Swelling of Paint Films in Water

VIII. Swelling of Linseed Oil Paints in Water and Organic Liquids

F. L. BROWNE

Chemist, Forest Products Laboratory,[1] Forest Service, U. S. Department of Agriculture

Compares the swelling effect of water and five organic liquids on films of unbodied linseed oil and of five linseed oil paints. All of the oil and paint films absorb, swell, and lose soluble ingredients in the organic liquids in much the same manner as they do in water. The order of increasing swelling power is nearly the same for all films, both before and after weathering artificially.

PREVIOUS PAPERS in this series (1)[2] have discussed the swelling of paint films and coatings in water. Of course, water is the swelling liquid of chief practical interest, but comparison of water with other liquid swelling agents should throw further light on the mechanism of swelling. Concern with swelling by organic liquids for paint removers (2) was not an immediate object of this work.

Swelling Liquids

Liquids were chosen whose relative capacity for swelling wood has been given by Stamm (6) as follows:

Liquid	Swelling relative to water Per cent
Water	100
Ethyl alcohol	83
Dioxane	62
n-Butyl alcohol	13.5
Benzol	0

Mineral spirits, which does not swell wood, was added to the list because of its common use as a paint thinner. The ethyl alcohol, butyl alcohol, and benzol were anhydrous, and of chemically pure grade. The dioxane was dehydrated and freed from peroxide by treatment with metallic sodium and redistillation. The water was distilled.

The density of distilled water at the temperature of the laboratory was considered to be 1.000, which is within the limits of accuracy required for the experiments. The specific graviy of the other swelling liquids was found by test to be:

Ethyl alcohol	0.790
Dioxane	1.035
Butyl alcohol	.812
Benzol	.878
Mineral spirits	.782

A few liquids swell wood more than water does. They are formic acid, compounds related to pyridine and morpholine, and some amines. A preliminary test showed that morpholine swells white lead linseed oil paint greatly, but makes a slimy film much too difficult to handle in the testing procedure, and it causes zinc oxide paint to disintegrate. Use of so highly acid a substance as formic acid was considered undesirable.

Preliminary tests also showed that dioxane and ethylene glycol monobutyl ether swell paint films markedly, but when the films are redried, much of the absorbed liquid is retained for a long time. The retained swelling liquid, however, can be removed by soaking the redried films in distilled water for three days and then redrying them.

Paint Films and Test Methods

Free films were made of unbodied linseed oil containing a lead-manganese paint drier, and of each of five linseed oil paints, all with a 30 per cent pigment volume, as follows: basic carbonate white lead, paint L; zinc oxide, paint Z; rutile titanium dioxide, paint T; white lead and zinc oxide, paint LZ_{35}; and titanium dioxide and zinc oxide, paint TZ_{35}. The subscript is the percentage of zinc oxide in the total pigment volume.

The paint films to be tested before weathering were spread on gummed paper by doctor blade and suction plate. The linseed oil was spread by brushing. The films were allowed to dry for 10 days and were then stripped from the gummed paper, cut into specimens 1½ by 2½ inches in size, marked with reference lines for measurement of length and width, and dessicated over calcium chloride. The films for tests in water and in mineral spirits were 19 days old when immersed in the swelling liquid; those for ethyl alcohol and benzol were 22 days old, and those for butyl alcohol and dioxane were 23 days old.

Weathered films were made by spreading the paints on tinplate. They were allowed to dry for 10 days, and then exposed in a weatherometer to ultraviolet light from a flaming carbon arc with a Corex D glass filter and sprayed three times an hour with distilled water for 15 days. After the artificial weathering, the films were stripped by amalgamation of the tin, cut to size, marked, and dessicated for testing.

Swelling tests were made as follows: the length and width of the film between reference marks were measured with a traveling microscope. The film was weighed first in air and then under distilled water to obtain the volume by displacement. After the water left on the surface from the brief immersion had evaporated, the film was submerged between two pieces of coarse-meshed glass cloth in 250 cubic centimeters of swelling fluid in a crystallizing dish. The glass cloth was weighted, and the dish was covered with a watch glass and sealed to prevent evaporation of the swelling liquid. The sealed dish was then placed in a water thermostat at 70° F. for three days.

After the film had soaked for three days, it was removed and immediately weighed under a fresh supply of the swelling liquid. The length and width between reference marks on the swollen film were measured with the film sandwiched between glass microscope slides. The film was then blotted quickly to remove excess swelling liquid from the surfaces, placed in a tared bottle, and weighed to determine the weight of the swollen film in air.

A few films were found to be too fragile when swollen to be straightened out between glass slides for the

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

The Author: Frederick L. Browne received B. Chem. degree from Cornell U., Ph.D. in colloid chemistry from U. of Wisconsin. He joined the Forest Products Lab staff in 1918, helped develop casein glues for wood airplanes of World War I. In 1921–22, he was a National Research Fellow at Wisconsin. Since 1929, Dr. Browne has edited the General and Physical Chemistry section of Chemical Abstracts.

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Table 2.—LIQUIDS ARRANGED IN THE ORDER OF THEIR VOLUMETRIC SWELLING OF WOOD AND OF UNWEATHERED AND WEATHERED FILMS OF EACH KIND OF OIL OR PAINT TESTED.

Material swollen	Liquids* in order of increasing swelling, left to right									
					Unweathered Films					
Clear linseed oil	Water	Min. sp.		EtOH		BuOH		Benzol		Dioxane	
White lead	Water	Min. sp.		EtOH		BuOH		Benzol		Dioxane	
Titanium dioxide		Min. sp.		EtOH	Water	Benzol		BuOH		Dioxane	
Zinc oxide		Min. sp.		EtOH		Benzol		BuOH	Water	Dioxane	
Lead-zinc		Min. sp.		EtOH	Water	BuOH		Benzol		Dioxane	
Titanium-zinc		Min. sp.		EtOH		BuOH		Benzol	Water	Dioxane	
					Weathered Films					
Clear linseed oil	Water	Min. sp.		Benzol		EtOH		BuOH		Dioxane	
White lead	Water	Min. sp.		EtOH		Benzol		BuOH		Dioxane	
Titanium dioxide	Water	Min. sp.		Benzol		EtOH		BuOH		Dioxane	
Zinc Oxide		Min. sp.		EtOH		Benzol	Water	BuOH		Dioxane	
Lead-zinc		Min. sp.	Water	EtOH		Benzol		BuOH		Dioxane	
Titanium-zinc		Min. sp.		EtOH	Water	BuOH		Benzol		Dioxane	
					Wood					
Wood		Min. sp.		Benzol		BuOH		Dioxane		EtOH	Water

*Abbreviations or symbols: Min. sp., mineral spirits; EtOH, ethyl alcohol; BuOH, butyl alcohol.

creased when the films were dried, except for films soaked in dioxane. Their density was not regained until the redried film had been leached with water and again redried.

Water and mineral spirits leached only moderate quantities of soluble substances from the films, but the other liquids dissolved large quantities, from 36.3 grams per 100 cubic centimeters for benzol to 55.5 grams per 100 cubic centimeters for butyl alcohol. Films that could be measured had swelled in area during soaking, but the ratio of areal to volumetric swelling varied widely (from 0.30 to 0.86). When the films were redried, they shrank to a smaller volume, area, and thickness than they had before soaking. This shrinkage corresponded at least roughly to the loss of soluble matter during soaking.

All of the organic liquids, even mineral spirits, swelled linseed oil films more than water did. Wood, in contrast, is more highly swollen by water than by the organic liquids. That might be expected if linoxyn is a gel of low polarity, wood is highly polar, and similar polarity between gel and liquid determines the swelling capacity of the liquids (2, 3, 4, 5). Such a consideration accounts for the closely related liquids, water, ethyl alcohol, and butyl alcohol, swelling linseed oil films increasingly in the order named and swelling wood in reverse order. But with dissimilar liquids, other factors not yet fully understood became important in the swelling of both wood and linseed oil films. Thus dioxane is less polar but swells wood more than butyl alcohol does, and mineral spirits, which is even less polar than benzol, swelled linseed oil films less than highly polar ethyl alcohol did and far less than benzol did.

The relative positions of the liquids for the swelling of wood and of the oil and paint films tested are indicated in Table 2. Graham (2) found the same order for water, mineral spirits, ethyl alcohol, butyl alcohol, and benzol in the swelling of films of bodied linseed oil.

White Lead Paint: Films of white lead in linseed oil absorbed less liquid and swelled less volumetrically than unpigmented films of linseed oil in all of the swelling liquids. The statement remains true when the absorption and swelling of unpigmented oil films are taken as 70 per cent of the values recorded in Table 1 because the pigmented films contained 70 per cent oil and 30 per cent pigment by volume. In water, white lead was the only pigment tested that effected such reduction. In the other liquids, however, all pigments reduced absorption and swelling to less than 70 per cent of the values for unpigmented linseed oil, and in that respect white lead was no longer more effective than other pigments.

The liquids stood in the same order of increasing absorption and swelling for films of white lead paint as they did for unpigmented films of linseed oil, as can be readily seen in Table 2. Swelling efficiencies were 91 and 95 per cent for ethyl and butyl alcohol, respectively, which indicate the development of slight porosity in the films, and 97 to 100 per cent for other liquids. The density of the films decreased when they swelled but was more than regained when they were redried. The increase in density of the redried films corresponded to a shrinkage in volume and a loss of soluble material during soaking.

Loss of soluble material from white lead paint films during soaking was relatively small, but it was larger than that for unpigmented linseed oil films in water and mineral spirits. In the other liquids, the solubility always exceeded 20 grams per 100 cubic centimeters, but it was much less for films of white lead paint than for films of unpigmented linseed oil.

The relation between swelling in area and swelling in volume was more nearly constant in all liquids for films of white lead paint ($\Delta Q_s/\Delta V_s$ = 0.28 to 0.39) than for films of unpigmented linseed oil. When they were redried, all films of white lead paint shrank to less than their volume before soaking. The shrinkage was approximately in proportion to the loss of soluble substances. There was a similar shrinkage in area when the films were redried except for dioxane, for which the area was greater and the thickness correspondingly less than before soaking.

Titanium Dioxide Paint: In water, films of titanium dioxide paint absorbed more liquid and swelled more volumetrically than films of unpigmented linseed oil or of white lead paint. In the other liquids, however, the absorption and swelling by films of titanium dioxide paint were less than by films of linseed oil, and did not differ greatly from films of white lead paint. A comparison of the liquids for their order of swelling (Table 2) of titanium dioxide paint film and clear linseed oil film shows that for the titanium dioxide paint, water moved from a position below mineral spirits to one above ethyl alcohol and that benzol and butyl alcohol changed places.

The swelling efficiency of water and mineral spirits for titanium dioxide paint film was 100 per cent and that of dioxane was 98 per cent. Ethyl alcohol, butyl alcohol, and benzol, however, had swelling efficiencies of 56, 80, and 87 per cent only, and presumably left the redried films markedly porous. These liquids removed much soluble matter from the films, but apparently did not plasticize the linoxyn sufficiently for the film to contract enough to close the voids when the swelling liquid evaporated. The fact that the redried films gained in density is not inconsistent with this view because the large quantity of soluble matter was much less dense than the pigment, which remained in the films.

In all liquids, films of titanium dioxide paint decreased in density when they swelled, but became denser and smaller in volume when they were redried than they were before they were soaked.

The solubility of films of titanium dioxide paint in each liquid was somewhat higher than that of white lead paint films, and was very nearly equal to 70 per cent of that of films of clear linseed oil (the proportion of linseed oil in the paint), except in water and in mineral spirits. In water and mineral spirits, the solubility of titanium dioxide paint films, like that of white lead paint films, was slightly greater than the solubility of the linseed oil films.

The ratio of swelling in area to swelling in volume for titanium dioxide paint films was 0.36 in water, which is within the range of ratios for white lead paint films, but was much higher, 0.55 to 0.85, in all other liquids in which the measurements could be made. When the films were redried, those that had been soaked in water remained slightly greater in area but were much thinner than they had been before soaking. The films soaked in other liquids shrank in both area and thickness.

Paints Containing Zinc Oxide: In water, films of the three paints that contained zinc oxide absorbed more liquid and swelled more in volume than titanium dioxide paint films. Among the three paints, the film of lead-zinc paint had the lowest absorption and swelling, followed by zinc oxide and then titanium-zinc with the highest. This order agrees with results previously reported.

In liquids other than water, however, the films containing zinc oxide did not differ significantly in absorption and swelling from the films of titanium dioxide or of white lead paints. The absorption and swelling by pigmented films was less than 70 per cent of that by unpigmented linseed oil in all liquids but water, except that films of straight zinc oxide absorbed more dioxane.

Comparison of the liquids for their order of swelling (Table 2) shows that, for zinc oxide and titanium-zinc paint films, water moved from a position below mineral spirits for clear oil and white lead paint films to a position just below dioxane. For the lead-zinc film, water took a position above ethyl alcohol, similar to its position for titanium dioxide film. The changes in the position of water among the swelling liquids suggest that white lead makes paint films less hydrophilic, titanium dioxide makes them more hydrophilic, and zinc oxide makes them still more hydrophilic.

The swelling efficiency of water for films of the three zinc-containing paints was 98 or 99 per cent. Mineral spirits had a swelling efficiency between 95 and 99 per cent for these films, and benzol had an efficiency of 96 or 98 per cent for titanium-zinc and lead-zinc films but only 74 per cent for straight zinc oxide film.

The efficiency of liquids other than water was as low as 59 and no higher than 95 per cent for straight zinc oxide films, and the efficiency of ethyl alcohol, butyl alcohol, and dioxane (after leaching with water) ranged from 69 to 95 per cent for films of lead-zinc and titanium-zinc paint. Thus the organic liquids tend to leave pigmented films porous after soaking and redrying, especially when the films contain zinc oxide. The tendency is less marked for mineral spirits, which also dissolves less, than for the other organic liquids, and for ethyl and butyl alcohols and benzol the tendency extends to zinc-free titanium dioxide paint. The tendency toward porosity is most marked for straight zinc oxide paint and least marked for straight white lead paint.

There is a distinct parallel between the tendency toward porosity and the stiffness and brittleness of the swollen films. Films that become highly flexible and tough when swollen do not become porous when redried, but films that become difficult to bend without breaking and often curl badly when swollen may be highly porous when redried. A conspicuous example was the film of zinc oxide paint in dioxane, which was hard, rigid though badly curled, and very brittle despite a 143 per cent swelling in volume. When it was redried, leached with water, and again redried, it had only 59 per cent swelling efficiency and a decidedly lower density than before soaking. Porosity may be caused by loss of soluble ingredients by the film when the swelling liquid fails to plasticize the film sufficiently (4) to permit it to shrink enough to close the voids.

Films of all three zinc-containing paints decreased in density when swollen in all liquids. When they were redried, they regained or exceeded their initial density, since they lost soluble material of low density, except for zinc oxide paint in benzol and all three paints in dioxane. The exceptions were always films that became porous, as indicated by low swelling efficiency of the swelling liquid.

Films of the three zinc-containing paints that had been soaked in dioxane retained from one-fourth to more than half of the dioxane when they were redried, and the redried volume was from 48 to 158 per cent greater than the volume before soaking. In contrast, the zinc-free films retained less than 6 per cent of the dioxane. The reason for this effect of zinc oxide is not clear, but it may be associated with the stiffness and brittleness of the zinc-containing films swollen in dioxane. A structure of hard, nearly impermeable walls enclosing cavities filled with dioxane may be formed after the soluble substances have been leached out of the films. When the redried films were soaked in water, they quickly became flexible and reasonably tough again, and the dioxane was leached out by the water. After another redrying, the films shrank considerably in volume.

The solubility of the zinc-containing films in water was moderate, but somewhat greater than that of the films with no zinc. In mineral spirits, the solubility was less than that of the white lead and the titanium dioxide films, and less to essentially the same as that of the unpigmented linseed oil film. The other liquids dissolved much more than mineral spirits or water did. Solubility of the zinc-containing films in ethyl alcohol, butyl alcohol, and benzol was always less than 70 per cent of the solubility of unpigmented linseed oil, and was less than the solubility of titanium dioxide film and not very different from the solubility of white lead film.

The solubility of the zinc-containing films in dioxane was overbalanced by retention of dioxane until the dioxane was leached out with water. After the films were leached the quantity dissolved by dioxane and the leach water came to 104.4 grams per 100 cubic centimeters for zinc oxide film, 65.3 grams per 100 cubic centimeters for titanium-zinc film, and 57.7 grams per 100 cubic centimeters for lead-zinc film. Most of this solubility must be attributed to the dioxane.

The solubility in dioxane of the zinc oxide paint film, and probably of the lead-zinc and titanium-zinc films, was so high that some of the dissolved material must have come from the pigment. The soaking liquid was not examined for presence of zinc compounds, but tests were made on the solubility of dry zinc oxide, white lead, and titanium dioxide in both dioxane and butyl alcohol. None of the pigments proved appreciably soluble in the liquids. Presumably, then, dioxane dissolves zinc soaps formed in the paint films by the reaction of the zinc oxide with acid decomposition products of linseed oil.

The ratio of areal to volumetric swelling, $\Delta Q_s/\Delta V_s$, for the titanium-zinc films varied from 0.32 to 0.69, much like the variation for titanium dioxide films. The ratio for zinc oxide films ranged from 0.29 to 0.88 in organic liquids, but was 0.24 in water. The ratio for lead-zinc films ranged from 0.20 to 0.38 only, much like the small range for white lead films. When $\Delta Q_s/\Delta V_s$ is large, the swelling in thickness is correspondingly less than would otherwise be expected.

When redried, films of the zinc-containing paints shrank below their volume before soaking, which corresponds to the loss of soluble material during soaking with adjustment for any development of porosity. The films soaked in water remained somewhat swollen in area, but became correspondingly thinner, as did also the

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film of lead-zinc paint soaked in dioxane and then leached with water. In the other cases, except when the dioxane was not leached out, the films shrank in area when redried, but usually to less extent than they shrank in thickness.

Results with Weathered Films

Results with films that had been weathered artificially are reported in Table 3.

Linseed Oil without Pigment: Weathered films of unpigmented linseed oil absorbed less water, dioxane, benzol, and mineral spirits, but about the same amount of ethyl alcohol and butyl alcohol, as the unweathered films. The swelling of weathered films was a little less than the absorption. Swelling efficiencies were 87 per cent in water, 92 per cent in ethyl alcohol and mineral spirits, 95 per cent in benzol, and 99 per cent in butyl alcohol and dioxane. Thus the weathered films were more inclined to become slightly porous than the unweathered films, which is further indicated by failure of the weathered films soaked in water and mineral spirits to regain their original density when redried.

The liquids stood in the same order for swelling weathered oil films as for unweathered films (Table 2), except that benzol, which fell between butyl alcohol and dioxane for unweathered films, dropped to a position between mineral spirits and ethyl alcohol. The solubility of the weathered films in water and in mineral spirits was greater than for the unweathered films, but in the other liquids the weathered films were considerably less soluble than the unweathered films. Nevertheless, the weathered films remained much less soluble in water and in mineral spirits than in any of the other liquids.

Weathered films of white lead paint absorbed less and swelled less than the unweathered films in all liquids. Swelling efficiencies for weathered films ranged from 83 to 94 per cent, which indicates the development of porosity. Nevertheless, all white lead films were higher in density after they were redried than before they were soaked because of loss of lightweight soluble matter to the soaking liquid.

The order of the liquids in swelling power (Table 2) was the same for the weathered as for the unweathered white lead films, except that benzol and butyl alcohol exchanged positions. Weathered films were more soluble than the unweathered films in mineral spirits, but were much less soluble than the unweathered films in the other liquids.

The ratio of areal to volumetric swelling was always less for the weathered than for the unweathered films of white lead paint. All weathered films of white lead paint shrank in volume when they were redried.

Titanium Dioxide Paint: Weathering greatly reduced the absorption and swelling of titanium dioxide paint films in water. The weathered film, in fact, swelled slightly less than weathered white lead or linseed oil films. In the other liquids, weathered titanium dioxide films absorbed and swelled less than the corresponding unweathered films, but the reduction was much less marked. Their absorption and swelling were greater than for weathered white lead films in ethyl alcohol, butyl alcohol, and benzol, and somewhat less than for white lead in dioxane and mineral spirits.

The swelling efficiency of the liquids for weathered titanium dioxide films ranged from 82 to 95 per cent except in dioxane, where it was 105 per cent. The high efficiency for dioxane may be erroneous, however, because the titanium dioxide film curled exceptionally badly in dioxane and proved very difficult to handle.

The order of the liquids in swelling power (Table 2) differed for weathered and unweathered titanium dioxide films in that water dropped from a position above ethyl alcohol for the unweathered films to a position below mineral spirits for the weathered film, and benzol changed places with ethyl alcohol. In all of the liquids, the solubility of the titanium dioxide films was less for weathered than for unweathered films.

The ratio of areal to volumetric swelling was less for the weathered than for the unweathered films in ethyl and butyl alcohols, but greater in water, benzol and mineral spirits. All weathered films of titanium dioxide paint shrank in volume when they were redried.

Paints Containing Zinc Oxide: Weathered films of the three paints that contained zinc oxide absorbed and swelled less than the corresponding unweathered films, except that the weathered straight zinc oxide paint absorbed and swelled slightly more in ethyl alcohol than did the unweathered film. The extent to which weathering decreased swelling, however, was usually greater for water than for the other liquids. Nevertheless, the weathered films of zinc-containing paints still swelled much more in water than did weathered films without zinc oxide.

In liquids other than water, the zinc-containing films did not differ greatly in swelling from the films of titanium dioxide or of white lead paint, and their swelling was less than 70 per cent of that of weathered linseed oil except in mineral spirits.

Water took a lower position in the series of liquids for swelling (Table 2) the weathered than the unweathered films of zinc-containing paint, as has already been noted with titanium dioxide paint. Perhaps this indicates that weathering in general diminishes the hydrophilic character of pigmented paint films. The order of liquids other than water was the same for weathered and unweathered films containing zinc oxide, except for a transposition of the neighboring liquids benzol and butyl alcohol for the lead-zinc films. This transposition occurred also for the weathered and unweathered films of white lead paint.

The swelling efficiency of water for the weathered film of zinc oxide paint was 90 per cent, and that for the lead-zinc and titanium-zinc paints was 98 per cent. Other liquids always had a lower swelling efficiency than water for the same zinc-containing paint. The swelling efficiencies for the weathered films closely parallel those for the unweathered films, and reveal a marked tendency for the zinc-containing paints to become porous when redried. Most of the films increased in density when redried because of a substantial loss of soluble ingredients of low density during the soaking. There was a decrease in density or failure to gain in density, however, for the three zinc-containing paints in water and for the zinc oxide and titanium-zinc paints in dioxane.

The weathered films of zinc-containing paints, like the unweathered films, retained dioxane after they were redried until the dioxane was leached out in water and the films were again redried. Such retention by the weathered films was proportionately less than by the unweathered films, although it was still substantial.

The solubility of the weathered films of zinc-containing paints was always less than that of the corresponding unweathered films in the same liquid. The solubility of the weathered films in water was low, from 0.5 to 1.8 grams per 100 cubic centimeters. In dioxane it was from 27.4 to 30.6 grams per 100 cubic centimeters and in the other liquids it was from 2.4 to 11.3 grams per 100 cubic centimeters.

The ratio of areal to volumetric swelling, $\Delta Q_s/\Delta V_s$, for weathered films of zinc-containing paints was always lower in water than in organic liquids, as was the case for unweathered films of all paints and of linseed oil. This was not always the case for weathered films that contained no zinc oxide, however. Weathering sometimes raised and sometimes lowered the ratio $\Delta Q_s/\Delta V_s$ for corresponding films of the zinc-containing paints without revealing any consistent pattern.

After films of zinc oxide and of titanium-zinc paints were soaked in water and then redried, they were larger in both volume and area than they had been before they were soaked. Films of lead-zinc paint were larger in area and only slightly smaller in volume than they had been before they were soaked.

All zinc-containing films soaked in dioxane were larger in both area and volume after they were redried than before they were soaked, but they shrank when subsequently soaked in water and redried. The films of zinc oxide paint still remained larger in volume and the film of titanium-zinc paint remained larger in both volume and area, however, than they had been before they were first soaked in dioxane. When the final volume of a film was larger than the original volume, the final density was lower than the density at the start of the soaking tests.

Conclusions

Films of linseed oil and of linseed oil paints absorb, swell, and lose soluble ingredients in a number of organic liquids in much the same manner as they do in water. The organic liquids can be arranged in an order of increasing swelling power that is nearly the same for all of the oil and paint films, both before and after the films have been weathered artificially. The order of the organic liquids in this series is mineral spirits, ethyl alcohol, butyl alcohol, benzol, and dioxane, except that for unweathered films the neighbors butyl alcohol and benzol may exchange places, and for weathered films benzol sometimes drops to a position between mineral spirits and ethyl alcohol.

The order of the liquids in the series differs greatly from their order for the swelling of a strongly hydrophilic gel such as wood. Mineral spirits and benzol fail to swell wood measurably, but both swell oil and paint films, with mineral salts at the bottom but benzol next to the top in the series for wood and at the top of the series for oil and paint films. The order of the series of homologous liquids (water, ethyl alcohol, and butyl alcohol) for wood is the reverse of the order for oil and paint films.

Polarity appears to be one of several properties of liquids that govern their swelling power. The more polar liquids swell hydrophilic gels to a greater extent and hydrophobic gels to a lesser extent than the less polar liquids. Thus oil and paint films seem to be less hydrophilic than wood, as might be expected.

But properties other than polarity also affect the swelling power of liquids. For oil and paint films, one of the other properties may be the solvent power of the swelling liquid for ingredients of the films, because the high-swelling organic liquids always

Table 3.—AFTER WEATHERING—ABSORPTION, SWELLING, AND RELATED DATA FOR FREE FILMS OF UNBODIED LINSEED OIL AND LINSEED OIL PAINTS WHEN SOAKED IN DIFFERENT LIQUIDS FOR THREE DAYS AND THEN REDRIED.

Paint	Swelling liquid	Density: Dry	Density: Swollen	Density: Redried	Initial thickness T_o	Absorption of liquid 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	Weight change from initial to redried condition S_r/V_o
					Mils	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Gm. per 100 cc.
Linseed oil	Water	1.18	1.17	1.17	2.5	6.2	5.4	6.4	-1.1	87	-1.9	-2.3	0	-3.4
	Ethyl alcohol	1.15	1.02	1.16	3.8	60.2	57.0	27.5	+10.0	92	-26.0	(1)	......	-29.6
	Butyl alcohol	1.15	.97	1.15	4.4	96.1	95.0	57.0	+30.5	99	-23.4	-15.8	-8.9	-26.1
	Dioxane	1.17	1.07	1.15	2.8	322	319	(1)	......	99	-28.3	(1)	......	-34.6
	Benzol	1.17	1.07	1.17	2.6	56.2	53.4	(1)	......	95	-19.7	(1)	......	-22.8
	Mineral spirits	1.18	1.14	1.17	2.9	11.0	10.1	3.1	+6.6	98	-.5	+.3	-.3	-12.4
White lead L	Water	3.02	2.95	3.03	3.1	6.2	5.3	.8	+4.4	85	-1.2	0	-.8	-2.6
	Ethyl alcohol	3.03	2.90	3.26	3.3	20.0	16.5	5.8	+11.2	83	-11.5	-2.6	-9.4	-14.0
	Butyl alcohol	3.06	2.70	3.27	3.1	31.4	28.5	8.5	+19.5	91	-10.5	-2.6	-8.2	-13.3
	Dioxane	3.07	2.04	3.16	2.9	117	110	31.4	+59.0	94	-8.2	+10.6	-17.0	-17.8
	Dioxane, then water	......	......	3.25	......	120	113	33.4	+60.7	94	-11.8	+8.6	-18.8	-21.8
	Benzol	3.06	2.87	3.26	3.0	22.3	18.9	(1)	......	85	-10.2	(1)	......	-13.2
	Mineral spirits	3.04	2.90	3.19	3.0	14.8	13.5	1.7	+11.8	91	-6.8	-.1	-6.6	-11.6
Titanium dioxide T	Water	2.28	2.22	2.28	3.0	5.3	4.9	3.7	+1.1	92	-.3	-1.7	+1.6	-.6
	Ethyl alcohol	2.26	2.05	2.35	3.1	29.7	24.6	19.0	+5.4	83	-9.1	-6.3	-2.8	-13.2
	Butyl alcohol	2.28	1.91	2.34	2.9	43.6	39.3	22.6	+14.7	90	-8.4	-6.3	-2.3	-13.2
	Dioxane	2.26	1.73	2.36	3.2	71.5	74.7	(1)	......	104	-10.0	(1)	......	-14.0
	Dioxane, then water	......	......	2.39	......	71.9	75.8	(1)	......	105	-11.1	(1)	......	-14.1
	Benzol	2.24	2.08	2.30	3.3	23.8	19.5	18.6	+1.2	82	-7.3	-5.9	-1.8	-11.2
	Mineral spirits	2.25	2.16	2.28	3.4	9.7	9.2	5.4	+3.6	95	-2.3	-3.0	+.7	-2.4
Zinc oxide Z	Water	2.60	2.34	2.57	3.0	33.1	29.7	8.2	+20.0	90	+.3	+1.2	-.8	-1.8
	Ethyl alcohol	2.59	2.35	2.69	3.2	26.2	22.4	11.6	+10.0	86	+6.5	-5.0	-1.2	-7.6
	Butyl alcohol	2.60	2.24	2.68	3.2	35.8	31.1	14.4	+15.7	87	-6.7	-5.4	-1.2	-9.5
	Dioxane	2.61	1.85	1.80	2.9	116	107	38.7	+49.0	92	+48.2	+3.2	+43.6	+5.5
	Dioxane, then water	......	......	1.71	......	141	107	38.7	+49.0	76	+34.5	-3.0	+38.7	-30.6
	Benzol	2.65	2.36	2.69	2.4	27.3	23.7	14.2	+8.9	87	-3.1	-3.2	+.2	-4.5
	Mineral spirits	2.60	2.42	2.62	3.1	15.3	12.7	3.9	+8.6	83	-1.2	-1.1	+.1	-1.4
Lead-zinc LZ_{25}	Water	2.87	2.60	2.86	3.5	17.3	16.9	2.5	+14.0	98	-.3	+1.2	-1.3	-1.3
	Ethyl alcohol	2.88	2.65	3.01	3.5	19.9	18.6	7.2	+11.4	93	-7.3	-3.2	-4.0	-8.5
	Butyl alcohol	2.88	2.50	3.01	3.5	30.4	28.7	9.7	+18.4	94	-7.4	-3.4	-3.9	-9.3
	Dioxane	2.89	2.08	2.79	3.3	89.0	79.5	28.0	+39.1	89	+.4	+1.8	-1.4	-8.4
	Dioxane, then water	......	......	2.98	......	107	91.8	29.9	+50.0	86	-12.2	-0.1	-12.3	-27.4
	Benzol	2.88	2.51	2.98	3.4	29.0	27.6	15.0	+11.5	95	-5.3	-1.1	-4.0	-5.8
	Mineral spirits	2.88	2.70	2.94	3.4	13.6	12.1	2.9	+9.8	89	-3.3	-.7	-1.0	-3.6
Titanium-zinc TZ_{25}	Water	2.24	1.97	2.24	3.6	28.3	27.7	12.3	+14.3	98	+.1	+0.7	-2.6	-.5
	Ethyl alcohol	2.27	2.09	2.39	2.9	23.9	22.0	16.9	+5.0	92	-9.2	-8.5	-.7	-10.7
	Butyl alcohol	2.26	1.94	2.37	3.7	37.5	35.6	22.5	+15.0	95	-9.4	-8.5	-.9	-11.3
	Dioxane	2.26	1.69	2.07	3.6	103	95.5	60.1	+22.2	93	+7.7	+2.0	+5.9	-3.2
	Dioxane, then water	......	......	2.21	......	129	106	(1)	......	82	-11.0	(1)	......	-29.8
	Benzol	2.26	1.90	2.32	3.5	40.5	39.3	31.3	+6.4	97	-4.1	-3.4	-.8	-4.2
	Mineral spirits	2.28	2.10	2.30	2.9	16.3	15.6	7.9	+7.3	96	-2.0	-3.0	+1.1	-2.4

[1] Film too fragile to measure.

dissolved relatively large quantities of soluble constituents from the films.

The position of water in the series of swelling liquids varies greatly with the composition of the film. For films of unpigmented linseed oil and of white lead paint, water has less swelling power than mineral spirits, but for unweathered films of zinc oxide and of titanium-zinc paint, water has a very high swelling power, and is exceeded only by dioxane. Water stands about in the middle of the series for unweathered films of titanium dioxide and of lead-zinc paints.

The marked shifting of the position of water suggests that its position is determined chiefly by the hydrophobic character of the film, and that titanium dioxide makes paint films less hydrophobic, zinc oxide makes them still less so, but white lead makes them more hydrophobic. If so, weathering partly offsets the effects of titanium dioxide and zinc oxide, because the position of water drops one or two places in the series after the titanium dioxide paint and the zinc-containing paints are weathered.

Organic liquids have less than 100 per cent swelling efficiency for oil and paint films more often than water does. This may be due largely to the greater quantity of soluble material leached from the films by most of the organic liquids. Low swelling efficiency probably results from voids left by dissolved material when the film fails to shrink sufficiently in volume as the swelling liquid evaporates. If so, a second factor in the development of porosity in films may be the plasticity of the remaining insoluble portion of the film, particularly the plasticity when the last portions of swelling liquid are evaporating. Voids may be readily closed in a highly plastic film, but remain in a more rigid film.

Consistent with this view are the facts that unpigmented films seldom become seriously porous, and weathering, which makes films harder and more brittle, also increases the tendency for the films to become porous when soaked and redried. It may then be concluded that the organic liquids do not plasticize the structural framework of paint films so well as water does.

Dioxane exhibits peculiar behavior toward zinc-containing films that may be related to the plasticity of the insoluble framework of the films. Zinc-containing films swollen in dioxane become stiff and brittle and when redried retain much of the dioxane for a long time.

Wood presents a parallel in that, when impregnated with organic liquids of high volatility but little or no swelling power, the liquids dry out much less rapidly than do less volatile liquids that swell wood appreciably. The nonswelling liquids do not penetrate the walls of the wood cells, and therefore must dry by the slow process of evaporation in place and escape of the vapor through the tortuous channels connecting the cavities. Dioxane, then, may be quite unable to penetrate and plasticize the insoluble framework of zinc-containing paint films left after the soluble components have been leached out, and thus remains trapped in the voids formed by loss of the soluble components.

The solubility of oil or paint films in mineral spirits is low, seldom much greater than their solubility in water. Their solubility in the other organic liquids, however, is high, more than 20 grams per 100 cubic centimeters for unweathered films, except those of zinc-containing paints in benzol, where it is about 15 grams per 100 cubic centimeters. Clear oil films are more soluble than pigmented films in the organic liquids other than mineral spirits, except that zinc-containing films are more soluble than clear oil films in dioxane.

Weathered films, which have already lost much soluble matter during the weathering, are less soluble in organic liquids other than mineral spirits than the corresponding unweathered films, but even the weathered films have moderate to high solubility.

The distribution of volumetric swelling between area and thickness of films varies widely in the organic liquids, just as it does in water. For unweathered films and for weathered films of zinc-containing paints, the ratio of areal to volumetric swelling, $\Delta Q_a/\Delta V_a$, seems always to be larger in organic liquids than it is for films of the same kind in water. The rule is generally true, but there are some exceptions for weathered films of white lead and of titanium dioxide paints. The difference in action between water and organic liquids may be related to the varying position of water when the liquids are arranged in order of swelling power, and to the greater tendency for films swollen in organic liquids to become porous when redried than is the case when they are swollen in water and then redried.

The volume, area, and thickness of films of linseed oil or paint are usually reduced when the films are swollen in organic liquids and then redried, as was found with water. The reduction is roughly proportional to the loss of soluble material to the soaking liquid. The shrinkage, however, is reduced in proportion to any porosity developed in the redried film, and, if the film becomes porous enough in relation to the solubility, its volume may actually be increased. When the films are redried, much the same irregularities in distribution of the volumetric shrinkage between area and thickness occur as are observed during swelling.

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