SOFTENING OF LINSEED OIL FILMS

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Linseed oil films which are dried and aged under a sunlamp at 78° F. and 50 per cent relative humidity exhibit an aftersoftening action. When such films are extracted with acetone, maximum acetone insolubility is reached a few days after maximum dryness is attained. On aging, the oils soften and the solid phase changes so that the film reverts to a condition of almost complete solubility in acetone, which indicates that syneresis is not the principal cause of the softening of linseed oil films. The less saturated linseed oils give dried films which soften less and are more insoluble in acetone. This shows that the composition of an oil affects not only the rate of drying but also the colloidal changes in the dried oil film. The presence of drier not only increases the drying rate but also delays the after-softening and decreases the degree of aftersoftening; likewise the acetone solubility is delayed and somewhat decreased. Linseed oil, when pigmented with white lead, gradually attains an acetone insolubility of 60 to 70 per cent which does not decrease on further aging.

The iodine number of the acetone-soluble phase drops quickly within 24 hours to less than one-third that of the original oil and then gradually decreases. Iodine number of the insoluble phase is similar to that of the soluble phase and is not related to the softening phenomenon or to the acetone solubility.

LINSEED OIL, when exposed as a film to the atmosphere and light, undergoes several progressive stages in the process of drying. These stages have been grouped by Long (*6*) as follows: (1) induction period; (2) oxidation and formation of colloidal nuclei sols; (3) polymerization, coagulation, and solvation of the nuclei with consequent "set" to a solid gel; and (4) subsequent changes in the solid gel film.

The drying of linseed oil has been subject to considerable research, and the mechanism of drying has been discussed by Auer (*1*), Eibener (*3*), Long (*5*), Morrell (*10*), and others.

This paper is principally concerned with the fourth stage which involves the colloidal changes in dried linseed oil films. From the viewpoint of colloids, a dried oil film consists of a dispersing or liquid phase and a dispersed or solid phase. The liquid phase may be adsorbed to a variable degree by the solid phase or xerogel. The film is therefore made up of three components: (*a*) liquid, (*b*) adsorbed liquid, and (*c*) solid. The physical nature of the film to a large degree is dependent upon the relative proportions of these components. It has been shown (*5–8*) that a dried oil film may be divided into a soluble and insoluble phase by means of various solvents, of which acetone has proved the most satisfactory. The acetone completely extracts the unpolymerized and unassociated liquid which has not been adsorbed by the xerogel but probably extracts only part of the liquid which has been adsorbed. Linseed oil films, as well as films of linolenic glyceride, have been extracted with acetone; and it has been found that, on aging, the solid phase becomes increasingly greater and the liquid phase decreases.

Before making the study described in this paper, it had been noticed that linseed oil films, exposed to the rays of a sunlamp and maintained under the constant conditions of 78° F. (25.6° C.) and 50 per cent relative humidity, dried moderately rapidly, but after a few weeks became tacky and on continued exposure in some cases almost liquid. This aftersoftening phenomenon was previously observed (*3, 9, 11*) and is attributed by several authors to syneresis, which would take place in the case of a dried linseed oil film system through the releasing of the adsorbed liquid without change in the solid phase. It is also thought that the softening may be due to depolymerization of the solid or the combined effect of syneresis and depolymerization.

This paper describes the study of the linseed oil films at various stages of aftersoftening. As it had been observed that different linseed oils varied as to the degree of aftersoftening, two pure linseed oils, differing in composition, were used. The two oils were exposed to the constant conditions of light, temperature, and humidity as thin films containing no drier, containing drier, and pigmented with white lead.

The films at intervals over a period of 9 months were extracted with acetone, and the acetone-soluble and -insoluble contents were determined. The iodine number of the acetone-soluble phase was also determined.

Composition of Linseed Oils

The raw linseed oils, which were used, were pure commercial oils representative of the raw linseed oil regularly used in the paint industry. The constants of the oils were:

	Linseed Oil 1	Linseed Oil 2
Sp. gr.	0.9320	0.9342
Acid No.	2.87	2.35
Iodine No. (Wijs)	175.7	186.9
Thiocyanogen No.	116.6	122.6

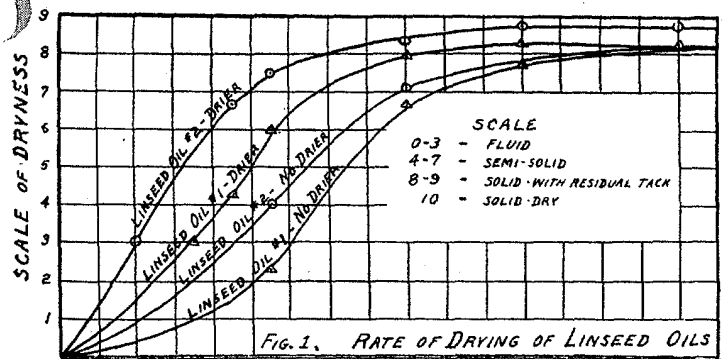


FIG. 1. RATE OF DRYING OF LINSEED OILS

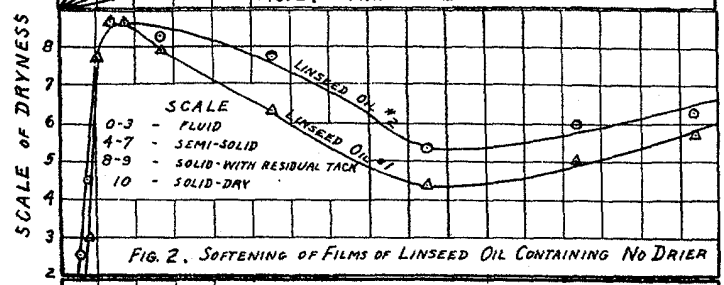


FIG. 2. SOFTENING OF FILMS OF LINSEED OIL CONTAINING NO DRIER

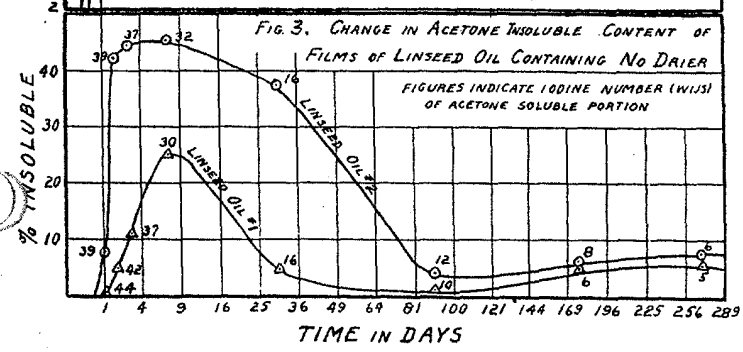


FIG. 3. CHANGE IN ACETONE INSOLUBLE CONTENT OF FILMS OF LINSEED OIL CONTAINING NO DRIER

The composition of the two oils on a fatty acid basis as calculated from the iodine number and the thiocyanogen number through a modification of Hoback's method (*4*) was found to be:

Acid	Linseed Oil 1	Linseed Oil 2
Saturated	7.02%	8.31%
Oleic	24.97	14.30
Linoleic	32.26	33.40
Linolenic	35.75	43.99

The relative drying characteristics of the two oils are illustrated in Figure 1. Linseed oil 2, with and without drier, proved to be the better drying oil. A comparison of the constants and composition of the oils shows that linseed oil 2 is less saturated and contains less oleic acid and more linolenic acid than linseed oil 1. This accounts for its faster drying properties. White lead paint made with oil 2 also had a faster drying rate (not plotted) than the paint made with oil 1, but the difference was not as pronounced as in the unpigmented films.

Conditions of Exposure

The oil films were exposed to the rays of a General Electric Company Type SI Sunlamp at a distance of 33 inches (83.8 cm.). This lamp transmits ultraviolet light ray in a range between 2800 and 3100 Å. (*2*). The light from this lamp in a general way corresponds to midsummer sunlight. The exposure was conducted in an air-conditioned laboratory in which the air was circulated and constantly changed. The temperature was maintained at 78° ± 1° F. (25.6° ± 0.56° C.) and a relative humidity of 50 ± 3 per cent.

Composition of Exposed Films

Films of the two oils containing drier and without drier were exposed. The films containing drier had 0.115 per cent lead and 0.011 per cent manganese present which were added as a liquid linoleate drier. White lead–linseed oil paint films were exposed and contained 71.1 per cent basic-carbonate white lead and 28.9 per cent linseed oil. The same liquid linoleate drier was used in amounts to give on the oil basis the same metal content as already described.

Experimental Procedure

Weighed quantities (0.65 ± 0.05 gram) of the linseed oils, with and without drier, were applied by a camel's hair brush on glass plates 4 × 6 inches (10.2 × 15.2 cm.). An uncoated 0.25-inch (0.635 cm.) margin was allowed to prevent the oils from flowing over the edges. The plates were placed on a flat, leveled board and were arranged in a circle so that the center of each plate was 33 inches (83.8 cm.) from the sunlamp.

The paints were exposed in the same manner and 2.5 ± 0.1 grams were applied on the glass plates. This quantity of paint contains approximately the same quantity of oil as was used in the oil films. The centers of the plates coated with paint were 36 inches (91.4 cm.) from the sunlamp.

The dryness was judged by touching the film with the finger. An arbitrary scale from 0 to 10 was used to rate both freshly applied and aged films for dryness. In this case 0 was taken to signify the paints and oils as applied, and 10 the dry condition without residual tack. When given ratings 0 to 3, the films were in a liquid condition. A rating of 1 was given when a slight thickening was noticed, 2 when the consistency had reached that of a heavy heat-bodied oil, and 3 when the film became so gelatinous that it would flow only with difficulty. When given ratings of 4 to 7 the films were not fluid but were in a plastic condition or various degrees of surface drying. At a rating of 4 the oils and paints were set and would not stick to the finger if touched very lightly. At 5 the film was more "solid" than at 4 and the weight of the finger would not remove any of it. At a rating of 6 the conditions were similar to those at 5 except that the film was firmer. At 7 practically all of the film was solid and only in a few places could the film be moved by pressure of the finger. When given ratings of 8 to 10 the films showed decreasing tackiness. At 8 the film contained no wet spots, but, if the hand was laid over the film, it would adhere. At a rating of 9 the films were not sticky but a residual tack could be easily felt when firmly pressed. When rated at 10 the films were dry and were without tack. Plus and minus signs were used to signify a condition slightly greater or slightly less than the rating. With some experience individual operators can use this scale and check one another within one point.

The method used to determine the percentage of the film insoluble in acetone was a modification of that used by Long and others. Continuous extraction was affected by using a Soxhlet rubber extractor. The acetone was boiled by placing the apparatus on a hot plate and condensed by means of a metal coil so as to drip on the thimble containing the sample. A piece of filter paper was folded so as to fit in the small Soxhlet thimble, and a small filter paper was folded to fit in the larger filter paper to hold the sample in place. These papers were placed in a glass-stoppered weighing vial which was placed in an oven at 95° C. for 2 hours, and the stopper was replaced while the vial was hot. When cool, the weighing vial and papers were weighed. The papers were then removed, placed in the Soxhlet thimble, allowed to come to equilibrium with the moisture in the air, which takes about 2 hours, and weighed.

From 0.6 to 0.7 gram of a dried oil film or 2.4 to 2.6 grams of a dried paint film were removed by a razor blade from the glass plate and placed in the filter paper in the thimble and weighed, and the weight of the sample was calculated. The thimble was then placed in the Soxhlet apparatus and 60 cc. of acetone were added to a previously weighed flask and allowed to reflux 4 hours.

The insoluble portion was prepared for weighing by placing the thimble in an oven at 95° C. for 1 hour and then removing the filter paper and insoluble portion and placing in the weighing vial

TABLE I. LINSEED OIL FILMS CONTAINING NO DRIER

Elapsed Time, Days	Rating of Dryness Oil 1	Rating of Dryness Oil 2	Per Cent Sol. in Acetone Oil 1	Per Cent Sol. in Acetone Oil 2	Per Cent Insol. in Acetone Oil 1	Per Cent Insol. in Acetone Oil 2	Per Cent Sol. Plus Insol. Oil 1	Per Cent Sol. Plus Insol. Oil 2	Iodine No. of Acetone-Sol. Oil 1	Iodine No. of Acetone-Sol. Oil 2
1	8−	8−	99.0	92.0	−0.3	7.5	98.7	99.5	43.9	39.1
2	9−	9−	92.8	54.2	4.7	42.8	97.5	96.0	42.0	39.4
3	9−	9−	88.6	48.5	10.3	44.1	98.9	92.6	37.0	37.3
7	8	8+	73.6	55.4	25.4	45.6	99.0	101.0	30.0	32.4
30	6+	8−	96.6	62.6	4.8	37.1	101.4	99.6	15.6	15.9
90	4+	5+	101.0	99.2	1.1	3.8	102.1	103.0	10.2	11.7
180	5	6	99.7	99.1	5.5	6.0	105.2	105.1	5.6	7.8
270	6−	6+	98.8	102.4	5.7	7.8	104.5	110.2	5.2	6.0

at 95° C. for 2 hours. The top of the vial was replaced and the weight obtained by difference. An advantage of this method is the elimination of the large error due to the absorption of moisture on the filter paper.

The weight of soluble portion was obtained by distilling off most of the acetone on a hot plate in a slow stream of carbon dioxide. When most of the acetone was distilled off, the distillation was continued with a rapid stream of carbon dioxide until the residual oil just began to darken. When the soluble portion from paint films less than one week old were extracted, some of the pigment went through the Soxhlet thimble into the flask. In this case the percentage of soluble portion was determined by making up the acetone solution to 100 cc., allowing the pigment to settle, pipetting off 50 cc., and determining soluble portion as before.

By weighing the insoluble paint film, the pigment loss could be calculated as the difference between the loss in weight of paint film after extraction and the weight of soluble portion extracted.

The iodine number was run on all soluble portions by the Wijs method after redissolving the weighed residue in glacial acetic acid.

The results of the acetone extraction of the films, the dryness rating, and the iodine number of the acetone-soluble portions at various ages are shown in Tables I, II, and III and are graphically illustrated in Figures 2 to 7, inclusive, where the time in days is plotted on a square root scale.

Linseed Oil Films Containing No Drier

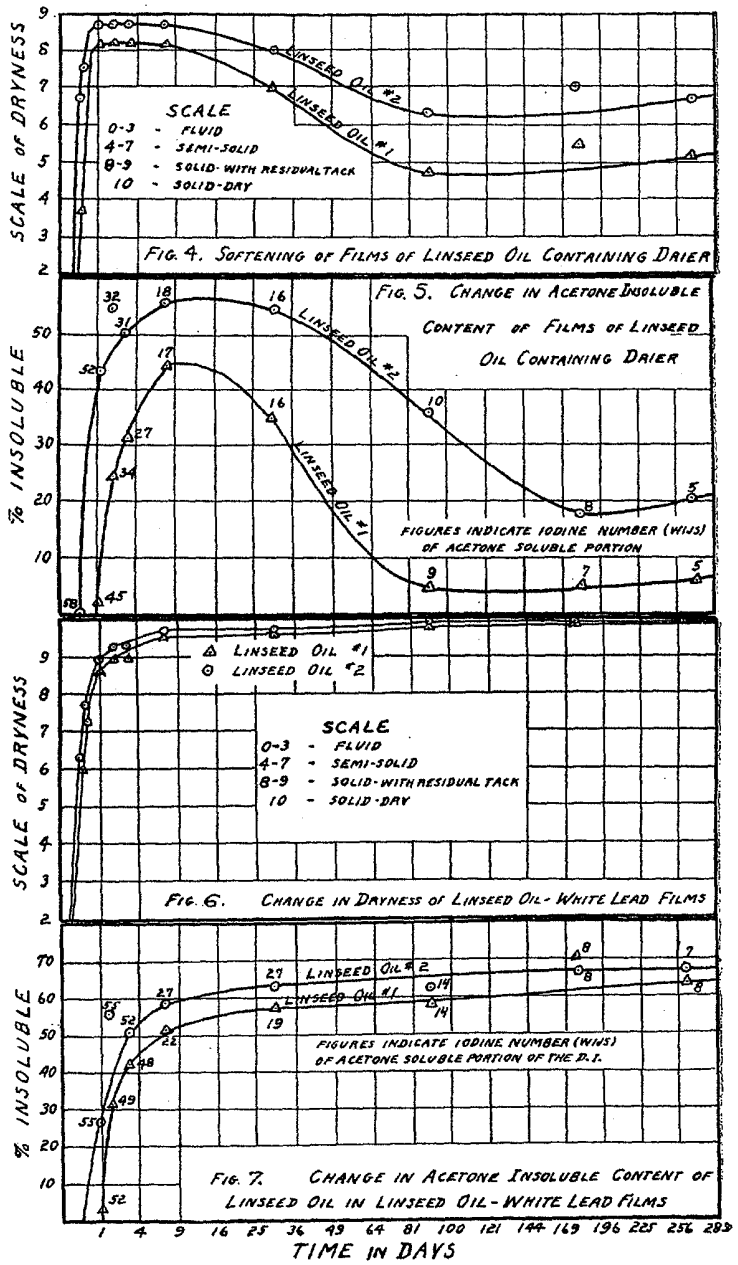
Figure 2 shows the changes in regard to softening which occurred in the linseed oil films which contained no drier. The oils at the end of 3 days began to soften, and Figure 3 shows that at this time the oils had not quite reached the maximum acetone-insoluble content which was actually reached at 7 days. After 3 days the oils definitely began to soften; at one month oil 2 was a tacky but solid film, and oil 1 was much softer and so plastic that the finger made a temporary imprint. At this time the film of oil 2, which is the better drying oil, contained 37 per cent acetone-insoluble material whereas the soft oil had only 5 per cent. After 90 days the films of both oils were extremely soft and contained but little material that was not soluble in acetone. On continued exposure of 9 months, the oils hardened somewhat but remained quite soft and were almost entirely soluble in acetone.

Linseed Oil Films Containing Drier

In Figure 4 the softening which occurred in the oil films containing drier is illustrated. These oil films acted similarly to the films without drier, except that the softening did not occur quite so early and the oils did not become so soft. The oil films with drier were more insoluble in acetone than the films without drier, as shown in Figure 5. The maximum acetone-insoluble content was reached for both oils shortly after 7 days of exposure. Following this, the better drying linseed oil, No. 2, appeared to have a reasonably high acetone-insoluble content but the other linseed oil, which was the more saturated, at the end of 90 days was largely soluble in acetone. On continued exposure to the constant conditions, oil 2 gradually became more soluble in acetone. Although these oils at this time were not as soft as those without drier, they were much softer than when they were only a few days old. They remained in this condition for the duration of the tests.

White Lead Paint Films

When the oils were pigmented with white lead, the paint films did not soften on aging. The initial drying rates and the dryness on aging of the two paints were almost identical (Figure 6). When the paints were one day old, the oils were quite soluble in acetone, but at the end of 7 days the oils in the paints had become much less soluble in acetone, as shown in Figure 7, and finally after 90 days the acetone-insoluble content reached a fairly constant range of 60 to 70



for both oils. However, even in paint form, linseed oil 1 consistently had a lower acetone-insoluble content than oil 2 which was the better drying oil.

Iodine Number of Acetone-Soluble Phase

In Figures 3, 5, and 7 the iodine number of the acetone-soluble portion is shown by figures on the curves. Upon exposure of the films, the iodine number of the acetone-soluble portion drops quickly and in 24 hours is one-third to one-fourth that of the original oil. It then gradually decreases to a minimum of about 6. Since the initial rate of drying of the more unsaturated oil is greater, the iodine numbers of the acetone-soluble portions from oil 2, with and without drier, is less after 1 day than similar portions from oil 1. However, upon continued exposure, the iodine numbers of soluble portions from the better drying oil again indicate greater unsaturation than for the other oil. The paints, having faster drying qualities, do not show this inversion at the 24-hour interval. The iodine number of the soluble phase is not related to the dryness or to the percentage acetone insoluble content.

drying oil 1 had lost twice as much pigment. After 3 days oil 2 showed no further loss of pigment, while oil 1 showed slight losses for one month. After 9 months of continued exposure, both oils again began to lose a trace of pigment due to changes in the oil structure.

Sum of Soluble and Insoluble Phases

The tables show that the sum of the soluble and insoluble phases up to one month exposure is from 97 to 99 per cent. The theoretical total is 100 per cent, but a lower figure is obtained because the volatile components of the film are lost upon the distillation of the acetone. After one month there is a reversal and the sums are above 100 per cent. This abnormality could be caused by a chemical reaction with acetone, variations in the technic of distilling off the acetone, or structural changes on aging in the soluble or insoluble phases. In the latter case, the acetone would be more strongly absorbed and its complete release prevented. It was found that benzene gave the same effect as acetone, since a film one year old extracted with benzene gave a soluble and insoluble sum of 108. The extractions were made over a considerable period of time and the technic of extraction was checked by extracting films at the same time the aged films were extracted. It therefore appears that absorption of the solvent by the colloidal structure is the reason why the sum of the soluble and insoluble portion is more than 100.

The study which has been described in this paper deals with linseed oil films exposed to but one set of conditions. Further interesting studies could be made on the colloidal structure

TABLE II. LINSEED OIL FILMS CONTAINING DRIER

Elapsed Time, Days	Rating of Dryness		Per Cent Sol. in Acetone		Per Cent Insol. in Acetone		Per Cent Sol. Plus Insol.		Iodine No. of Acetone-Sol.	
	Oil 1	Oil 2	Oil 1	Oil 2	Oil 1	Oil 2	Oil 1	Oil 2	Oil 1	Oil 2
1/2	7+	7+	98.2	99.0	−0.2	0	98.0	99.0	61.2	57.6
1	8+	9−	97.8	54.0	1.9	43.1	99.7	97.1	45.0	52.2
2	8+	9−	73.1	43.5	24.3	55.3	97.4	98.8	34.4	32.4
3	8+	9−	69.1	48.1	31.0	50.4	100.1	98.5	26.6	31.0
7	8+	9−	52.6	41.7	44.5	56.1	97.1	97.8	17.3	17.8
30	7	8	66.5	48.5	35.3	54.1	101.8	102.6	16.1	15.9
90	5−	6+	100.6	65.9	4.0	36.1	104.6	102.0	9.1	9.9
180	6	7	99.0	87.7	4.8	17.4	103.8	105.1	7.3	7.8
270	5+	7−	99.4	87.0	6.2	20.2	105.6	107.2	5.0	5.3

TABLE III. WHITE LEAD PAINT FILMS

Elapsed Time, Days	Rating of Dryness		Per Cent Oil-Sol. in Acetone		Per Cent Oil-Insol. in Acetone		Per Cent Sol. plus Insol.		Per Cent Pigment Loss		Iodine No. of Acetone-Sol.	
	Oil 1	Oil 2	Oil 1	Oil 2	Oil 1	Oil 2	Oil 1	Oil 2	Oil 1	Oil 2	Oil 1	Oil 2
1	9−	9	96.7	73.3	3.3[a]	26.7[a]	...	...	10.7	6.4	51.8	55.2
2	9	9+	68.4	44.0	31.6[a]	56.0[a]	...	...	6.0	2.5	49.0	55.4
3	9	9+	57.0	49.2	43.0[a]	50.8[a]	...	...	2.0	0	47.6	52.4
7	10−	10−	48.9	40.4	51.1[a]	59.6[a]	...	...	0.4	0	21.7	27.3
30	10−	10−	42.5	35.7	57.6	63.9	100.1	99.6	0.1	0	19.4	26.9
90	10	10	41.0	37.7	58.9	62.5	99.9	100.2	0	0	13.8	14.3
180	10	10	34.2	45.6	70.6	66.7	104.8	111.3	0	0	7.5	7.6
270	10	10	41.2	38.0	64.6	66.1	105.8	104.1	Trace	Trace	8.1	7.1

[a] Calculated value by subtracting per cent soluble from 100 per cent

Iodine Number of Acetone-Insoluble Phase

The iodine number of the insoluble and soluble phases were compared in a separate experiment. The acetone-soluble portion of a raw linseed oil exposed under the sunlamp 6 days was extracted as previously described, and its iodine number was found to be 30. The insoluble portion was refluxed with glacial acetic acid for 15 hours, at which time three-fourths of it had gone into solution. After subtracting a control blank, the iodine number of the insoluble portion was found to be 31. Thus, the iodine numbers of the insoluble and soluble phases may be assumed to be virtually the same. This assumption is borne out by other workers who have found the carbon, hydrogen, and oxygen content of the solid phase to be the same as the liquid.

Pigment Loss

A difference in the "binding" power of the two oils is shown by the percentage pigment loss. At 24 hours the poorer drying oil allowed 10.7 per cent of the pigment to escape, whereas under similar treatment only 6.4 per cent was lost from the more unsaturated oil. After 48 hours the percentage pigment loss was less for both oils, but the poorer

of dried linseed oil films under other conditions. Also a study of the effect of various pigments on the colloidal structure of linseed oil might lead to useful information on the behavior of paints on aging.

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RECEIVED June 7, 1935. Presented before the Division of Paint and Varnish Chemistry at the 89th Meeting of the American Chemical Society, New York, N. Y., April 22 to 26, 1935.