

NRL Report 4803

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# MECHANISM OF LINSEED OIL FILM DEGRADATION UNDER ULTRAVIOLET IRRADIATION

S. B. Crecelius and A. L. Alexander  
Protective Coatings Branch

R. E. Kagarise  
High Polymers Branch

Chemistry Division

July 31, 1956



NAVAL RESEARCH LABORATORY  
Washington, D.C.

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## ABSTRACT

Two films of linseed oil, one thick and the other relatively thin were irradiated with ultraviolet light in a closed cell filled with oxygen. Periodically infrared spectra of the gaseous content were obtained through the films during irradiation. The data indicate that the films break down into carbon dioxide, carbon monoxide, and low molecular weight aldehydes and ketones. The spectra showed that the rate of formation of carbonyl and OH and/or OOH groups for the thick film differed from that of the thin film. Methyl alcohol was identified in the gaseous phase of the decomposition of the thick film.

## PROBLEM STATUS

This is an interim report; work on the problem is continuing.

## AUTHORIZATION

NRL Problem C03-09  
Project No. NS 061-017  
BuShips ltr S19/1(347) Ser 347-767 of 21 July 1951  
BuShips ltr S19/1(347) Ser 347-491 of 29 April 1952

Manuscript submitted June 29, 1956

## MECHANISM OF LINSEED OIL FILM DEGRADATION UNDER ULTRAVIOLET IRRADIATION

### INTRODUCTION

It has been observed empirically for many years that drying oil films exposed to sunlight are subject to a much more rapid and different type deterioration than when retained indoors where there is very little ultraviolet light. This deterioration is manifested by a gradual wasting away of the film together with other well known aspects of film failure such as checking, cracking, blistering, peeling, etc. This wasting away of the film is most obvious when it is pigmented since the binding matrix of the film gradually disappears on the surface leaving the pigment in the form of chalk. This chalk is then washed away by the erosive action of wind and rain.

The chemical mechanism of deterioration induced by ultraviolet light has received little attention, possibly because it is rather difficult to study *in situ*. D'Ans and Merzbacher (1) attempted such a study by coating the inside of two flasks with drying oil which they sealed and exposed one to sunlight. By analyzing the contents of this flask, after several months exposure, they were able to detect a much higher content of carbon dioxide in the flask which had been exposed to sunlight than in the one which had not been exposed.

Kaufmann and Berger (2) observed that oil films sealed in ampules in the presence of oxygen required daylight for true film formation, while aging of similar films in darkness gave only soft gels. Elm (3) postulated that scissions in oil film structures which have been exposed to sunlight probably result in the formation of fragmentary products such as aldehydes, ketones, acid, and hydroxyl compounds. Such scission of a chain projecting from the main structural center probably produces small fragments without particular damage to the film. Scission in a chain connecting two molecular centers, however, results in considerably reduced molecular weights which would damage the film seriously. Elm did not base his theory on experimental chemical evidence but on empirical observations of films exposed to sunlight and compared with similar films retained indoors. In previous work at the Naval Research Laboratory (4) it was noted that films of linseed and dehydrated castor oil exposed to intense ultraviolet light, including rather short wavelengths ( $2600 \text{ \AA}^0$ ), lose weight continuously throughout exposure until they almost completely disappear. Infrared spectra were obtained simultaneously with weight checks. The results were as follows:

(1) The 2.93-micron band, indicating the existence of OH and/or OOH groups, decreased rather rapidly during the first six hours and reached a plateau beyond which there was no decrease from 6 to 14 hours. Subsequently this band decreased at a uniform rate throughout the remainder of the exposure.

(2) Absorbance at 3.4 microns, identifying  $\text{CH}_2$  groups, decreased uniformly throughout the entire exposure period.

(3) Absorbance at 5.73 microns, showing the presence of carbonyl groups also diminished uniformly throughout the exposure. A dehydrated castor oil film exhibited a slight increase in absorbance at this wavelength during the first two hours of irradiation followed by a uniform decrease thereafter.

This disappearance of the groups indicated by the spectra agreed with the total weight loss in both films. Together these facts suggest that there is a strong tendency of ultra-violet light to accelerate the decomposition of oil films and that this decomposition apparently occurs at a number of points.

## EXPERIMENTAL PROCEDURE

### Measurement of Thick Film Degradation

The ultimate products of decomposition from the drying oil films irradiated as above apparently are volatile and therefore do not remain in the film. In order to learn something of the nature of these products an experiment was designed to attempt their identification by infrared spectroscopy. Since the products are volatile, it was obvious that some means must be devised by which the breakdown of the film could be accomplished within a closed system. Such an arrangement would permit the determination of the nature and concentration of these volatile products following various periods of exposure. To accomplish this a cell was designed as shown in Fig. 1. Several cells were constructed from 5.5-cm glass tubing, sealed together in such manner as to provide four openings, any one of which was opposite another. A two-way stopcock was installed on two such cells. The edges of the openings were ground smooth to permit sealing by cementing onto them windows of potassium bromide crystals.

A film of linseed oil containing 0.3% Pb and 0.03% Co drier, based on the weight of the oil, was applied to one window. This film was rather thick (about 0.2 mm) to assure the evolution of sufficient gaseous products for study. The film was allowed to dry 24 hours at 25°C and 50% relative humidity following which the window was cemented to an opening of the cell with the oil film on the inside. The three remaining openings had been sealed previously by cementing potassium bromide crystals over them. The cell was evacuated to approximately 1/2 mm of Hg and filled with oxygen at a pressure slightly below atmospheric. Oxygen was used to insure an excess over that required for reaction with the film over a prolonged period. The slightly reduced initial pressure was intended to permit some additional pressure resulting from the formation of gaseous decomposition products within the cell.

As a point of reference, an infrared spectrum was obtained for the gas (oxygen) filled cell through the pair of clear windows. This spectrum is shown in curve A<sub>1</sub>, Fig. 2. The cell was then revolved through a 90-degree angle and a second infrared spectrum obtained through the window coated with the linseed oil film. This spectrum is shown as curve A, Fig. 2, and represents the spectrum of the film plus that of the cell (gas filled). The linseed oil film was then exposed to ultraviolet light from a No. 343 Mineral-Light lamp through the KBr window for periods of 2, 6, 14, and 30 hours, respectively, and an infrared spectrum was obtained at the end of each period. These spectra are illustrated in Figs. 2 and 3 by curves B, B<sub>1</sub>, C, C<sub>1</sub>, D, D<sub>1</sub>, E, and E<sub>1</sub>, respectively.

Interpretation of the Spectra — It is obvious from an inspection of the spectra in Figs. 2 and 3 that the film was too thick to permit a direct, comprehensive, and quantitative interpretation of changes occurring in the film. This excessive thickness extends absorption into the region below 10% transmission, which permits only a low degree of accuracy in determining the quantitative changes in absorbance. Hence, any quantitative significance attributable to changes in the film itself as illustrated by these shifts in absorbance, is minimized. The situation is further complicated by the fact that some absorption bands appearing as a result of changes in the gaseous phase coincide with similar bands resulting from absorbance of the film. Thus, any spectral reading through the cell reflects the additive effect of both the gas and film. This made it necessary to subtract the gas absorbance values from those of the film, where there were overlapping bands, before absorbance due to the film could be assigned any significance. Absorbance values for the film along with percent change from original values are shown in Table 1. These values are based, as before, on absorption bands at 2.93 micron (OH and/or OOH groups),

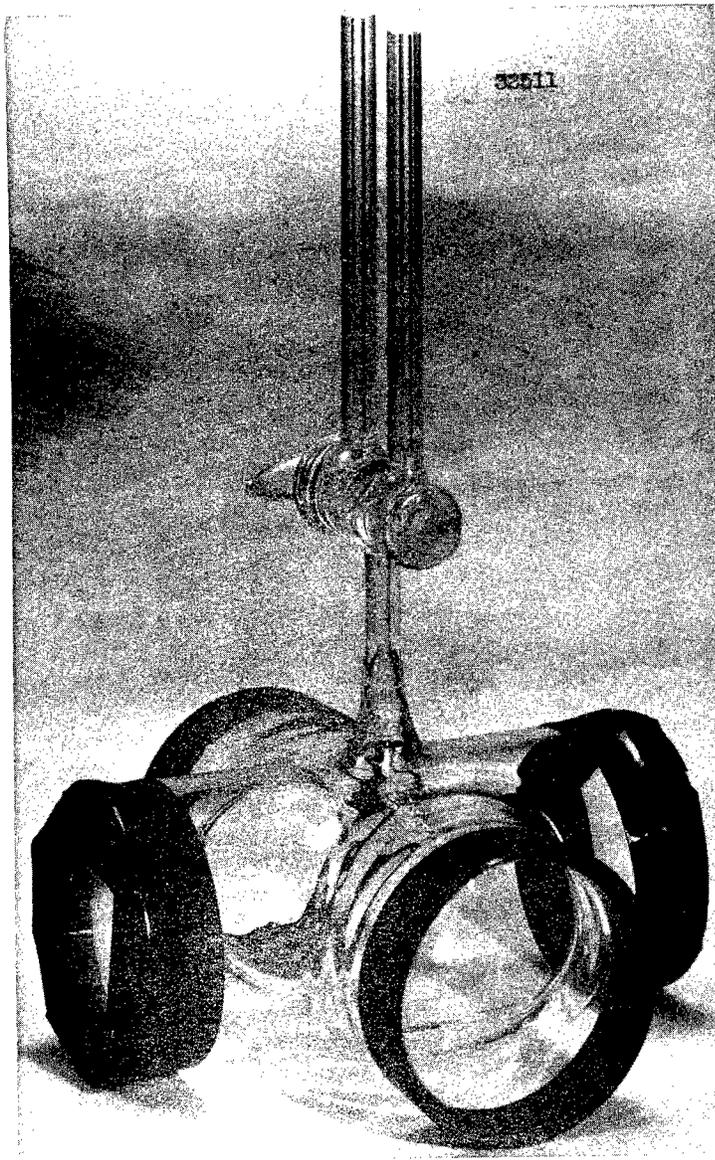


Fig. 1 - Infrared degradation cell

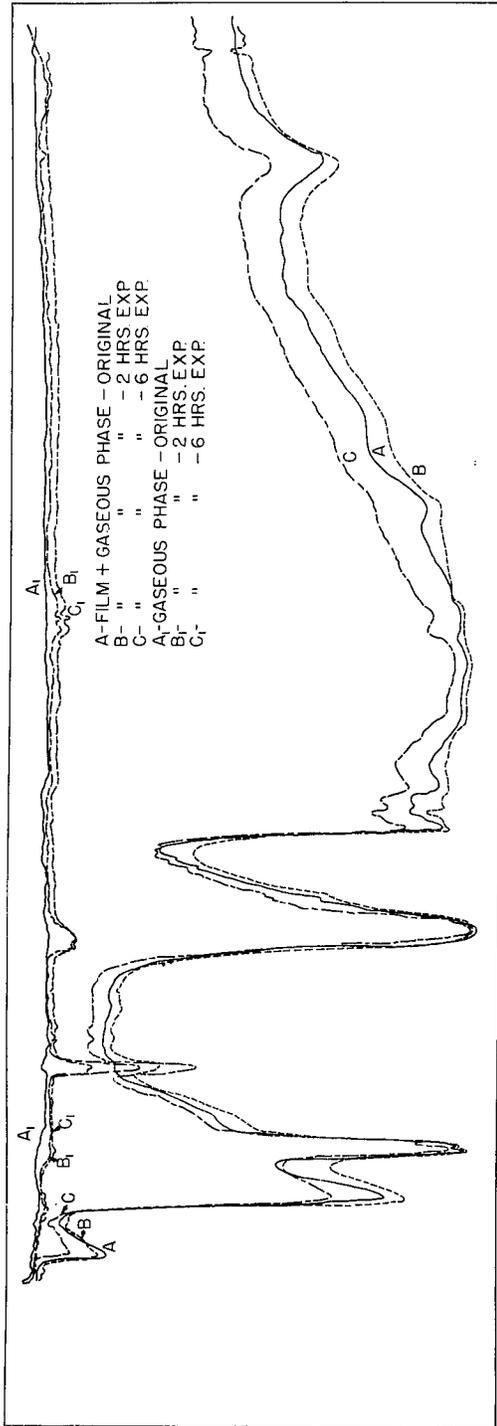


Fig. 2 - Infrared spectra of thick film degradation

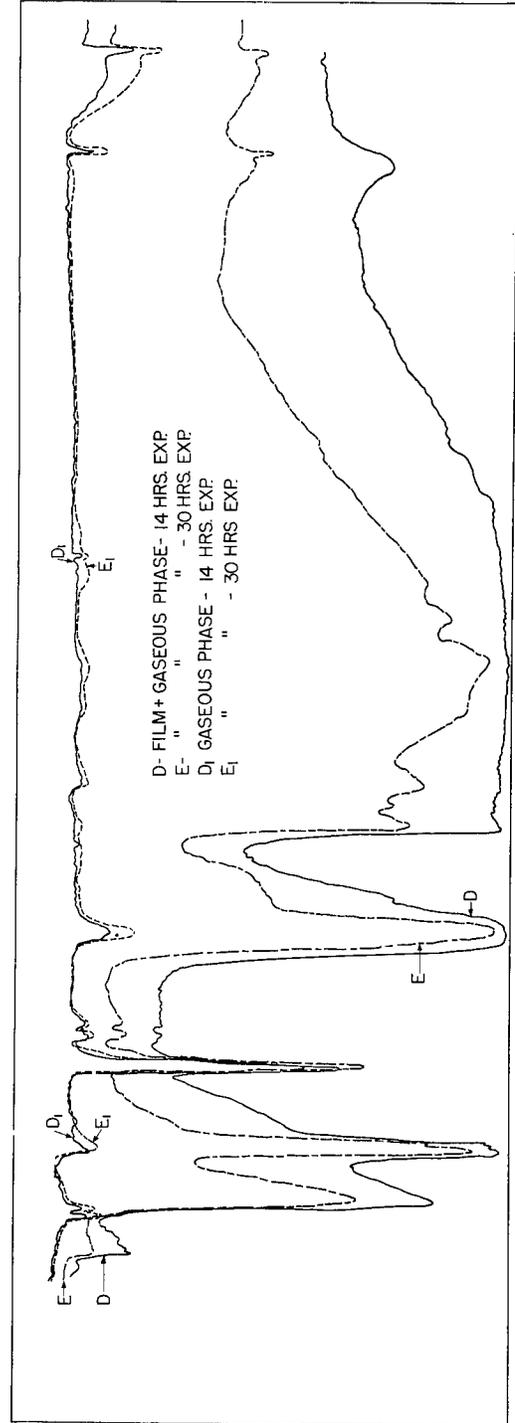


Fig. 3 - Infrared spectra of thick film degradation

3.4 microns (CH<sub>2</sub> groups), and 5.75 microns (carbonyl groups). It was at these points that the more significant changes in film absorbance took place, disregarding those bands which were due obviously to the gaseous components. Figure 4 shows the percent change in absorbance at these points plotted against time of exposure to ultraviolet. It must be kept in mind that as a result of the excessively thick film these values are relative only and are not truly proportional to absolute changes in weight due to shifting of the groups.

TABLE 1  
Film Phase on Exposure to Ultraviolet Light

Type Film	Exposure Time (hours)	Absorbance Values (corrected*)			% Change in Absorbance from Original					
		2.93 μ (OH)	3.4 μ (CH <sub>2</sub> )	5.7 μ (Carbonyl)	2.93 μ (OH)		3.4 μ (CH <sub>2</sub> )		5.7 μ (Carbonyl)	
					Gain	Loss	Gain	Loss	Gain	Loss
Thick (0.2 mm)	0	0.597	1.19	1.22	-	-	-	-	-	-
	2	0.670	1.16	1.083	12.2	-	-	2.5	-	11.25
	6	0.440	0.982	1.128	-	26.3	-	17.5	-	7.5
	14	0.730	-	-	22.3	-	-	-	-	-
	30	0.430	0.909	1.268	-	28	-	23	2.1	-
Thin (0.02 mm)	0	0.202	0.545	0.899	-	-	-	-	-	-
	4	0.210	0.364	1.054	3.9	-	-	33.2	17.2	-
	12	0.194	0.184	0.959	-	3.95	-	62.0	6.7	-
	30	0.104	0.058	0.282	-	69.5	-	89.0	-	69
	52	0.00	0.016	0.001	-	100.0	-	97.0	-	99.1

\*(Film A + Gaseous A) - Gaseous A = Film A

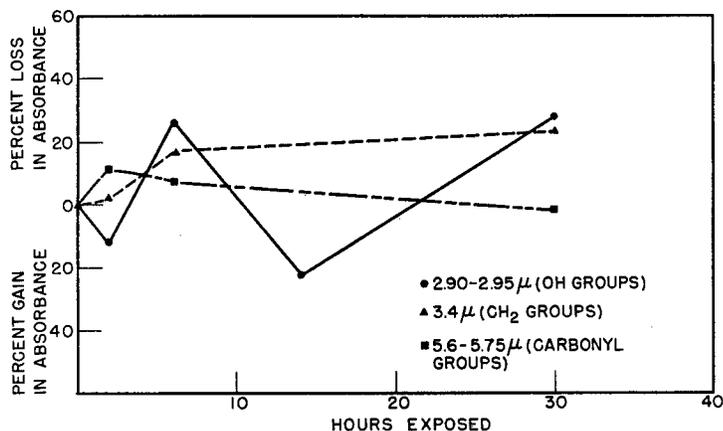


Fig. 4 - Film phase of thick film degradation

Infrared spectra of the gaseous products, obtained by passing the beam through the two clear windows, are shown in Figs. 2 and 3. The absorbance values of the several bands observed are given in Table 2. In Fig. 5 absorbance values are plotted against time of exposure.

TABLE 2  
Gaseous Phase on Exposure to Ultraviolet Light

Type Film	Exposure Time (hours)	Absorbance Values				
		3.4 $\mu$ (CH <sub>2</sub> )	4.27 $\mu$ (CO <sub>2</sub> )	5.65-5.75 $\mu$ (Carbonyl)	8.9-9.1 $\mu$ (Formic Acid)	9.7 $\mu$ (MeOH)
Thick (0.2 mm)	0	0	0	0	0	0
	2	0.010	0.054	0.027	0.018	0
	6	0.018	0.108	0.032	0.027	0
	14	0.046	0.332	0.065	0	0.027
	30	0.051	0.407	0.092	0	0.038
Thin (0.02 mm)	0	0	0	0	0	0
	4	0.042	0.073	0.086	0.06	0
	12	0.046	0.092	0.131	0.089	0
	30	0.067	0.147	0.163	0.089	0
	52	0.097	0.155	0.300	0.105	0

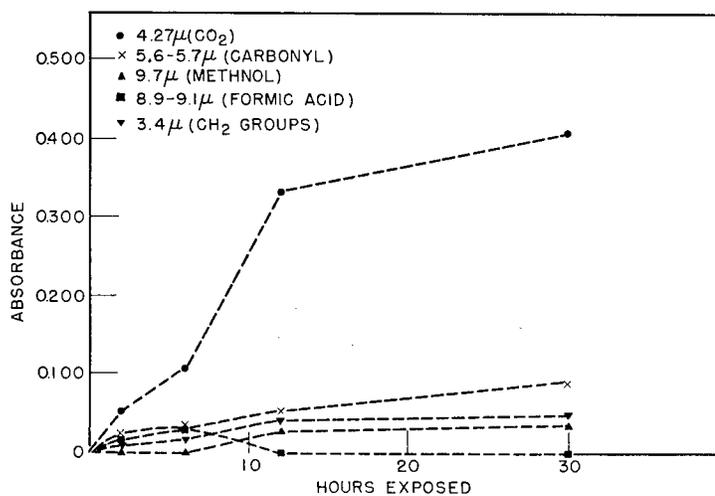


Fig. 5 - Gaseous phase of thick film degradation

Film Phase — Interpretation of the film spectra in Fig. 5 follows:

1. Absorbance at 2.9 to 2.93 microns (indicating OH and/or OOH groups) was essentially absent in the gaseous phase and hence no additive effect was involved. Absorbance increased slightly during the first 2 hours of irradiation indicating an increase in the number of these groups. A subsequent loss in absorption after 6 hours suggests that the decomposition rate of OH and/or OOH groups exceeded the rate at which they were formed. On the other hand, after 14 hours there was a substantial gain at 2.93 microns indicating that OH and/or OOH groups again were being formed faster than they were being decomposed; at 30 hours there was a substantial decrease in absorbance from which it can be concluded that decomposition again exceeded the rate of formation resulting in a net loss. This is at some variance with the previous study (4) where a plateau was reached between 6 and 14 hours exposure. Apparently the thick film allows the OH and/or OOH groups to be formed at a rate which exceeds the rate of deterioration at the film surface. This may account for the earlier observation (4) that the number of OH and/or OOH groups evidently remained the same while general deterioration was steadily continuing. As indicated by the plateau these groups probably were being replaced at about the same rate which they were being destroyed.

2. Absorbance at 3.4 microns ( $\text{CH}_2$  groups), after correction for that attributable to the gas, decreased rather rapidly up to 6 hours, and then decreased at a reduced rate throughout the remainder of the exposure. This suggests that  $\text{CH}_2$  groups were being lost during the entire exposure which corresponds to the earlier results (4). This is to be expected since there is little possibility of any formation of new  $\text{CH}_2$  groups.

3. Absorbance at 5.73 microns (carbonyl), after correction, showed a marked decrease up to 2 hours, beyond which there was a net gain of 2.1% over the original value. This behavior was in contrast to the previous work (4) where a decrease in carbonyl throughout was observed. An explanation may lie in the fact that the thick film held some of the volatile carbonyl components in solution as the deterioration occurred resulting in a net increase for the carbonyl in the film. Such a view is enforced by the fact that the ultraviolet light was applied through the window to the underside of the film. Since deterioration probably would take place more rapidly on the underside of the film, the chance of some carbon dioxide and degradation products being held within the film was increased. In the previous experiment (4) the ultraviolet light had been applied directly to the outside of the film.

Gaseous Phase — The spectra obtained through the clear windows involving only the gaseous products are interpreted as follows:

1. Absorbance at 3.4 microns, denoting  $\text{CH}_2$  groups, increased at a rather uniform rate throughout the entire exposure, indicating that an organic gaseous component containing these groups was being formed.

2. Absorbance at 4.27 microns, identified as carbon dioxide, increased uniformly during exposure up to 6 hours and then showed a rapid rate of increase up to 14 hours.

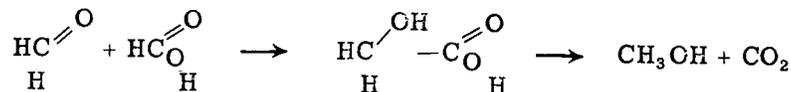
3. A parallel band which appeared at 4.65 microns after 14 hours exposure suggested the presence of carbon monoxide. This band remained at about the same strength after 30 hours exposure.

4. Absorbance at 5.64 to 5.75 microns (carbonyl) increased at a gradual rate throughout the entire exposure period.

5. A perpendicular band at 9.05 microns was apparent after 2 hours, increased very slightly by 6 hours, and then disappeared completely after 14 hours. This band was interpreted as characteristic of formic acid.

6. A perpendicular band at 9.7 microns, which appeared after 14 hours, increased slightly by 30 hours. This band was identified as characteristic of methanol.

The following postulation may be made from the above observations. Formic acid is produced during the first part of the exposure, while simultaneously another low molecular weight carbonyl compound, probably formaldehyde, is being formed. The formic acid then reacts with the formaldehyde to produce carbon dioxide, which increased rapidly between 6 and 14 hours, and methanol which also appeared after 14 hours.



Formaldehyde was not identified positively but it was assumed to be present by implication from the increase in the absorbance due to carbonyl groups in the low molecular weight range, and this view is supported further by the formation of methyl alcohol and carbon dioxide. The  $\text{CH}_2$  absorbance band at 4.27 microns increased at a much slower rate than the carbon dioxide band which suggests a more rapid conversion to carbon dioxide.

#### Measurement of Thin Film Degradation

In order to determine the effect of film thickness on the results from the foregoing experiment and to compare them with the previous work (4) where a thin film was exposed in the open, an experiment was repeated in the closed cell using a much thinner film (0.02 mm). Comparable measurements were made by irradiating the thin film with ultraviolet light for successive periods of 4, 12, 30, and 52 hours. The infrared spectra for the several exposure periods are shown by the curves in Figs. 6 and 7. Curves F and  $F_1$  are the spectra of the film plus gaseous and gaseous phases, respectively, before exposure to ultraviolet light. Curves G,  $G_1$ , H,  $H_1$ , I,  $I_1$ , J, and  $J_1$  show the spectra of the film plus gaseous and gaseous phases for exposures of 4, 12, 30, and 52 hours, respectively. Absorbance values at each pertinent wavelength were determined from these curves. These values are shown in Tables 1 and 2. The percent change in absorbance from the original also is shown in Table 1 and plotted against the time of exposure in Fig. 8. The increase in absorbance with exposure for the gaseous phase is shown in Fig. 9. Absorbance values for the film were corrected to compensate for the absorbance from the gaseous phase.

Film Phase — Interpretation of the film spectra in Fig. 8 follows:

1. Absorbance at 2.93 microns (OH and/or OOH groups) increases slightly in 4 hours, then decreases rather rapidly for the remainder of the exposure until it virtually disappears. This differs from the behavior in the thick film where the OH and/or OOH decreased and increased alternately throughout the experiment but such behavior does correspond closely with earlier work (4) in which a similar thin film was exposed in the open. This further enhances the assumption that in the thicker film OH and/or OOH groups are produced faster than they are decomposed at the film surface.
2. Absorbance at 3.4 microns ( $\text{CH}_2$  groups) diminishes throughout the entire exposure at a gradually decreasing rate until it has virtually disappeared. This also corresponds closely to the exposure of the thin film in the open. The percent loss based on the original was much greater than that for the thick film exposure.
3. Absorbance at 5.7 to 5.75 microns (carbonyl) showed a rather sharp rise for the first 4 hours. It decreased slightly after 12 hours but remained somewhat above the original. From this point on it decreased rather rapidly until a negligible amount remained.

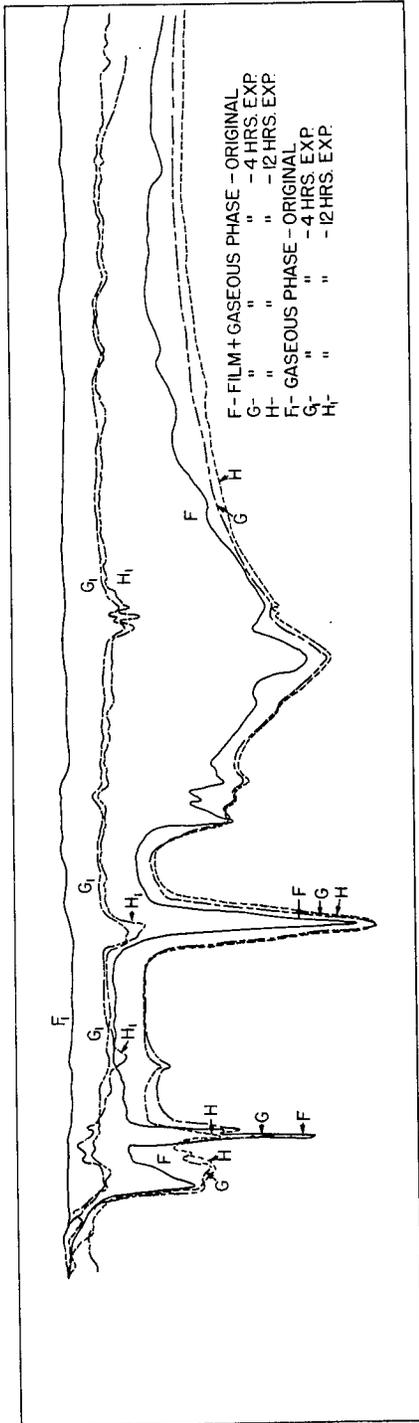


Fig. 6 - Infrared spectra of thin film degradation

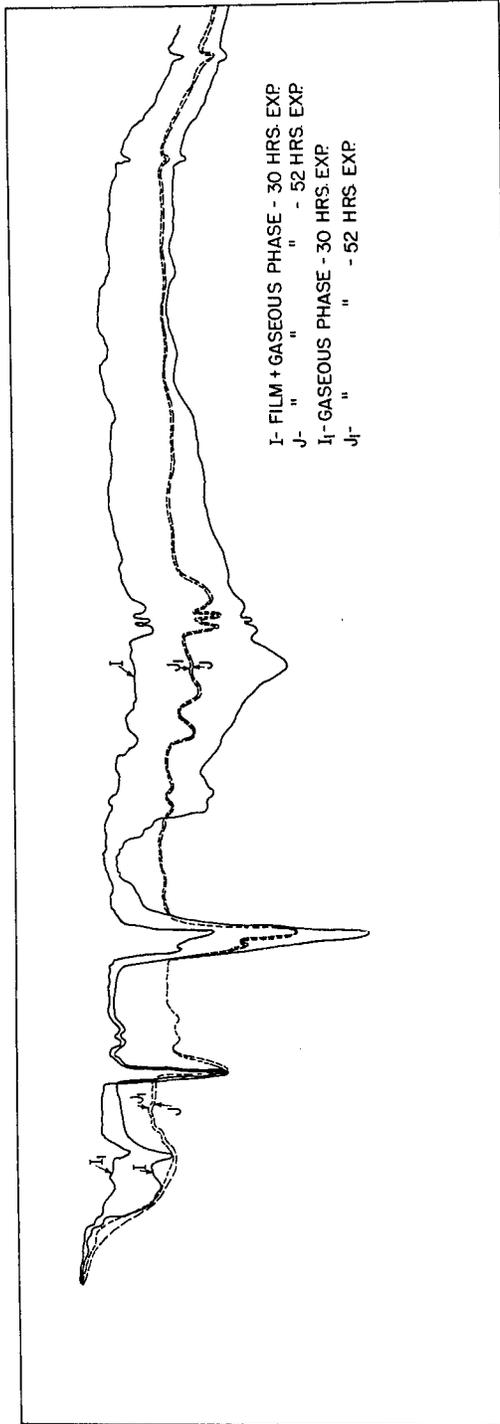


Fig. 7 - Infrared spectra of thin film degradation

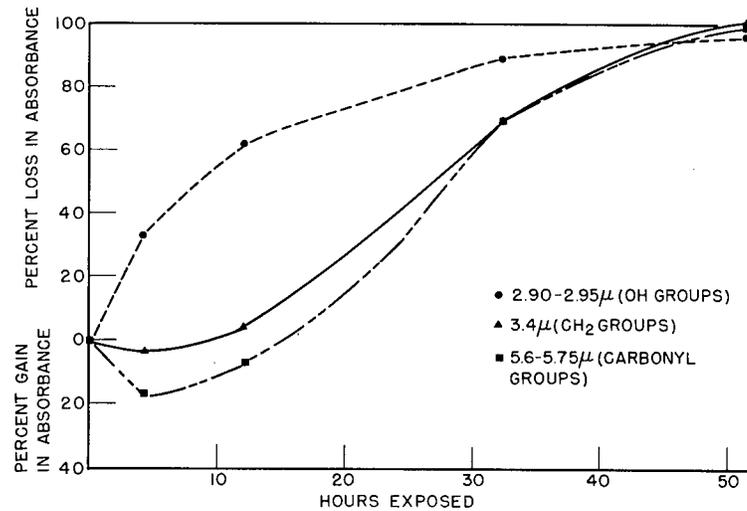


Fig. 8 - Film phase of thin film degradation

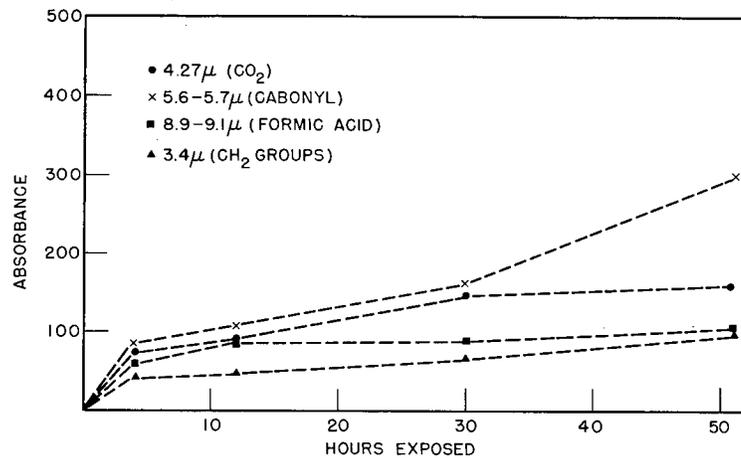


Fig. 9 - Gaseous phase of thin film degradation

Apparently enough film is present in the beginning to hold in solution some of the carbonyl produced by decomposition as in the thick film. As decomposition progresses and the film volume is reduced, the carbonyl is lost into the gaseous phase more rapidly than it is formed. This will be seen more clearly during the discussion of the gas spectra.

Gaseous Phase — Interpretation of the gas spectra from the curves in Fig. 9 follows:

1. Absorbance at 3.4 microns (CH<sub>2</sub>) appears at 4 hours exposure and continues to increase gradually at a uniform rate throughout the entire exposure.

2. Absorbance at 4.27 microns (CO<sub>2</sub>) was observed at 4 hours, increased moderately up to 12 hours exposure, and then increased only slightly during the remainder of the experiment. This varies from the thick film experiment where carbon dioxide increased rapidly between 6 and 14 hours and continued to increase throughout the experiment.

3. A parallel band at 4.65 microns, indicating the presence of carbon monoxide, began to appear after 52 hours of exposure.

4. Absorbance at 5.6 to 5.7 microns (carbonyl), on the other hand, appeared at 4 hours exposure and continued to increase rather rapidly during the entire experiment, with an increase in rate after reaching 30 hours.

5. Absorbance at 8.9 to 9.1 microns suggesting formic acid appeared at 4 hours, increased somewhat by 12 hours, and remained steady to the end of 30 hours. After 52 hours, however, it had shown a further increase. This is in contrast to the behavior of this band in the thicker film which had disappeared altogether at the end of 14 hours exposure.

6. No absorbance was evident at 9.7 microns, and hence no methyl alcohol was indicated. No categorical reason can be given for the appearance of methyl alcohol in the thick film irradiation and its absence in the thin film. Possibly as a result of the thickness of the film, more ultraviolet light was absorbed before it reached the gaseous layer thus producing less intensity in the gaseous layer and thereby setting up different conditions for reaction. This, however, is only speculation and offers little real basis for a valid conclusion.

#### SUMMARY AND CONCLUSIONS

The conclusions as substantiated by the results of this experiment may be summarized as follows:

The irradiation by ultraviolet light of two linseed oil films, one fairly thick (0.2 mm) and one thin (0.02 mm), produced a number of gaseous deterioration components some of which were identifiable.

Those products definitely identifiable during the irradiation of the thick film were as follows:

1. Carbon dioxide (3.4 microns) increased generally throughout the irradiation. This rate increase was most marked when the formic acid band (8.9 to 9.1 microns) disappeared and the methanol band (9.7 microns) appeared.
2. Carbon monoxide (4.65 microns) was observed after 14 hours and remained at approximately the same level during the remainder of the exposure.
3. Formic acid (8.9 to 9.1 microns) was apparent after 2 hours irradiation, increased at 6 hours, and disappeared completely after 14 hours.
4. Methanol (9.7 microns) was detected after 14 hours irradiation, coincidentally with the disappearance of the formic acid, and increased after 30 hours.
5. The  $\text{CH}_2$  band (4.27 microns) increased generally throughout the exposure, indicating that gaseous compounds containing  $\text{CH}_2$  were being produced. Formaldehyde was not identified definitely, but by implication it was concluded to be present based on the following reasoning.
  - a. The appearance and subsequent increase in intensity of the  $\text{CH}_2$  band, which cannot be attributed to any other gaseous compound containing  $\text{CH}_2$ , most strongly suggests formaldehyde.
  - b. The increase in carbonyl absorbance, all of which could not be attributed to formic acid, suggests formaldehyde.

- c. The apparent reaction of some compound with formic acid to produce carbon dioxide and methanol strongly suggests formaldehyde.

The products identifiable in thin film irradiation were as follows:

1. Carbon dioxide (4.27 microns) appeared here but to a lesser degree than in the thick film, and its rate of formation was more uniform throughout.
2. Carbon monoxide (4.65 microns) appeared definitely after 52 hours exposure.
3. Formic acid (8.9 to 9.1 microns) was present, continued to increase with prolonged exposure, and did not disappear as in the thick film experiment.
4. No methanol (9.7 microns) appeared at any time during the irradiation.
5. The  $\text{CH}_2$  band (4.27 microns) appeared more strongly than in the thick film and increased in intensity throughout the exposure.
6. Formaldehyde was present by inference for the same reasons mentioned before, except there was no evidence of its reaction with formic acid to form methanol and carbon dioxide.

The appearance of gaseous products was accompanied by changes in the film in both cases. These changes did not follow the same pattern in the thick film as they did in the thin one. In the former the production of OH and/or OOH fluctuated throughout the time of irradiation indicating that at times these groups were being produced in the film faster than they were deteriorating. In the thin film the OH and/or OOH increased slightly during the first four hours and decreased rapidly thereafter. Carbonyl groups (5.75 microns) in the thick film decreased slightly during the first two hours and increased thereafter, resulting in a net increase in the carbonyl of the film for the entire exposure. Two explanations are suggested: (a) more carbonyl groups are being formed in the body of the film itself; (b) the gaseous carbonyl fragmentary compounds are being held within the film in a soluble state. The increased carbonyl content of the gas phase from the thin film over that of the thick one points to the latter. The carbonyl content of the thin film increased only slightly during the first four hours and decreased rapidly thereafter.

The  $\text{CH}_2$  content of both films decreased throughout exposure. Percent loss in the thin film was much greater than that of the thick one.

The over-all deterioration was practically complete in the thin film at the end of 52 hours.

Generally, it may be said that continued irradiation of a linseed oil film with ultra-violet light will cause it to deteriorate into gaseous components composed for the most part of carbon dioxide and low molecular weight aldehydes and acids, with the possible formation of methyl alcohol depending upon the conditions.

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