in area than they were before soaking, 2 were unchanged in area, and 5 decreased in area. Of course, failure to shrink in area when the volume shrank caused correspondingly large shrinkage in thickness. All seven films that were no larger in area after redrying than before soaking were either clear films or films pigmented only with white lead or with antimony oxide. When high-swelling pigments were present, the redried area was always greater than the presoaked area.

Loss in Weight While Soaking: If allowance is made for the differences in film thickness, the solubilities of the films of clear unbodied and bodied linseed oil and alkyd-resin vehicle may be considered about equal at 5.8 grams per 100 cubic centimeters for 3.7-mil thickness. The phenolic-resin varnish was much less soluble, 1.3 grams per 100 cubic centimeters. For the 70 per cent by volume of vehicle in the pigmented films, the solubility, if the pigments had no effect, should be 4.1 grams per 100 cubic centimeters for the first 3 vehicles and 0.9 gram per 100 cubic centimeters for the phenolic-resin varnish.

In unbodied linseed oil, the solubilities for paints with pigments other than zinc oxide were not far from 4.1 grams per 100 cubic centimeters, but zinc oxide raised the solubility to 5.9 grams per 100 cubic centimeters. In bodied linseed oil, no paint was higher than 1.9 grams per 100 cubic centimeters in solubility. In alkyd resin, the solubility of all paints was more than 1.9 grams per 100 cubic centimeters, but only the zinc oxide and the titanium-zinc paints were much more soluble than 4.1 grams per 100 cubic absorption by the pigmented films took place in the vehicle, without any effects from the pigments, the absorption should have been 15.3 per cent for all films with unbodied linseed oil, 6.3 per cent for all films with bodied oil, 5.4 per cent for all films with alkyd resin, and 1.0 per cent for all films with phenolic resin. Pigmentation, however, resulted in higher or lower absorptions, according to the nature of the pigments.

To see whether absorption of water by pigments in the absence of vehicle could account for the effects of pigments on absorption by paint films, 3- to 4-gram samples of white lead, zinc oxide, titanium dioxide, and magnesium silicate were each soaked in 150 cubic centimeters of distilled water for 3 days. The water was then decanted and the pigments allowed to dry at room temperature until the weight was constant. The white lead gained 0.044 per cent by weight or 0.3 per cent by volume, zinc oxide gained 0.48 per cent by weight or 2.69 per cent by volume, titanium dioxide gained 0.023 per cent by weight or 0.09 per cent by volume, and magnesium silicate lost 0.18 per cent by weight. Thus the magnesium silicate contained a small proportion of water-soluble matter and the other pigments retained slight amounts of water that was presumably adsorbed. Zinc oxide, as was to be expected, retained more water than white lead or titanium dioxide, but the amount was far too small to account for the large effect of zinc oxide on the absorption of water by paint films.

With paint films of any one pigmentation, the absorption was nearly always highest for the unbodied linseed oil vehicle and lowest for the phenolic-resin vehicle, and was always higher for the alykd-resin vehicle than for the bodied linseed oil vehicle. The differences attributable to kind of vehicle, however, proved less than differences caused by kind of pigment.

Antimony oxide, in all four vehicles, reduced the absorption below the ab-

Table 1.—DATA FOR FREE, UNWEATHERED FILMS OF DIFFERENT OIL OR VARNISH VEHICLES WITH AND WITHOUT PIGMENTS—CHANGES IN DENSITY; ABSORPTION OF WATER AND SWELLING IN VOLUME, AREA, AND THICKNESS WHEN SOAKED IN WATER FOR 3 DAYS. SWELLING EFFICIENCY; SHRINKING IN VOLUME, AREA, AND THICKNESS WHEN REDRIED; AND LOSS IN WEIGHT BY LEACHING DURING THE SOAKING PERIOD

Vehicle	Density of nonvolatile in liquid paint	Density of film: Dry	Density of film: Swollen in water	Density of film: Redried	Initial thickness of film T_o	Absorption of water A/V_o	Swelling: In volume $= \Delta V_s$	Swelling: In area ΔQ_s	Swelling: In thickness ΔT_s	Swelling efficiency $\frac{\Delta V_s V_o}{A}$	Redried: Volume ΔV_r	Redried: Area ΔQ_r	Redried: Thickness ΔT_r	Loss in weight soaking S_2/V_o
					Mils	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Gr. per 100 cc.
CLEAR VEHICLES CONTAINING NO PIGMENT														
Linseed oil, not bodied	0.93	1.11	1.09	1.12	3.1	21.8	22.0	9.8	10.8	101	-6.0	-4.9	-1.3	5.8
Linseed oil, heat bodied	.97	1.11	1.09	1.11	3.6	9.0	9.2	6.1	1.4	102	-4.9	-2.6	-2.2	5.1
Alkyd vehicle	1.00	1.11	1.10	1.12	5.6	7.7	8.9	6.0	-.7	116	-4.0	+2.1	-5.7	3.3
Phenolic-resin varnish	1.02	1.11	1.10	1.11	3.9	1.5	1.7	1.0	-.3	113	-1.3	-.1	-1.3	1.3
BASIC CARBONATE WHITE LEAD, SINGLE-PIGMENT PAINTS, PIGMENT VOLUME 0.30														
Linseed oil, not bodied	2.70	2.87	2.74	2.90	3.8	8.9	9.3	2.1	5.3	104	-2.5	+.1	-2.1	3.8
Linseed oil, heat bodied	2.71	2.82	2.78	2.87	4.8	3.1	4.2	.8	1.0	135	-2.3	0	-2.5	1.9
Alkyd vehicle	2.79	2.91	2.80	2.98	3.1	9.7	10.0	2.7	3.8	103	-3.3	+.3	-3.5	3.0
Phenolic-resin varnish	2.76	2.80	2.79	2.82	4.8	1.8	2.3	.5	.6	128	-1.2	0	-1.2	.6
ANTIMONY OXIDE, SINGLE-PIGMENT PAINTS, PIGMENT VOLUME 0.30														
Linseed oil, not bodied	2.38	2.54	2.52	2.61	3.4	5.3	5.8	2.9	.3	109	-4.3	-1.4	-2.9	4.7
Linseed oil, heat bodied	2.39	2.42	2.42	2.42	5.6	.8	.7	.7	-.5	87	-.7	+.2	-.9	.8
Alkyd vehicle	2.46	2.57	2.56	2.61	3.3	2.2	2.7	1.8	-.9	123	-2.4	-.7	-1.5	2,4
Phenolic-resin varnish	2.44	2.47	2.48	2.50	5.2	.9	1.2	1.2	-2.0	133	-1.8	+.3	-2.0	1.3
RUTILE TITANIUM DIOXIDE, SINGLE-PIGMENT PAINTS, PIGMENT VOLUME 0.30														
Linseed oil, not bodied	1.91	2.06	1.80	2.11	3.5	34.9	35.5	17.1	12.4	102	-4.2	+3.3	-7.1	4.1
Linseed oil, heat bodied	1.93	1.99	1.94	2.02	5.2	6.8	7.7	5.7	0	113	-2.2	+.3	-2.1	1.2
Alkyd vehicle	2.05	2.11	1.97	2.15	3.4	16.6	17.2	10.3	3.5	103	-2.9	+.4	-3.2	3.0
Phenolic-resin varnish	1.97	1.99	1.97	2.00	6.6	2.5	3.2	2.5	-.5	128	-1.2	+.4	-1.5	.5
ZINC OXIDE, SINGLE-PIGMENT PAINTS, PIGMENT VOLUME 0.30														
Linseed oil, not bodied	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
Linseed oil, heat bodied	2.35	2.45	2.10	2.46	4.3	31.8	31.5	10.9	17.3	99	-1.0	+3.0	-4.0	1.6
Alkyd vehicle	2.41	2.55	1.96	2.58	3.0	61.8	61.5	21.5	29.6	100	-3.6	+6.0	-9.2	6.4
Phenolic-resin varnish	2.39	2.44	2.32	2.45	5.0	9.8	9.9	4.7	4.0	101	-1.5	+1.3	-2.8	1.6
MAGNESIUM SILICATE, SINGLE-PIGMENT PAINTS, PIGMENT VOLUME 0.30														
Linseed oil, not bodied	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
Linseed oil, heat bodied	1.53	1.60	1.47	1.62	5.2	28.0	28.5	14.0	10.7	102	-2.1	+1.7	-3.8	1.7
Alkyd vehicle	1.57	1.68	1.49	1.69	3.2	40.3	40.0	16.1	17.6	100	-3.6	+2.8	-6.3	4.5
Phenolic-resin varnish	1.57	1.62	1.54	1.63	5.2	15.3	15.7	7.1	6.2	102	-1.4	+.7	-1.9	.9
LEAD-ZINC, MIXED-PIGMENT PAINTS LZ_{25}, PIGMENT VOLUME 0.30														
Linseed oil, heat bodied	2.63	2.72	2.48	2.74	4.5	16.3	16.5	5.9	9.0	101	-1.0	+.9	-1.8	.9
Alkyd vehicle	2.69	2.82	2.06	2.84	3.1	73.5	72.6	26.9	34.4	99	-1.9	+11.5	-12.2	3.8
Phenolic-resin varnish	2.67	2.73	2.67	2.74	4.9	4.5	4.7	2.8	.8	104	-.8	+.4	-1.0	.5
ANTIMONY-ZINC, MIXED-PIGMENT PAINTS AZ_{25}, PIGMENT VOLUME 0.30														
Linseed oil, heat bodied	2.30	2.45	2.24	2.47	5.3	18.0	18.3	8.8	8.1	102	-1.0	+1.5	-2.5	.5
Alkyd vehicle	2.44	2.57	1.96	2.55	3.1	64.2	62.3	34.0	21.2	97	0	+13.4	-11.5	3.3
Phenolic-resin varnish	2.44	2.46	2.38	2.48	5.0	7.3	7.5	4.6	1.4	103	-1.3	+.7	-2.2	1.3
TITANIUM-ZINC, MIXED-PIGMENT PAINTS TZ_{25}, PIGMENT VOLUME 0.30														
Linseed oil, heat bodied	2.04	2.11	1.90	2.12	4.8	23.3	23.5	11.0	10.1	101	-1.1	+2.4	-3.3	.9
Alkyd vehicle[1]	1.85	1.97	1.52	1.95	3.3	86.4	84.0	36.4	33.0	97	-2.5	+15.2	-15.3	7.3
Phenolic-resin varnish	2.09	2.11	2.05	2.13	5.2	6.4	6.5	5.9	-.8	102	-1.6	+1.6	-3.3	1.8
TITANIUM-ANTIMONY-MAGNESIUM SILICATE PAINT $TA_{25}X_{57}$, PIGMENT VOLUME 0.30														
Alkyd vehicle	1.86	2.02	1.84	2.04	3.0	22.8	23.4	8.1	11.5	103	-3.0	+.8	-3.6	3.4

[1]The pigment in this paint contained titanium dioxide, zinc oxide, and magnesium silicate; paint $TZ_{25}X_{57}$, p/nv 0.30.

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centimeters. In phenolic resin, no paint reached 1.9 grams per 100 cubic centimeters in solubility, and only the zinc oxide, titanium-zinc, antimony-zinc, and antimony oxide paints exceeded the solubility expected of the clear vehicle, 0.9 gram per 100 cubic centimeters.

There seems to be a rough relation between the effect of pigments on the solubility of paint films and on film absorptions and swelling (7). Meier and Schulz (16) found that removal of water-soluble ingredients from pigments reduces the swelling of paints made with them, but that paints with some pigments, particularly zinc oxide, still swell more than the clear vehicle, even if the pigments have been thoroughly leached. It may well be that pigments affect film swelling at least in part by altering the formation of water-soluble substances formed from the vehicles during oxidation, aging, or hydrolysis (1, 15).

Weathered Films

Table 2 gives the effects of weathering on oil-type paints that were weathered artificially for 15 days (1,200 kilowatt-hours of electric input), and the subsequent effects of soaking on these artificially weathered films.

Loss in Weight While Weathering: All films lost weight during the 15-day period of artificial weathering, as other workers have found (1, 13). Among the clear vehicles, the losses per 100 cubic centimeters were 28.1 grams for unbodied linseed oil, 12.7 grams for bodied linseed oil, 6.1 grams for alkyd-resin vehicle, and 2.3 grams for phenolic-resin varnish. For the proportion of vehicle in the pigmented films, the losses would be 19.7, 8.9, 4.3, and 1.6 grams per 100 cubic centimeters, respectively, if the pigments exerted no effect.

In unbodied linseed oil vehicle, all pigments except zinc oxide made films that lost more than 19.7 grams in weight while weathering. Zinc oxide decreased the loss materially. In bodied oil vehicle, on the other hand, all pigments except magnesium silicate reduced the loss to less than 8.9 grams. Zinc oxide or any pigment mixture that included zinc oxide was particularly effective in reducing this weight loss. Magnesium silicate increased the loss slightly. In alkyd-resin vehicle, pigments usually increased the weight loss to more than 4.3 grams, but zinc oxide and mixtures containing zinc oxide gave only slight increases or even slight decreases in the weight loss. In phenolic-resin varnish, pigments usually increased the weight loss, and zinc oxide increased it as much or more than other pigments.

Since water extracts appreciable quantities of zinc oxide from films of linseed oil paints, but extracts little or none of the other pigments used in these tests (3, 7, 12), it might be expected that the loss of weight on weathering would be higher for the paints that contain zinc. The fact that zinc oxide tends instead to reduce the weathering loss indicates that the effect of zinc on the solubilization of the vehicle is more important than the reaction of zinc with acid decomposition products of the vehicle to form soluble soaps (1, 15).

Density: All films were higher in density after the weathering period than they had been when dried for 10 days but not yet weathered. The increase was due to further contraction in volume on aging and weathering and to loss of vehicle constituents that are much less dense than the pigments.

When clear films of the four vehicles were weathered, the density increased 5.4, 4.5, 3.6, and 4.5 per cent for unbodied oil, bodied oil, alkyd vehicle, and phenolic-resin varnish, respectively. For the films of unbodied oil paints, the density increase was 7.8 to 15.7 per cent, and was always greater than that for the clear oil without pigment. For the films of pigmented phenolic-resin varnish, on the other hand, the density increase was only 2.5 to 3.5 per cent, and was always less than that for the clear varnish. For the films of bodied oil paints and alkyd-resin paints, except those containing zinc oxide, the density increase always exceeded that of the clear vehicle. The increase was 6.0 to 7.5 per cent for bodied oil paints, and 4.2 to 7.8 per cent for alkyd-resin paints. When the paint contained zinc oxide, the density increase was always less than that for films containing any other pigment in the same vehicle.

In general, pigments exerted an effect on density increase during weathering that was opposite to their effect during film formation and drying. Pigmentation delayed the density increase during drying of the liquid paint, but when the pigmented films were weathered, they tended to catch up with the increase in density of the clear vehicles. A comparison of the density of the weathered films with the density of 10-day-old films calculated on the assumption that pigments do not alter the behavior of the vehicle shows that weathered films of unbodied oil paints reached a density 2 to 12 per cent greater than theoretical for 10-day-old films, weathered bodied oil or alkyd-resin paints came within 2 per cent above or below theoretical, and phenolic-varnish paints failed to reach theoretical by 1 to 4 per cent.

When the weathered films were soaked in water for 3 days, the density decreased roughly in proportion to the quantity of water absorbed, unless the absorption was less than 2.5 per cent. After redrying, the density returned to its value before soaking, or slightly higher, for all but seven films, six of which became somewhat porous, as indicated by their lower swelling efficiency and larger volume after redrying.

Absorption of Water: Weathering had little effect on the absorption of water by clear films of unbodied linseed oil and of phenolic-resin varnish. It diminished the absorption by clear films of alkyd-resin vehicle only slightly, and greatly increased the absorption by clear films of bodied linseed oil so much that the bodied oil films absorbed more water after weathering than the unbodied oil films did before they were weathered.

Pigmented films that absorbed more than 9.0 per cent of water before weathering always absorbed less water after they were weathered. They absorbed much less if their absorption before weathering exceeded 20 per cent. Weathering also diminished the absorption of most pigmented films that absorbed less than 9.0 per cent before weathering. The exceptions were white lead in unbodied and bodied oils, antimony oxide in bodied oil, alkyd resin, and phenolic resin, and lead-zinc in phenolic resin. For these exceptions, weathering increased the absorption slightly or failed to decrease it.

In weathered films of unbodied linseed oil, the only pigment that caused absorption as great or greater than that to be expected of the proportion of clear vehicle in the film was zinc oxide. In weathered films of bodied oil, clear films were so much more absorptive after weathering than before that all pigments reduced the absorption below that expected of the proportion of vehicle in the films. In weathered films of alkyd resin or phenolic resin, however, the absorption was as great or greater than that expected of the proportion of vehicle in the films, except with antimony oxide, with which the absorption was slightly less.

Swelling: For nearly half of the weathered films, the volumetric swelling was less than the absorption of water, and the swelling efficiency was therefore less than 100 per cent. That was the case with all unbodied oil paints, although the unbodied oil without pigments had 100 per cent swelling efficiency. The tendency for weathering to reduce swelling efficiency has been observed repeatedly in previous work, and is attributed to the development of voids within the film that are capable of holding free water that causes no swelling.

Weathered films of bodied oil were the only unpigmented films to have less than 100 per cent swelling efficiency. Bodied oil paints that contained white lead had only 75 per cent swelling efficiency, and the zinc oxide and lead-zinc paints had a 99 per cent efficiency. Bodied oil paints with antimony oxide, titanium dioxide, or magnesium silicate had at least a 100 per cent swelling efficiency. Weathered films of unpigmented alkyd resin, like the corresponding unweathered films, swelled beyond the volume of water absorbed, which may indicate a release of internal stresses acquired when the films originally dried. If such a release did occur, these internal stresses were absent or less significant in the films of weathered alkyd-resin paints, none of which had much more than 100 per cent swelling efficiency, and three of which had less than 100 per cent efficiency. Weathered films of phenolic-resin varnish, with or without pigments, were too low in absorption and swelling to permit reliable deductions from the variations in swelling efficiency.

The swelling in area and thickness of weathered films exhibited much the same variations from proportionality to volumetric swelling that have already been discussed for unweathered films.

Shrinkage on Redrying: On redrying after soaking, all but one of the weathered films shrank to a volume closer to that of the film before soaking than was the case with the unweathered films. For the one exception, the redried volume was within 0.7 per cent of the initial volume for both unweathered and weathered films. As a rule, the redried volume was less than the volume before soaking, but for weathered films of six paints, the redried volume slightly exceeded the initial volume. The smaller residual shrinkage of weathered films may be attributed to less solubility during soaking, and perhaps to less swelling during the soaking period.

On redrying, weathered films, like the unweathered films, tended to

Table 2.—DATA FOR FREE, WEATHERED FILMS OF DIFFERENT OIL OR VARNISH VEHICLES WITH AND WITHOUT PIGMENTS—CHANGES IN DENSITY; ABSORPTION OF WATER AND SWELLING IN VOLUME, AREA, AND THICKNESS WHEN SOAKED IN WATER FOR 3 DAYS. SWELLING EFFICIENCY; SHRINKING IN VOLUME, AREA, AND THICKNESS WHEN REDRIED; AND LOSS IN WEIGHT BY LEACHING DURING THE SOAKING PERIOD

Vehicle	Weight loss while weathering S_1/V_o	Density of film: Dry	Density of film: Swollen in water	Density of film: Redried	Initial thickness of film T_o	Absorption of water A/V_o	Swelling: In volume ΔV_s	Swelling: In area ΔQ_s	Swelling: In thickness ΔT_s	Swelling efficiency $\frac{\Delta V_s V_o}{A}$	Redried: Volume ΔV_r	Redried: Area ΔQ_r	Redried: Thickness ΔT_r	Loss in weight soaking S_L/V_o
	Percent				Mils	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Gr. per 100 cc.
CLEAR VEHICLES CONTAINING NO PIGMENT														
Linseed oil, not bodied	28.1	1.17	1.14	1.17	3.7	20.4	20.5	4.4	15.5	100	-2.2	-1.7	+0.3	2.9
Linseed oil, heat bodied	12.7	1.16	1.13	1.19	4.1	28.1	27.5	10.1	14.9	98	-.7	+2.1	+.2	1.8
Alkyd vehicle	6.1	1.15	1.15	1.15	5.1	4.8	5.5	3.5	1.0	114	-1.4	-.3	-1.2	.5
Phenolic-resin varnish	2.3	1.16	1.16	1.14	3.9	1.5	2.0	1.0	0	133	-1.0	-.2	-1.0	.5
BASIC CARBONATE WHITE LEAD, SINGLE-PIGMENT PAINTS, PIGMENT VOLUME 0.30														
Linseed oil, not bodied	21.0	3.26	3.06	3.11	2.8	9.9	8.7	.7	8.8	88	+2.3	-.7	+2.1	2.9
Linseed oil, heat bodied	7.6	2.99	2.92	2.96	4.0	4.8	3.6	1.0	3.2	75	+.4	-.6	+1.0	2.0
Alkyd vehicle	4.9	3.05	2.98	3.06	2.9	4.2	4.3	1.4	2.7	102	-.8	-.8	0	1.6
Phenolic-resin varnish	2.3	2.87	2.85	2.88	4.7	1.5	1.5	0	.9	100	-.7	-.5	-.2	1.1
ANTIMONY OXIDE, SINGLE-PIGMENT PAINTS, PIGMENT VOLUME 0.30														
Linseed oil, not bodied	34.4	2.94	2.97	2.97	2.9	2.5	2.3	2.3	-.7	92	-1.5	-.8	-.3	1.5
Linseed oil, heat bodied	5.3	2.60	2.58	2.61	4.8	1.5	1.5	1.3	-1.0	100	-.6	-.2	-.8	1.0
Alkyd vehicle	11.0	2.77	2.74	2.77	3.1	2.4	2.2	2.1	1.0	92	-.4	-1.0	+.7	.3
Phenolic-resin varnish	2.9	2.54	2.54	2.55	4.8	.9	.7	.9	0	76	-.7	-.9	+.6	.9
RUTILE TITANIUM DIOXIDE, SINGLE-PIGMENT PAINTS, PIGMENT VOLUME 0.30														
Linseed oil, not bodied	24.1	2.34	2.32	2.37	3.1	8.3	5.7	3.6	1.9	69	-1.8	-1.3	0	1.0
Linseed oil, heat bodied	7.3	2.14	2.10	2.14	4.2	3.9	3.9	3.9	1.0	100	-.5	-1.1	+1.0	.8
Alkyd vehicle	7.4	2.22	2.18	2.23	3.2	3.4	3.1	2.9	1.3	91	-.4	-1.3	+1.3	.4
Phenolic-resin varnish	1.4	2.06	2.04	2.07	4.5	1.9	2.0	1.6	-.4	110	-.7	0	-.9	.3
ZINC OXIDE, SINGLE-PIGMENT PAINTS, PIGMENT VOLUME 0.30														
Linseed oil, not bodied	11.7	2.63	2.30	2.61	3.8	28.2	26.0	7.4	26.0	92	0	+1.4	-.3	.8
Linseed oil, heat bodied	3.3	2.55	2.36	2.55	4.3	14.2	14.0	3.6	10.3	99	+.1	-.1	0	.3
Alkyd vehicle	6.3	2.63	2.40	2.62	2.8	17.8	16.8	4.4	11.9	94	+.3	+.3	0	.5
Phenolic-resin varnish	3.6	2.52	2.45	2.53	4.3	5.3	5.5	1.3	3.7	104	-.7	-.4	-.5	.6
MAGNESIUM SILICATE, SINGLE-PIGMENT PAINTS, PIGMENT VOLUME 0.30														
Linseed oil, not bodied	28.4	1.89	1.81	1.89	2.4	9.9	9.8	5.0	6.7	99	-2.1	-3.4	+.1	3.4
Linseed oil, heat bodied	10.5	1.71	1.61	1.72	4.8	14.9	15.3	6.8	7.3	102	-1.0	+1.0	-2.1	.6
Alkyd vehicle	11.4	1.75	1.69	1.78	3.2	12.1	12.2	4.3	5.4	101	-2.2	+.5	-2.5	.9
Phenolic-resin varnish	2.3	1.66	1.61	1.67	5.1	8.9	9.4	2.0	6.2	105	-.9	-.1	-1.2	.3
LEAD-ZINC, MIXED-PIGMENT PAINTS LZ_{55}, PIGMENT VOLUME 0.30														
Linseed oil, heat bodied	1.6	2.82	2.58	2.82	4.5	15.7	15.3	4.6	9.9	98	-.3	+.9	-1.1	.9
Alkyd vehicle	4.8	2.92	2.60	2.93	3.0	20.3	20.2	5.1	13.6	99	-.9	+1.5	-2.3	1.2
Phenolic-resin varnish	2.2	2.76	2.69	2.78	4.6	5.4	5.4	2.1	2.4	100	-1.2	-.2	-1.3	1.4
ANTIMONY-ZINC, MIXED-PIGMENT PAINTS AZ_{25}, PIGMENT VOLUME 0.30														
Linseed oil, heat bodied	1.8	2.55	2.35	2.53	5.0	14.7	14.0	5.6	8.6	95	+.2	-.9	+1.0	1.0
Alkyd vehicle	3.9	2.64	2.37	2.65	2.9	20.2	20.3	9.3	9.3	100	-.7	+3.3	-3.8	.5
Phenolic-resin varnish	3.7	2.54	2.47	2.55	4.6	4.2	4.5	1.6	2.4	107	-.7	-.4	-.7	.7
TITANIUM-ZINC, MIXED-PIGMENT PAINTS TZ_{25}, PIGMENT VOLUME 0.30														
Linseed oil, heat bodied	1.2	2.19	2.02	2.17	4.6	16.1	15.9	6.5	8.7	99	+.7	+1.2	-.7	.5
Alkyd vehicle[1]	3.1	2.02	1.85	2.02	3.2	20.2	20.1	6.9	12.0	100	-.6	+3.2	-3.8	.7
Phenolic-resin varnish	2.3	2.16	2.12	2.17	4.7	4.3	4.8	2.0	1.9	111	-.8	-.3	-.8	.3
TITANIUM-ANTIMONY-MAGNESIUM SILICATE PAINT $TA_{25}X_{57}$, PIGMENT VOLUME 0.30														
Alkyd vehicle	7.6	2.07	2.04	2.10	3.1	4.8	4.8	2.2	2.0	100	-1.5	-.9	-.7	.8

[1] The pigment in this paint contained titanium dioxide, zinc oxide, and magnesium silicate; paint $TZ_{25}X_{57}$ p/sv 0.30.

shrink less in area and more in thickness, rather than in proportion to the volumetric shrinkage. The discrepancy generally was less for the weathered than for the unweathered films, however. Thus only 10 of 34 weathered films remained larger in area after redrying than before soaking, compared to 27 of the 37 unweathered paint films. Weathered paint seems to be less able to readjust the ratios among length, width, and thickness during changes in volume than is unweathered paint.

Loss in Weight While Soaking: The solubility of most weathered films during soaking was less, usually much less, than that of the corresponding films before weathering. Exceptions were four bodied linseed oil paints and two phenolic-resin paints, among which the solubility of the weathered film exceeded that of the unweathered film by more than 0.2 grams per 100 cubic centimeters only when the solubility of the weathered film was no greater than 1.4 grams per 100 cubic centimeters.

Among the weathered films, the solubility was always higher for unbodied linseed oil films than for the corresponding films with any other vehicle. Bodied linseed oil films stood second in solubility unless they contained zinc oxide, in which case the corresponding alkyd-resin films usually were more soluble than the bodied oil films. The solubility of weathered phenolic-resin films was less than 1.0 gram per 100 cubic centimeters except when the pigment was white lead or lead-zinc, for which the solubilities were 1.1 and 1.4 grams per 100 cubic centimeters, respectively.

Conclusions

The formation and hardening of films results in increased density, and the density increases still further when the films are weathered. Ten-day films of all four of the clear vehicles had densities of 1.11. After weathering artificially for 15 days, the densities ranged between 1.15 and 1.17, although the densities of the liquids before spreading varied from 0.93 to 1.02.

When pigments are incorporated in the vehicles, the density increase during formation and hardening of films is diminished. The increase in density during drying is always less than that calculated on the assumption that the vehicle in paint undergoes the same changes in weight, volume, and density as the clear vehicle without pigment.

Pigments alter the course of drying of bodied oil and of phenolic-resin vehicles relatively more seriously than they do that of unbodied oil and alkyd-resin vehicles. White lead, antimony oxide, and zinc oxide exert more effect than titanium dioxide and magnesium silicate. During weathering, however, pigments have an opposite effect because the density increase of pigmented films tends to catch up with that of the corresponding clear vehicle.

The four dissimilar vehicles resemble one another in that their films absorb water, swell, and lose soluble matter when soaked in distilled water for 3 days and, on redrying, shrink to a volume usually smaller than that before soaking. The changes are usually much the greatest in magnitude for unbodied linseed oil (21.8 per cent absorption), least for phenolic-resin varnish (1.5 per cent absorption), and about the same intermediate magnitude for bodied linseed oil and alkyd-resin vehicle. Weathering leaves the changes nearly as great for unbodied oil and for phenolic-resin varnish, reduces them slightly for alkyd-resin, but increases them for bodied oil to as much or more than those for unbodied oil.

Pigmentation greatly alters the absorption of water by films of all four vehicles. Even the low-absorbing phenolic-resin varnish, which absorbs only 1.5 per cent when the film contains no pigment, absorbs 15.3 per cent when pigmented with magnesium silicate. Absorptions greater than 83 per cent in unbodied oil films, 31 per cent in bodied oil films, and 86 per cent in alkyd-resin films can occur with some pigments. Although weathering materially decreases the absorption by pigmented films, it may remain well above that of the vehicle without pigment.

Among the pigments, zinc oxide, magnesium silicate, and titanium dioxide increase absorption in all vehicles, but antimony oxide and white lead reduce absorption or at least fail to increase it very much. In mixture, high-absorptive pigments dominate over low-absorptive pigments.

Unweathered films, either without pigments or pigmented at 30 per cent pigment volume, usually swelled in volume by the volume of water absorbed; that is, their swelling efficiency is 100 per cent within the experimental error. There are perhaps rare cases of more than 100 per cent swelling efficiency that may be attributed to internal compression stresses from absorption of oxygen after initial formation and hardening of a film. Release of these stresses adds slightly to volume as soon as absorbed water plasticizes and softens the film.

Swelling efficiency less than 100 per cent, which is sometimes exhibited by unweathered films containing zinc oxide and more generally in weathered films, is attributed to development of porosity when soluble material is leached from the film. When redried, however, the film fails to shrink enough to close the voids.

Volumetric swelling is distributed anisotropically and not very reproducibly between area and thickness of both pigmented and unpigmented films, both before and after weathering.

When the films are redried after soaking, nearly all unweathered films and most weathered films shrink to less than the volume before soaking because of loss of soluble material during soaking. Similarly, the density of the wet film decreases in proportion to the water absorbed. When the film is redried the density usually exceeds the density before soaking, because the soluble materials lost are relatively light in weight. Failure of a redried film to shrink to its volume or less than its volume before soaking, which is usually coupled with failure of the redried density to exceed the density before soaking, is taken as an indication of development of porosity within the film.

All films lose weight while weathering. The unpigmented films of the 4 vehicles lose weight in the decreasing order, unbodied oil, bodied oil, alkyd-resin, phenolic-resin. Pigments usually tend to increase the weight loss by unbodied oil, alkyd-resin, and phenolic-resin films, but they tend to decrease the loss by bodied oil paints films. Zinc oxide, however, reduces the weight loss or fails to increase it as much as other pigments in all vehicles except phenolic-resin, in which zinc oxide causes greater loss than other pigments.

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