Studies in the Drying Oils

XVII. Influence of Several Factors on the Mechanism of Drying of Oil Films[1]

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The first stage in the drying of linseed oil films is a matter of oxidation or, more generally, of making polar molecules. The mechanism of reaction in this stage is greatly influenced by factors such as temperature and humidity. High humidity greatly inhibits and modifies the reactions occurring.

The second stage in the drying involves association of the polar molecules produced in the first stage to form the solid gel-like coherent structure of the film. Some further oxidation occurs after the oil has "set," but the film is soon oxidized to a stage corresponding to the addition of two oxygen atoms at each double bond, and the percentage of oxygen remains practically constant thereafter.

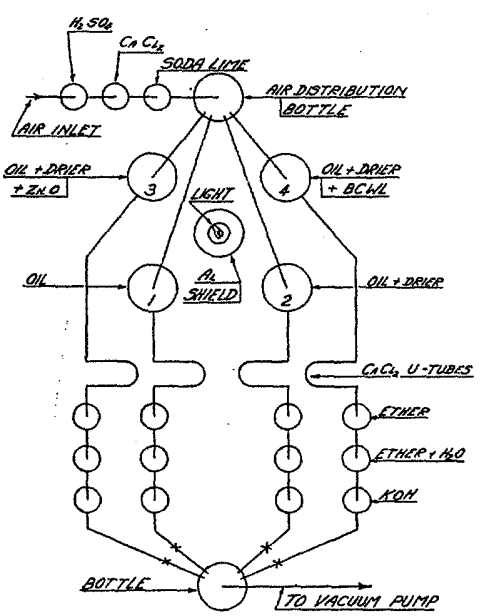
The aging of films of linseed oil or of trilinolenic glyceride consists in a gradual transition of polar liquid phase to solid phase of substantially the same ultimate analysis. Embrittlement and failure of drying oil films is primarily a matter of reduction of the percentage of liquid phase to low values.

PREVIOUS work has indicated that the serviceable life of a paint film is determined in no small measure by the mechanism of the drying process. This in turn is greatly dependent on the composition of the oil used and on the drying conditions, especially humidity and temperature. Abnormal environment, particularly in early stages, stunts the life of the film. This paper describes certain experiments on (1) the mechanism of the so-called drying process and (2) the influence of humidity and temperature. It is a part of a long investigation being carried on, one objective of which is the lengthening of the serviceable life of paint and other protective coating films in exterior exposure.

It is well known that in the first stage of transition from liquid drying oil to solid film as carried out by exposure to air, oxidation plays a major role. The interesting ability of linseed oil to change to a solid film was known as far back as the tenth century. Understanding of the part played by the air waited until after the discovery of oxygen in 1774. Since that time we have had a fair picture of the nature of the process although, until recent years, investigators failed to see that the later stage of the process is not oxidation but is a matter of building up or association of the primary particles to form the solid film or gel. This part of the drying comes under the realm of colloid chemistry and should be considered in the light of colloid behavior. The later stage of drying and the aging of films involves some oxidation but this is not the most important feature, and this oxidation is masked by the other phenomena.

If we recognize that the later stages in the setting and aging are colloidal association processes, then the process of the setting and aging of bodied oils, varnishes, and resins can be considered with that of paints and other products containing raw oil. We simply recognize that the first stage of the process is somewhat different in the different cases. In the case of raw linseed oil, the first stage is largely a process of oxygen addition. Direct addition of oxygen at the double bonds has used up the free energy of the oil. In the case of bodied oils the free energy of the double bonds has been partially used up by the association or polymerization process, the union of oil molecule to oil molecule. In either case a larger, more complicated, and polar molecule has been formed which has a strong tendency to associate with neighboring molecules to form a solid gel. The process consists of two major phases irrespective of whether we are considering raw oil, bodied oils, or varnishes.

This view of the situation seems helpful because it means one picture instead of several. However, there are definite differences in the primary molecules built in the first part of the process. This means that the constitution and structure of the resultant film will be different in the various cases and suggests the possibility of producing desired differences in a product by purposed variation of one of the factors affecting the result; also it seems that the possibilities inherent in combination processes have not been exhausted. This applies especially to combinations of heat-bodying and oxidation, of varnishes from oils processed to various extents, etc.



First or Oxidation Stage

The simple idea of catching the volatile oxidation products given off and of determining the weight of each was extended to include comparison of the effects of high and low temperatures and high and low humidity as follows (Figure 1):

Holes were bored in the bottom and lids of screw-top mason jars to admit

[1] The first seven articles of this series appeared as unnumbered papers in Ind. Eng. Chem. as follows: 17, 138, 905 (1925); 18, 1245, 1252 (1926); 19, 62, 901, 903 (1927). Parts VIII to XVI appeared in

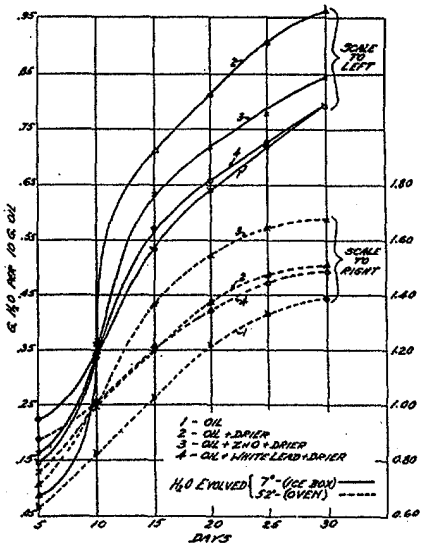


FIGURE 2. WATER EVOLVED DURING RUN I (DRY AIR)

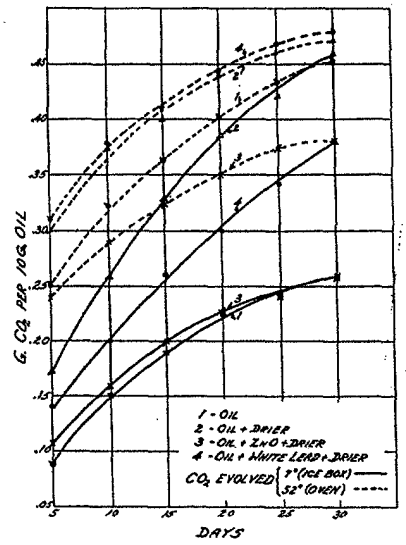


FIGURE 3. CARBON DIOXIDE EVOLVED DURING RUN I (DRY AIR)

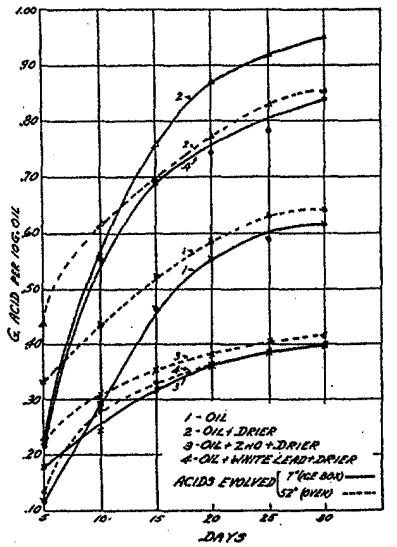


FIGURE 4. ACIDS EVOLVED DURING RUN I (DRY AIR)

were sealed on to the jars with de Khotinsky cement. Each jar was filled loosely with glass wool which had been carefully sprayed with the oil, oil + drier, or oil + drier + pigment. The weight of oil or paint sprayed on to the glass wool was adjusted so that each jar contained the same weight of oil. Precautions were taken that oil did not run down off the glass wool and collect on the bottom. In the beginning difficulty was experienced at this point. The loose packing of glass wool permitted light from the lamp to reach all parts of the jar with fair uniformity. The results of duplicate experiments agreed within 5 per cent.

Air let in the bottom of each jar struck a shield of wire gauze to distribute it uniformly through the glass wool. Volatile products of oxidation of the oil passed with the excess air to a train consisting of (1) a calcium chloride tube to absorb moisture, (2) gas-washing bottles containing ether, ether + water, and potassium hydroxide to absorb fatty acids and carbon dioxide. At regular intervals these were replaced by fresh ones and the weights of water, carbon dioxide, and fatty acids determined. Aldehydes were found in the gaseous products in every case, but the weight of these were so much smaller that it was finally decided not to involve quantitative determination of aldehydes.

For run I, samples were made up as follows:

	Grams		
1	60	Raw linseed oil	
	2	Benzene (equivalent to that in the drier in 2-4)	
2	60	Raw linseed oil	
	2.4	Drier	
	110	Paste →	54.5% XX black zinc oxide 45.5% raw linseed oil
3			
	2	Drier	
	143	Paste →	73.4% basic carbonate white lead 26.6% raw linseed oil
4			
	1.5	Drier	

Samples 2 to 4 contained drier equivalent to 0.2 per cent metal (lead, cobalt, manganese) based on the weight of the oil.

The drier contained:

	Grams		Grams
Lead resinate	25	Linseed oil	35
Manganese resinate	5.62	Benzene	92
Cobalt resinate	1.75		

In run I weights of these to give 5 grams of oil in each case were sprayed on the glass wool in the jars, and air was bubbled through sulfuric acid and calcium chloride to dry it, and over soda lime to remove carbon dioxide, and was passed through the four samples at the same rate of 2.5 liters per hour for 30 days. Two sets of jars were included in this run. The first set was kept in an electric refrigerator at 7° C., the second set in an oven at 52° C. Each set was exposed to indirect light reflected from the white walls of the oven or the refrigerator from a 100-watt Mazda lamp, surrounded by an aluminum cylinder which protected the samples against direct light and thus tended to equalize the effect of light in the different parts of the jars.

At the end of 30 days, or when the weight of volatile products coming off had decreased to a small figure, the jars were broken and the films examined. In all cases the oil or paint on the glass wool was thoroughly dry. The results are plotted graphically in Figures 2 to 4.

In run II, the jars held the same materials as in run I, but the air led through them was saturated with moisture by bubbling it through water in a series of gas-washing bottles. Results of this run are given in Figures 5 and 6. In this case water evolved could not be determined, but only carbon dioxide and fatty acids. However, these serve sufficiently for comparison.

1. Oils or paints exposed in diffuse light to very dry air, dry thoroughly at either moderately high or moderately low temperatures. The temperatures used are representative of the extremes likely to be met in painting practice. It is doubtful whether it would be logical to paint when the temperature is much below 7° C. Yet the oils and paints dried perfectly. True, as expected, there is a difference in the rates of drying at 7° and 52° C., but the oil or paint dried thoroughly in each case. The weights of volatile products are, however, quite different, thus indicating very real differences in the mechanism of drying and in the composition and nature of the resultant films.

An interesting side light on this is afforded by the following experiment: Using sample 1, raw linseed oil alone was to all indications of touch perfectly dry after 30 days in the refrigerator. It had given off 1.654 grams of volatile oxidation products. This jar and sample were then put in the oven at 52° C., and the air stream was continued. After 5 days in the oven the sample had given off:

	Gram/10 grams oil
Fatty acids	0.240
CO_2	0.146
Moisture	0.495
Total	0.881

Adding this to 1.654 grams gives 2.535 grams. The corresponding sample in the oven gave off 2.475 grams in 30 days. The agreement is close.

2. Excessive moisture or humidity in the air inhibits drying of the oil or paint. When the jars were opened after 30

days, the oils and paints which had been exposed to air practically saturated with moisture at the two temperatures were still undried or wet. They had been "drowned" by the high humidity. Drying had been inhibited to a large degree. This series brought out in striking fashion the inadvisability of painting under conditions of continued high humidity. This is not new but the work furnished quantitative data to substantiate the work of Schmutz and Palmer (*4*).

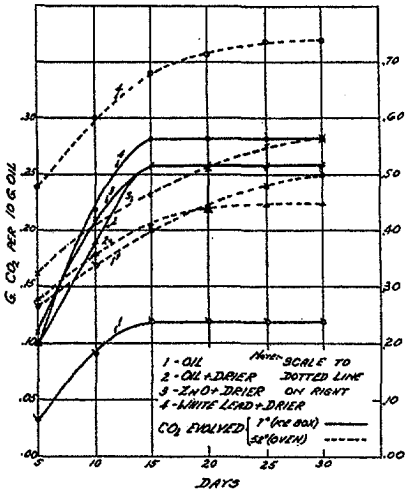
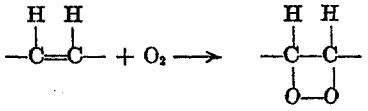


FIGURE 5. CARBON DIOXIDE EVOLVED DURING RUN II (WET AIR)

3. Pigments and driers exert definite influence on the drying process. In some experiments not reported, the percentage of pigment or pigment-vehicle ratio was varied and was found to produce appreciable differences in the volatile products evolved.

SECOND STAGE OR ORIENTATION AND ASSOCIATION OF THE MORE COMPLICATED POLAR MOLECULES TO FORM THE SOLID FILM

After the oil has absorbed oxygen corresponding to the formation of one peroxide group per molecule of acid,



or three peroxide groups per molecule of oil, it sets or gels.

A more general statement would be that, when the molecules have grown to a certain degree of complexity or polarity or both, they associate and form solid gel. After this stage some further oxidation occurs, but this is outweighed by other considerations and soon becomes very small.

The oxidation has practically run its course before the film begins to undergo appreciable changes leading to failure. As shown by the data below, ultimate analysis seems to indicate that oxidation has stopped or decreased to a very low rate before the films begin to undergo appreciable changes in physical character. Rather the gradual embrittlement or final failure of the films seems to be closely associated with steady and progressive change of the fully oxidized liquid phase to solid association products with only small changes in composition.

METHOD OF STUDY OF SECOND STAGE. After the oil has set to what is called a "film," a new feature enters the situation. The so-called solid film really contains both solid and liquid. Oil films exposed indoors contain appreciable percentages of liquid oil even after a year. Exposed outside, the liquid changes to solid more rapidly under the stimulus of the sun's rays. Complete detailed study of the film after the oil has set will naturally involve separation of the solid from the liquid and a study of each phase separately. Fortunately, this can be done simply, though it is a time-consuming job. If the film is removed from the surface and put in an extractor, such as a Soxhlet extractor, the liquid oil portion can be extracted from the film by means of organic solvents. Whitby has used acetone. The present authors' experience with it has been rather satisfactory though they have also used other solvents. The process called "solution" savors of chemical reaction in many instances, and in this extraction of the film with solvents it is felt that the solvent exerts a disassociating effect on the solid phase to some extent. The results are therefore relative or comparative rather than absolute. However, as the film ages from its initial set-up to its final failure, there is a steady and interesting decrease in the percentage of (liquid) material extracted by a solvent such as acetone. This is true for both inside and outside exposure. It has been followed for many series of films. In other words, as time goes on, one thing of major importance in the film is the steady increase in the percentage of the insoluble solid part. The film is becoming harder and more rigid. It is losing elasticity. These changes which are of interest in determining the life of the film may be conveniently observed by following the change in the percentages of liquid and solid in the film. In several cases it has been found that failure on outside exposure started soon after the percentage of liquid had decreased to low values.

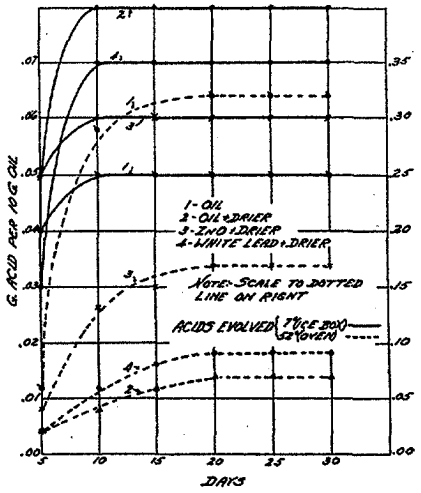


FIGURE 6. ACIDS EVOLVED DURING RUN II (WET AIR)

Duplicate films inside were still perfect and contained much larger percentages of extractable liquid oil. These findings are at least suggestions. They led further to the question, what factors determine the gradual change from liquid to solid? Is it a matter of slow oxidation catalyzed by the driers? Is it a change prompted by absorption of light energy, particularly of certain wave lengths or, more exactly, certain quanta of energy? Finding the cause may supply the means of hindering the transition of liquid to solid and thus increase the life of paint and other protective coatings.

Nelson (*2*, *3*), from criticisms of stress-strain curves, premised and discussed the disappearance of liquid phase in films as they age.

Linseed oil is a mixture of glycerides of at least four acids, stearic, oleic, linoleic, and linolenic. In starting this more detailed study, it was decided to avoid all possible complications due to mixtures and deal with pure substances.

Trilinolenic glyceride was chosen as the material: (1) because it is the most active and therefore the most interesting component of linseed oil and (2) because the authors had learned how to make it in a relatively pure condition. Therefore, this material was synthesized through the bromine derivative and was used to make up a number of series of panels, a few of which were on wood, but most of which were on glass since this permitted samples to be scraped off with a razor blade for extraction and study at regular intervals.

TABLE I. VOLATILE PRODUCTS FORMED DURING DRYING PERIOD OF TRILINOLENIC GLYCERIDE

(Determined as carbon and hydrogen)

Drier	Time of Run	O in Film	Increase in Weight	C Evolved	H_2 Evolved	Total Evolved	Ratio C:H
%	Hours	%	%	%			
None	100	27.15	18.10	3.19	(1.65)	...	...
0.2	100	28.25	17.75	3.08	0.61	3.69	5.05:1
None	150	31.10	22.80	8.10	1.42	9.52	5.7:1
0.2	150	29.41	19.20	7.50	1.00	8.50	7.5:1
1.0	150	28.00	16.50	6.02	0.99	7.01	6.1:1

TABLE II. SOLID AND LIQUID PHASES OF TRILINOLENIC GLYCERIDE FILMS

Solvent	B. P. of Solvent	Liquid Phase	Oxygen Content Solid phase	Oxygen Content Liquid phase
	°C.	%	%	%
38 DAYS WITH 0.2 PER CENT DRIER				
Ethyl acetate	77	44.4	31.56	[a]
Methyl acetate	57	36.6	30.80	33.73
Isopropyl ether	67	11.4	...	[a]
Methyl alcohol	66	50.8	29.04	35.20
Ethyl alcohol	78.4	50.1	29.10	30.43
N-propyl bromide	71.5	15.3	30.47	[a]
Ethylene dichloride	84	32.9	28.84	35.92
Carbon tetrachloride	76	1.5	...	[b]
Chloroform	61.6	30.6	30.75	32.40
Benzene	80	13.4	29.40	25.72
Acetone	56.6	29.5	29.80	38.34
42 DAYS WITH NO DRIER				
Petroleum ether	35–75	7.70	31.10	[a]
Ethyl alcohol	78.4	100	...	36.85
Carbon tetrachloride	76.0	...	...	[b]
Chloroform	61.6	35.80	29.95	41.50
Benzene	80.0	26.00	30.10	26.92
Acetone	56.6	36.70	28.15	[a]

[a] Sample too small. [b] Decomposition occurred.

In some series driers were present, in others no driers were used. Supplementary experiments to confirm various leads were run at intervals. Results are given in Tables I to VII. Certain features of the process seem to be established by the data already in hand. These refer to trilinolenic glyceride, not oil, unless otherwise stated. Although this material is in no sense of the word commercial, a study of it throws light on the drying of commercial products.

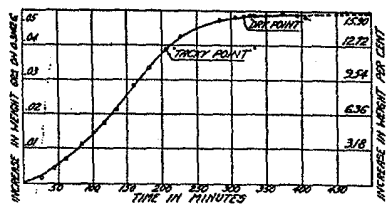


FIGURE 7. INCREASE IN WEIGHT, WITH TIME, OF TRILINOLENIC GLYCERIDE WITH 0.2 PER CENT METAL DRIER

CHANGES IN WEIGHT

The gain in weight (Figure 7) for trilinolenic glyceride with drier equivalent to 0.2 per cent metal shows that there is practically no induction period. Oxidation begins at once and proceeds steadily until the film is dry to touch. The net gain in weight amounts to 15 per cent at this point, which corresponds to a take-up of 8.1 atoms of oxygen per molecule of glyceride. When no drier is present, the net gain in weight up to the dry point is 19.25 per cent. It took 30 hours to reach the dry-to-touch point in contrast to 5 when drier was present. Drier therefore accelerates the rate of absorption of oxygen, but the results seem to indicate that the drier has other functions than that of an oxidation catalyst. Elm (*1*) has previously determined the gain in weight *vs.* time curve for trilinolenic glyceride. Figure 7 and Table VII give further data on this, extending Elm's work to show the influence of metallic driers. A smaller percentage increase in weight of the films up to the dry point or after 12 days is obtained as the percentage of drier increases. The differences are striking; thus, the percentage increase in weight when 3 per cent of metal is present is less than half of that when no metal is present. As shown by Table VIII, variation in

TABLE III. PERCENTAGE OF SOLID PHASE IN TRILINOLENIC AND TRIOLEIC GLYCERIDE FILMS AT VARIOUS FILM AGES

(0.2 per cent cobalt-manganese-lead drier)

Oil Composition Linolenic	Oleic	Percentage of Acetone-Insoluble Phase after Days: 4	7	18	29	47	68	92	114	175	365
%	%										
100	0	38.5	54.6	55.5	57.5	69.4	..	74.8	83.7	78.2	82.0
94.65	5.35	..	34.9	58.0	59.4	57.9	70.4	74.8	79.6	81.9	81.0
89.20	10.80	20.6	36.0	60.0	59.8	70.0	66.7	74.2	75.0	73.8	76.0
77.70	20.30	23.8	31.7	60.8	66.5	58.6	54.5	65.0	64.6	64.7	68.0
66.20	33.80	6.8	23.5	39.9	43.7	52.8	51.3	54.1	55.8	48.3	63.0
49.60	50.40	0.0	20.2	24.5	33.1	36.1	40.1	38.5	41.3	35.8	..
31.90	68.10	[a]	10.2	15.9	29.2	29.3	34.1	34.7	23.2	32.4	..
11.20	88.80	[a]	12.4	12.4	14.7	20.0	18.6	..	..	22.4	..

[a] No determination, films not dry.

TABLE IV. OXYGEN IN ACETONE-INSOLUBLE PHASE OF FILMS OF TRILINOLENIC AND TRIOLEIC GLYCERIDES

(0.2 per cent drier, exposed inside)

Composition Linolenic	Oleic	Percentage of Oxygen after Days: 4	7	18	29	47	68	92	114	175	365
%	%										
100	None	29.50	28.71	28.48	31.59	32.47	31.13	31.12	30.88	31.50	31.20
94.65	5.35	29.48	30.00	29.48	30.92	31.91	31.66	30.55	30.44	30.04	29.76
89.20	10.80	30.40	29.78	32.15	31.35	33.54	29.48	30.63	31.80	31.90	37.10
79.70	20.30	30.28	29.65	32.94	29.80	32.72	31.50	31.61	31.74	30.90	30.97
66.20	33.80	...	31.18	32.64	34.12	34.08	32.90	32.49	32.67	33.40	34.75
49.60	50.40	...	32.16	32.44	32.78	31.72	31.35	34.13	34.06	34.27	...
31.90	69.10	...	34.52	32.64	31.45	34.90	32.58	32.45	32.42	32.29	...
11.20	88.10	...	35.22	31.25	33.30	36.12	37.48	...	36.36	38.05	...

The method of study used consisting in (1) extraction to determine percentages of solid and liquid and (2) ultimate analysis of the separated phases to see whether the change from liquid to solid took place only after the liquid phase had been oxidized to a certain composition.

percentage of drier does not produce any definite drift in oxygen content. The figures vary slightly as is to be expected from the technic used, but are substantially constant at any given time. In one series (Table I, column 3) a downward drift in oxygen content with increase in drier was observed. These two observations taken together indicate that increase in the percentage of metallic driers increases the volatile oxidation products evolved during the early stages of drying.

TABLE V. SOLID PHASE IN FILMS
(0.2 per cent drier exposed outside)

	Acetone-Insoluble Phase			Acetone-Insoluble Phase	
Film Age	Linseed	Trilinolenic glyceride	Film Age	Linseed	Trilinolenic glyceride
Days	%	%	*Days*	%	%
3	6.0	75.5	73	38.0	74.5
7	5.8	86.5	100	56.2	78.2
16	13.0	82.8	123	60.2	79.6
35	14.3	81.2	165	53.8	..
52	41.2	79.6			

TABLE VI. OXYGEN IN SOLID AND LIQUID PHASES AFTER ACETONE EXTRACTION OF FILMS OF LINSEED OIL AND TRILINOLENIC GLYCERIDE

	Linseed Oil outside, 2% drier		Oxygen in Trilinolenic Glyceride inside, no drier		Oxygen in Trilinolenic Glyceride outside, 0.2% drier	
Film Age	Solid phase	Liquid phase	Solid phase	Liquid phase	Solid phase	Liquid phase
Days	%	%	%	%	%	%
3	...	26.60	...	30.14	28.83	32.43
7	...	30.08	29.90	30.79	26.30	
16	...	34.29	29.70	31.05	29.65	37.88
35	...	33.30	30.48	34.13	30.76	33.40
52	...	30.88	...	37.04	32.06	...
73	...	...	32.45	35.80	34.10	...
100	32.87	34.55	...	...	34.78	...
123	38.40	40.72	29.90	35.00	34.45	...
165	34.10	....	...	31.16	...	...

TABLE VII. INCREASE IN WEIGHT, WITH TIME, OF TRILINOLENIC GLYCERIDE FILMS

		Increase in Weight			Loss on Heating
Drier	Drying Time	At dry point	After 12 days	After heating	
%	*Hours*	%	%	%	%
None	40:00	19.30			
0.1	6:14	14.90	16.00	4.83	11.17
0.2	5:21	14.80	...	...	...
0.5	2:56	13.00	14.50	3.55	10.95
1.0	2:33	11.89	13.90	1.75	12.15
3.0	2:13	9.43	12.25	0.95	11.30

TABLE VIII. OXYGEN CONTENT OF TRILINOLENIC GLYCERIDE FILMS

	Percentage of Oxygen				
Drier	At dry point	3 days	8 days	12 days	After heating[a]
%					
0.0	...	27.15	...	...	...
0.1	23.67	27.40	27.85	28.05	27.90
0.5	24.67	27.90	27.50	27.15	28.02
1.0	23.07	26.44	27.25	28.30	29.10
3.0	23.24	26.70	27.70	28.85	20.25

[a] 12-day films were heated at 130° C. for 20 hours.

The effect of light in promoting gelation by polymerization or association rather than oxidation is shown by the data from trilinolenic glyceride with drier equal to 0.2 per cent metal. This showed a gain in weight of 15.3 per cent before it set in the dark, whereas the duplicate samples dried at the same time in diffuse daylight in the room showed a net gain of only 12.1 per cent when dry to touch.

The gain in weight measured is the net gain. Volatile oxidation products are being given off at the same time but at a very slow rate. However, after the film is dry to touch, the two rates become nearly equal, the net loss in one week being only one per cent.

As shown by Figure 7, the change in slope of the curve for trilinolenic glyceride is sharp enough so that the time when the film is dry to touch may be determined by following the gain in weight.

If the dry films are heated, there is definite loss of weight with evolution of corresponding amounts of water and carbon dioxide. Thus, 16-day films heated for 3 hours at 130° C. lost 8.17 per cent, and 40-day films heated for 20 hours at 130° C. lost 7.63 per cent.

The mechanism of drying characteristic of the glyceride was not appreciably changed by the presence of a red iron oxide pigment; thus, a mixture of 32.3 parts by weight iron oxide (99.4 per cent Fe_2O_3) and 67.8 parts by weight trilinolenic glyceride showed a gain of 8.15 per cent up to the dry point. This is equivalent to (100/67.8) × 8.15 = 12.0 per cent on the basis of the glyceride.

When baked for 20 hours at 130° C., this film lost 9.0 per cent calculated on the basis of the oil. These results are quite comparable to those for the glyceride above.

CHANGES IN COMPOSITION

Although the net change in weight is small after the glyceride is dry to touch, oxidation is proceeding at first rapidly, but the rate soon falls off to a very low value, and after some months the values for ultimate analysis remain sensibly constant. After this point further changes in the film are a matter of change of liquid phase into solid with little or no change in percentage of oxygen, rather than an oxidation. Further, the physical changes in the film which are considered as film failure occur long after gain in percentage of oxygen has ceased, as far as the writers are able to detect. This leads to the thesis that failure of films is not a matter of progressive oxidation catalyzed by metallic driers but of progressive change of liquid to solid by reactions of an "association" nature. Substances which decrease the velocity of this change will be of service in prolonging the life of films. From this viewpoint, increasing the life of paints is not a hopeless task but is a matter of patient search for materials which will not retard the initial oxidation phase of the drying process, but will retard the latter stages of transition of fully oxidized liquid oil into solid gel.

The first work had been done on films exposed in the laboratory. A second series which has been outside on the roof exposed at an angle of 45° facing south has so far given identical results.

The percentage of liquid phase extractable from the film by acetone or other solvents decreased much more rapidly than in the indoor samples. The films also reached the maximum oxygen content much more rapidly but have not yet failed physically although they have reached what seems to be the maximum degree of oxidation.

The work on the gross films has been supplemented by studies on the separate phases after extraction with acetone. The figures for the composition of the solid, acetone-insoluble phase are constant to an unexpected degree, showing that the solid fundamental structure of the film is fairly definite and constant in composition but that the percentage of it simply increases as time goes on.

On the basis of the formation of a peroxide group at each double bond, one molecule of trilinolenic glyceride would take up 9 × 2 = 18 atoms of oxygen. If no volatile oxidation products were evolved, the solid oxidized product would contain 33.1 per cent oxygen. It is known that some carbon dioxide, water, and other volatile products are evolved, but such measurements as have been already completed (Table I) indicate that the quantity is small and that this loss should decrease (Table IV) the percentage of oxygen in the solid film to approximately 31–32 per cent.

With the smaller percentages of trioleic glyceride, the figures agree closely with this. In those cases where the percentages of admixed trioleic glyceride are high, there is a definite drift of the figures towards 34 per cent. Apparently the presence of fluid trioleic glyceride facilitates complete

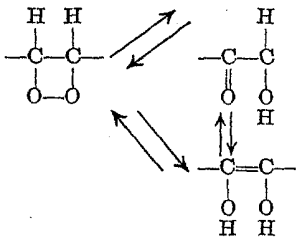
oxidation and minimizes the formation of volatile oxidation products.

Whole unextracted films of trilinolenic glyceride with drier equivalent to 0.2 per cent metal (lead, cobalt, manganese) contained 31.55 per cent oxygen (exposed inside 288 days) and 32.27 per cent oxygen (exposed outside 164 days).

These figures indicate that the composition of the entire unextracted film is nearly the same as that of the acetone insoluble (solid) phase and has apparently not only reached a maximum, but the maximum is nearly the theoretical maximum for this material.

It was logical also to follow the changes in the liquid phase by changes in ultimate analysis. However, the acetone apparently reacts with the liquid or else dissolves preferentially from the "embryonic structure" those portions richer in oxygen. At any rate, the acetone-soluble phase contains a higher percentage of oxygen than the solid insoluble phase (Tables II and VI). This helps to justify the premise that the liquid is not simply waiting for progressive oxidation to reach the percentage corresponding to the solid phase and then change over to solid.

It has been previously established by other workers that the peroxides first formed during the early stages of oxidation, as mentioned in the foregoing, undergo rearrangements involving formation of C=O and O—H groups as typified by the equation:



Gelation and film formation (drying) are ascribed to the attraction and association of these polar groups. If it is a matter of association (secondary attractions) rather than polymerization (primary valence change) or condensation, it should be possible to disassociate the films by use of solvents. Accordingly, the action of different types of solvents on films was studied. The results not only seem to strengthen the general premise of association but, on the basis that "like dissolves like," offer specific evidence of the existence of the polar C=O and O—H groups. This is brought out in Table II in which a series of different types of solvents was used which had boiling points as close together as practicable.

The larger percentages of liquid phase were obtained with those solvents that contained C=O or O—H groups. Hydrocarbons and ethers extracted a smaller percentage of the film.

In the course of this work many gels and films made from linseed oil were also extracted. The action of solvents on these was somewhat different from that in the case of trilinolenic glyceride. This is to be expected if we keep in mind that linseed oil is a mixture of mixed glycerides of stearic, oleic, linoleic, and linolenic acids. Acetone is a good solvent for raw linseed oil and for its polar oxidation products as discussed. Acetone therefore attacks the linseed oil films strongly. Alcohol is not a good solvent for linseed oil. The linseed oil films at various stages in their oxidation contain some O—H groups which would be attacked by alcohol. The film, however, contains up to 10 per cent of stearic acid chains which do not oxidize and 10 to 15 per cent more of oleic chains which can have only one polar spot as against three in the linolenic chains of the trilinolenic glyceride. In general, therefore, alcohol has less action on the linseed oil films than on trilinolenic glyceride films, but, on the other hand, the stearic and oleic chains increase the percentage of the film disassociated and dissolved by hydrocarbon solvents.

Tables III and IV should be considered together. In running down any vertical column, it can be seen that the percentage of acetone-insoluble solid phase decreases as the percentage of oleic acid increases. Trioleic glyceride, like other fatty oils, is soluble in acetone. The results are therefore exactly as expected. They are, however, suggestive of the conditions in oil films, particularly those containing high percentages of oleic and stearic chains.

In running along any horizontal line, the percentage of acetone-insoluble solid phase increases steadily as time goes on. This is not paralleled by steady increase in percentage of oxygen. On the contrary, the percentage of oxygen in the films, after reaching a maximum early in the life of the films, remains constant or decreases slightly except in the case of the films ridiculously high in oleic.

Acknowledgment

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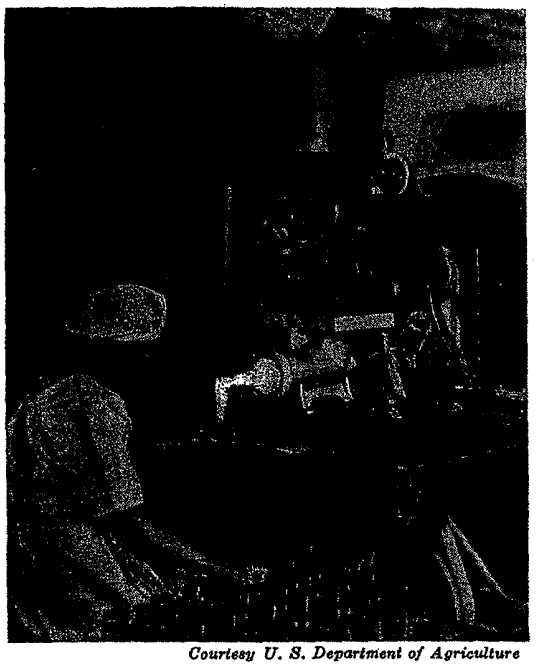

Courtesy U. S. Department of Agriculture

Peanuts Drop into the Tin Can at the Top of the Peanut Butter Machine and Are Forced Along by a Revolving Screw Which Carries the Peanut Mass through a Pair of Grinding Disks to the Discharge Spout