**Chemical kinetics of photo-oxidative degradation of dried trilinolein film**
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# CHEMICAL KINETICS OF PHOTO-OXIDATIVE DEGRADATION OF
# DRIED TRILINOLEIN FILM

BY

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# CINETIQUE CHIMIQUE DE L'ALTERATION PAR OXYDATION A LA LUMIERE D'UNE PELLICULE DE TRILINOLEINE SECHEE

## SOMMAIRE

En vue de mieux connaître les processus fondamentaux de l'altération que subissent les revêtements extérieurs de peinture, des pellicules de trilinoléine séchée, détachées de leur support, ont été soumises à une altération dirigée. Les pellicules ont été exposées dans un espace fermé à diverses doses d'oxygène, de rayons ultra-violets et de vapeur d'eau, et la composition chimique des pellicules et des produits volatils dégagés a été déterminée périodiquement par spectrophotométrie à l'infrarouge.

La formation des composés carbonylés dans la pellicule de trilinoléine et le dégagement de composés carbonés volatils ont été attribués respectivement à des fractionnements de la chaîne moléculaire et à des coupures de l'extrémité de cette chaîne. L'ensemble de ces réactions permet d'obtenir une estimation de l'altération et des réactions non formatrices de pellicule qui se produisent à l'intérieur de la couche de trilinoléine durant les premiers temps de l'exposition.

# Chemical Kinetics

# Of Photo-Oxidative Degradation

# Of Dried Trilinolein Film

By R. S. YAMASAKI

National Research Council of Canada*

In a continuing effort toward better understanding of the basic degradation processes taking place in exterior paint coatings, free films of dried trilinolein were subjected to controlled degradation. Films were exposed to oxygen, ultraviolet radiation, and water vapor in a closed system in various combinations, and the changes in chemical composition of the film and of the volatiles evolved were analyzed periodically by infrared spectrophotometry.

The formation of carbonyl compounds in the film and the evolution of volatile carbon compounds were attributed to internal body scissions and end chain-scission reactions, respectively. Combined, these reactions give the measure of the deterioration and non-film formation reactions occurring in the film in the early stages of exposure.

## INTRODUCTION

A better understanding of the degradation processes that take place in paint film has become essential with the demand for more durable protective coatings. With respect to exterior house paint and in particular to its binder, linseed oil, Elm[1] has summarized the work on dried linseed oil film up to 1949; and Crecelius et al have since studied the chemical effects of ultraviolet radiation and oxygen on thick and thin dried linseed oil films by infrared spectroscopy.[2,3] Miller[4] and Cowan[5] have written more recent reviews. These show that when linseed oil is exposed to oxygen it oxidizes to form hydroperoxides at carbons adjacent to the double carbon-to-carbon bonds. Free radicals are formed and become carriers of film reactions. The hydroperoxides may, in turn, combine with the unreacted esters to form dimers and polymers (with perhaps peroxide or ether linkages) and solidify, or they may initiate chain reactions to split oil and polymers. On exposure to oxygen and ultraviolet radiation the polymers may further cross-link and gradually form brittle films or may break down to produce, among other substances, carbon dioxide and low molecular weight aldehydes and acids. Thus reactions pertaining to formation, non-formation and deterioration of film take place simultaneously.

The brief summary of the film reactions serves to show that reactions occurring in linseed oil are complex, although only oxygen and ultraviolet radiation have been considered, and are far from adequately understood. The important area of the effects of moisture has not been studied. Furthermore, towards obtaining a more balanced picture of the relative effects of the various degradative agents, the effects of radiation whose spectral distribution is similar to that of the sun should be considered. Because of the complexity of the film reactions, study of a system simpler than that of linseed oil, which is a mixture, would be desirable. These considerations led to the present investigation of the chemical kinetics of the photo-oxidative degradation of dried film of one of the components of linseed oil, trilinolein.

## EXPERIMENTAL

### Selection of Film Material

As linseed oil is a complex mixture of seven component fatty acids, it was decided to study a simpler replacement substance. The primary reactions involved in the drying and deterioration of linseed oil are oxidative[4] and the site of this oxidation is the double bond. It follows, therefore, that the reactivity of the oil is determined by the concentration of these bonds. Linseed oil consists mainly of triglycerides of three, two, and one double-bonded acids: linolenic, linoleic and oleic, respectively. The individual esters may be pure or mixed. Thus, esters with $(2 \times 3 = 6)$ six double bonds should represent the average reactivity of the components in oil. There are three possibilities (including one incorporating a saturated fatty acid), but only one ester consisting of three fatty acid radicals

all the same. Because the unmixed ester can be obtained in a purer state than the mixed one, glyceryl trilinoleate, or trilinolein, was chosen as the film material.

For driers, octoates of lead and cobalt were employed because they are non-oxidizing and can be obtained in pure form. They were added in minimum amounts to reduce contamination and yet produce a satisfactory dried film.

Free films rather than supported films were selected for study in order to provide double the surface for reaction and subsequent analysis, and to facilitate infrared analysis by obviating the difficulty of finding a substrate both inert and adequately transparent to IR radiation.

### Selection of Degradative Agents

Of the weathering agents to which exterior paint films are normally exposed, oxygen, ultraviolet radiation, and water vapor were considered for study. Gaseous tank oxygen (99.7%) was used for the test atmosphere.

The ultraviolet radiation should in the first instance simulate that of the sun with respect to spectral distribution. To isolate possible reactions promoted by different wavelengths, however, appropriate monochromatic radiations should be used. Radiations at two wave lengths were employed simultaneously, one at 3130Å to simulate short UV from the sun, the other at 3660Å to simulate long UV, with intensities comparable to those of the noon-day sun. Specifically, a Hanovia high-pressure, mercury-quartz lamp (435 watts) in conjunction with filter 6527B and heat-deflecting vycor 6527F was used. Prior to the exposure test the radiation output of the lamp was measured by the Division of Applied Physics of the National Research Council.[6,7]

It is known that water contributes to the degradation of paint films by causing swelling and leaching of the solubles.[8] Here the effect of the atmosphere initially saturated with water vapor was studied.

### Apparatus

CONTROLLED-ATMOSPHERE BOX—To minimize premature deterioration of trilinolein by oxygen prior to film preparation, it was desirable to prepare solutions in an inert atmosphere. A controlled-atmosphere box was designed and constructed of Lucite,® as is shown in *Figure* 1, in which necessary manipulations could be carried out in dry nitrogen, free of oxygen.

In operation the main chamber (127 litres) and an auxiliary transfer chamber (12 litres) were purged with certified high-purity, dry nitrogen ($O_2$ max. 20 ppm, $H_2O$<10 ppm) until the oxygen content in the effluent, as monitored with a Beckman Oxygen Analyzer, fell to 0.00%. Objects, some of which were flushed out with nitrogen beforehand, were introduced
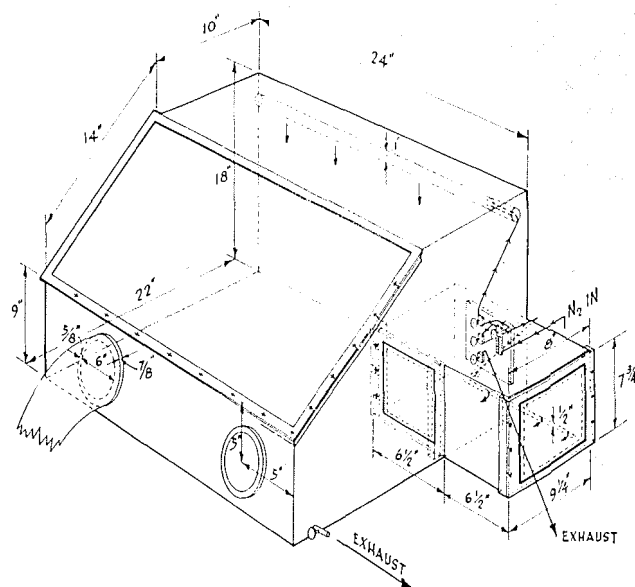
Figure 1—Controlled-atmosphere box for preparing drier-trilinolein solution in absence of oxygen

into the transfer chamber, purged of oxygen, then transferred into the main chamber. Gas valves were closed to prevent subsequent suction of air into the box and solutions were prepared gravimetrically. The box was repurged in the middle of operations to remove oxygen that had diffused into the system during manipulation, mainly through the rubber gloves. The oxygen content increased typically from 0.00 to 0.2% after use.

The box was constructed of 0.25-in. (0.64 cm) Lucite sections press-sealed with chloroform as solvent. Ports and the front window were made of 0.37-in. (0.94 cm) Lucite; the latter was removable and sealed with a 0.030-in. (0.076 cm) rubber gasket and wing nuts. Neoprene® gloves were used, and gloves and ports were sealed with 0.25-in. (0.64 cm) O-rings and 0.50-in. (1.27 cm) rubber tubings, respectively. Hollow gas inlet cylinders with 0.015-in. (0.038 cm) diameter holes spaced 2 in. (5.1 cm) apart were used to facilitate nitrogen gas distribution. The main chamber required 5.5 volumes of nitrogen at 3.6 litres/min to lower the oxygen content from 20.7 to 0.01%. Plumbing was of 0.25-in. (0.64 cm) copper tubing and vacuum-pressure valves.

EXPOSURE-INFRARED CELL—For the present kinetic study a non-destructive, relatively rapid method of analysis was required with a minimum of system disturbance. The infrared method was therefore chosen for film and gas analyses.

A number of exposure-infrared cells as illustrated in *Figure* 2 were designed and fabricated. The film is exposed in an appropriate atmosphere to radiation at position 1. At suitable intervals the cell is removed and placed in the infrared spectrophotometer and with the aid of ordinate scale expansion (20X) the spectrum of the gas is determined for analysis. The film is
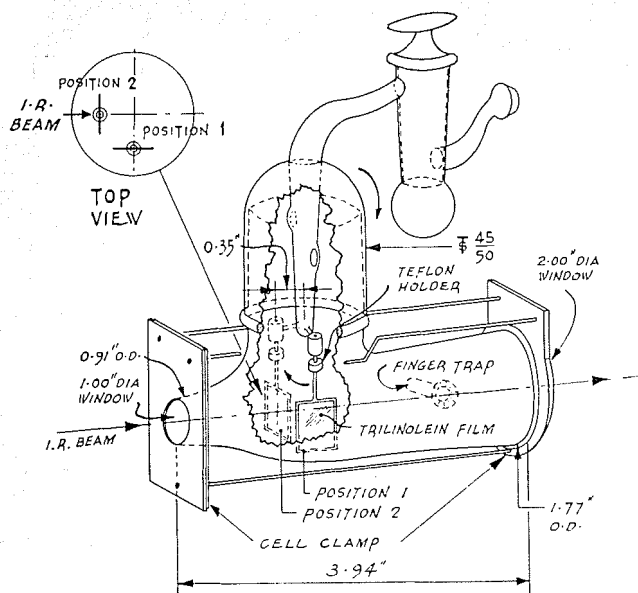
**Figure 2—Exposure-infrared cell in which both the exposure of the film and _in situ_ infrared analysis of the film and its volatile products may be carried out**

then moved to position 2 and the film and the gas are scanned at 1X. To obtain the spectrum of the film only, the gas spectrum is next run at 1X with film at position 1 and subtracted from the combined spectrum.

For exposure in a dry atmosphere, sodium chloride windows were usually used and sealed with Glyptal.® For a humid atmosphere, water-insoluble Irtran® 2 windows were employed. To maintain the original dry atmosphere the finger was kept cooled with liquid nitrogen.

Spectra from 10,000 to 650 cm$^{-1}$ were taken on a Perkin-Elmer Model 221 infrared spectrophotometer with sodium chloride prism optics.

### Study of Degradation

Experiments were designed so that the effect of each degradative agent could be studied. An ampoule containing 5 g of trilinolein (97% +) * sealed in nitrogen was opened in the controlled-atmosphere box in the absence of oxygen and a solution containing 0.030% lead and 0.025% cobalt as octoates was prepared gravimetrically. Drier solutions were previously de-oxygenated by bubbling nitrogen through them. About 1-ml portions of the solution were then dispensed in gas-tight, nitrogen-filled vaccine bottles and stored at —20 C to minimize deterioration.

Prior to initial film preparation trilinolein solutions were aged at room temperature for about 48 hrs. to allow driers to reach full effectiveness.[9] About 0.1-ml portions of the solution were removed with a syringe and free films 25$\mu$ thick were prepared by

Glyptal is a registered trademark of General Electric Co. Irtran is a registered trademark of Eastman Kodak Co.
* Hormel Foundation, Austin, Minnesota.

drawing the solution on a tin panel with a 12$\mu$ doctor-blade. The coating was allowed to dry overnight for 17 hr at 22± 1 C, relative humidity of 53± 1%, and under normal indoor illumination. It was subsequently loosened by mercury amalgamation of the substrate. Films were cut to suitable size and placed on rectangular (2.0 x 1.5 cm) pyrex rod frames with handles. Films relatively free of imperfections were selected for study to minimize premature rupture. The frame with the film was then mounted in the cell with the aid of a flexible Teflon® holder (_Figure_ 2) .

Cells containing one film each were evacuated and filled with the appropriate atmosphere at slightly less than atmospheric pressure: i.e., 69 cm of mercury. Atmospheres used were dry oxygen, water-vapor saturated (25 C) oxygen, and dry nitrogen. Dry oxygen was obtained by passing tank oxygen through a dry ice-acetone trap. Moisture-laden oxygen was generated by bubbling the gas via filter stick through water that had previously been oxygenated. Certified high-purity dry nitrogen was used without further purification.

Films were subjected to test exposure and infrared spectra of the films and atmospheres were taken at suitable intervals. Non-irradiated films were air-thermostated at 25± 1 C under normal indoor illumination. The irradiated films were maintained at 27± 1 C (higher due to radiation heating) . Exposures were usually run in duplicate. Films were followed up to 120 and 1200 hrs. for radiation—exposed and unexposed—films, respectively. The former period was short because of film rupture. As the primary volatile products may subsequently undergo further chemical changes, auxiliary check runs were made. Finally, calibration curves were determined for each volatile product and the analytical results were interpreted in terms of chemical changes in the film.

## RESULTS AND DISCUSSION

### Analysis of Volatile Products

The volatile products observed, identified and studied kinetically were formic acid vapor, carbon dioxide, carbon monoxide and water vapor. They were

Teflon is a registered trademark of E. I. du Pont de Nemours & Co., Inc.

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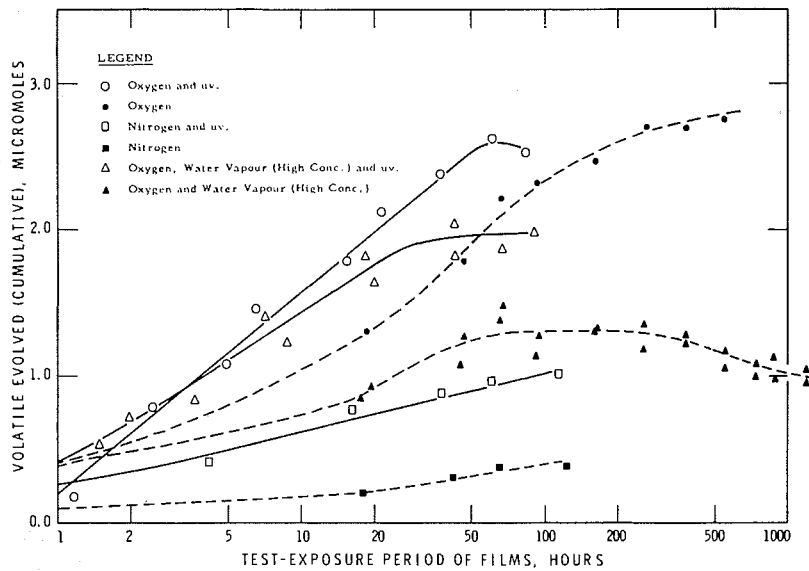
Figure 3—Kinetics of evolution of formic acid from trilinolein films exposed to different degradative agents

Figure 4—Kinetics of evolution of carbon dioxide from trilinolein films exposed to different degradative agents
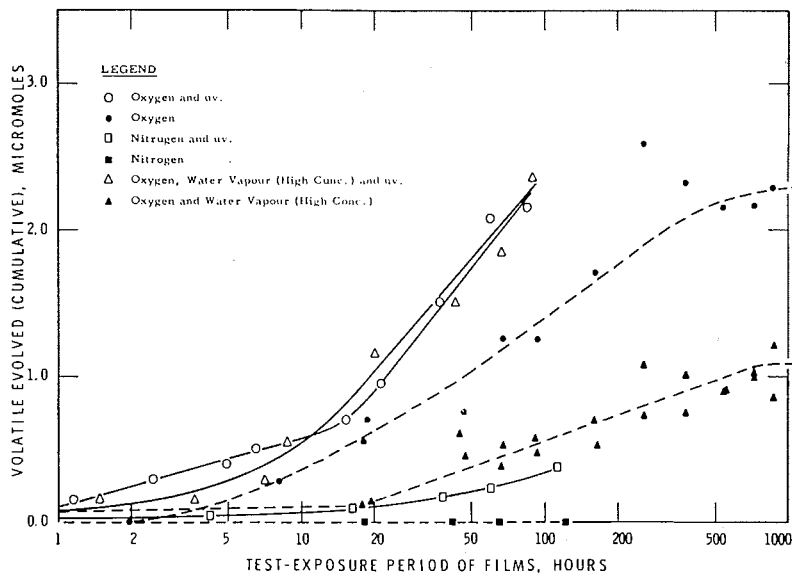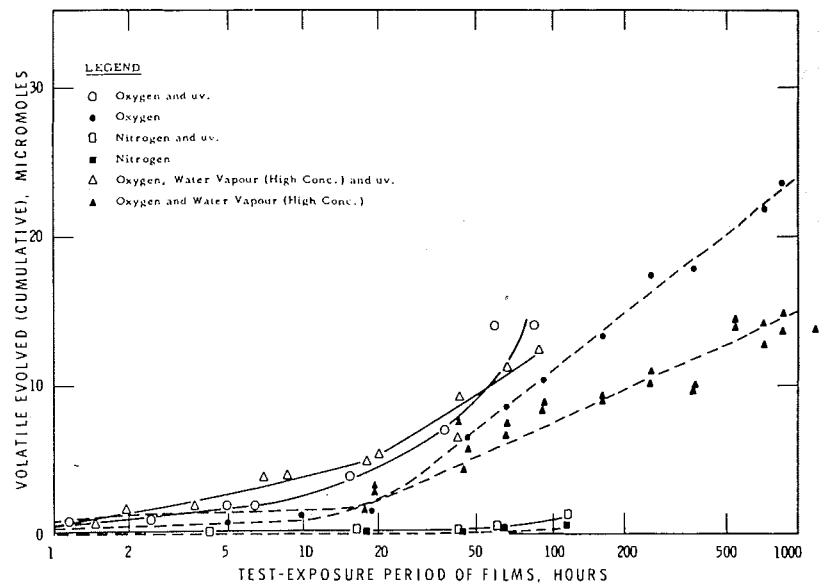
Figure 5—Kinetics of evolution of carbon monoxide from trilinolein films exposed to different degradative agents
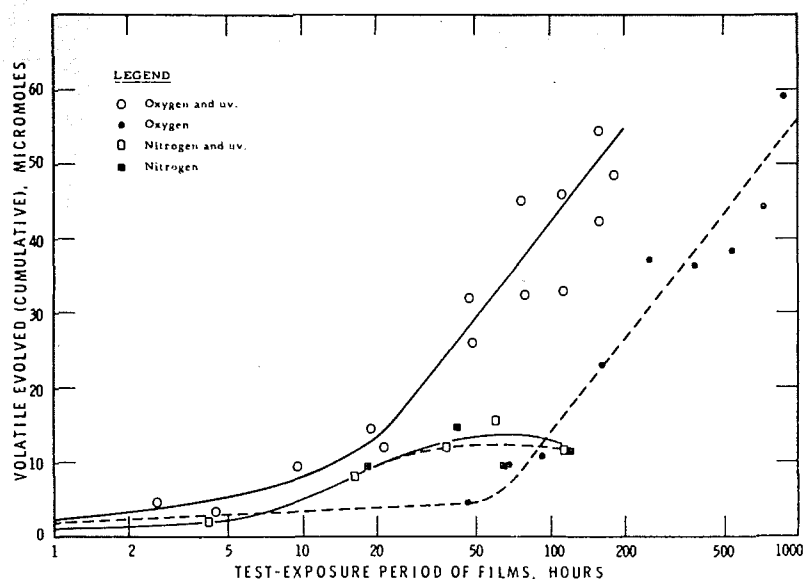
Figure 6—Kinetics of evolution of water vapor from trilinolein films exposed to different degradative agents

quantitatively analyzed by their bands at 1770 and 1122, 2300, 2250, and 1550 cm$^{-1}$, respectively.

Calibration curves for formic acid vapor were determined using 98% formic acid. Those of carbon dioxide and carbon monoxide were obtained by employing gas mixture G-7 (Phillips Petroleum Co., Special Products Div., Bartlesville, Okla.). Air of known relative humidity was mixed with dry nitrogen to draw up the water vapor curve.

The kinetic results for formic acid vapor, carbon dioxide, carbon monoxide, and water vapor are shown in *Figures* 3, 4, 5, and 6, respectively. The results for formic acid vapor are uncorrected for possible subsequent loss of the vapor in the test condition. For example, in an auxiliary run in oxygen atmosphere un-

der UV radiation, formic acid vapor concentration decreased as a first order reaction with specific reaction rate constant of 0.011 hr$^{-1}$. The other volatiles were not affected.

**Film Analysis**

As an illustration of changes observed, the infrared spectrum for the trilinolein oil and working spectra for the dried film and its corresponding atmospheres (before and after exposure to radiation and dry oxygen for 85 hrs.) are given in *Figure* 7. The bands at 967 cm$^{-1}$ and 910 cm$^{-1}$ show the presence of isolated *trans-trans* and *cis-cis* double bonds, respectively, in the original trilinolein oil. For the dried film subjected to ex-



A. Trilinolein Oil.    B. Cell and Atmosphere Before Exposure.    C. Cell and Atmosphere After Exposure of Film for 85 hr.

D. Dried Trilinolein Film, Cell and Atmosphere Before Exposure.    E. Dried Trilinolein Film, Cell and Atmosphere After Exposure of Film for 85 hr.
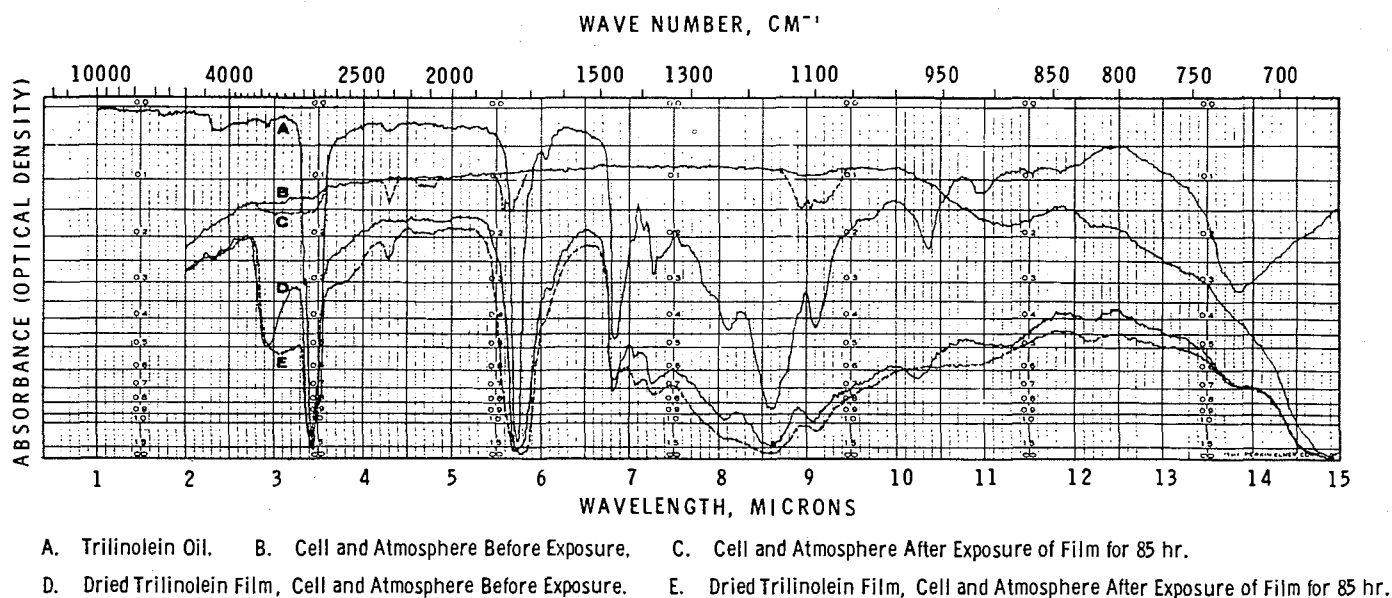
Figure 7—Infrared spectra of trilinolein oil; dried film and its environmental atmosphere before and after exposure to UV radiation in oxygen

Table 1—Composition* of Tack-Free Trilinolein
Film Dried for 13 Hours†[12]

| Functional Groups | Dried Film Wt. or Number 10⁻⁶ Mole | Original Oil (Theory) |
|---|---|---|
| 1. Peroxide* | 22 | 0 |
| 2. Hydroxyl | 28 | 0 |
| 3. Alpha glycolic group | 10 | 0 |
| 4. Unsaturated double bonds | 39 | 84 |
| 5. Carbonyl (ketonic, aldehydic) | 4-8 | 0 |

* For 14X10⁻⁶ mole equivalent in monomeric trilinolein. By analysis of reduced fatty acids.

† Dried at 21°C and 61% relative humidity. Drier content 0.025 per cent Co and 0.03% Pb.

** Analysis on original oxidized film.

posure the main changes occurred with bands at 3400, 1740 and 980 cm⁻¹. These consisted of changes in band intensity, band width and band peak frequency.

To make the intensity results of the bands amenable to comparison among films of different thickness and to allow for thickness changes of the film in the course of exposure, each absorbance value was corrected with reference to that of the corresponding methylene group at 1460 cm⁻¹ (a function of thickness). This is possible because the methylene group is relatively stable to oxidation and much of the population of the film is composed of this group; even if some of it is lost during degradation, absorption will primarily depend upon film thickness.[10] The baseline method[11] was employed to determine absorbance of the bands.

To aid in the interpretation of the spectra chemical analytical results for tack-free trilinolein film $31\mu$ in thickness and dried for 13 hrs. were used and are given in Table 1.[12]
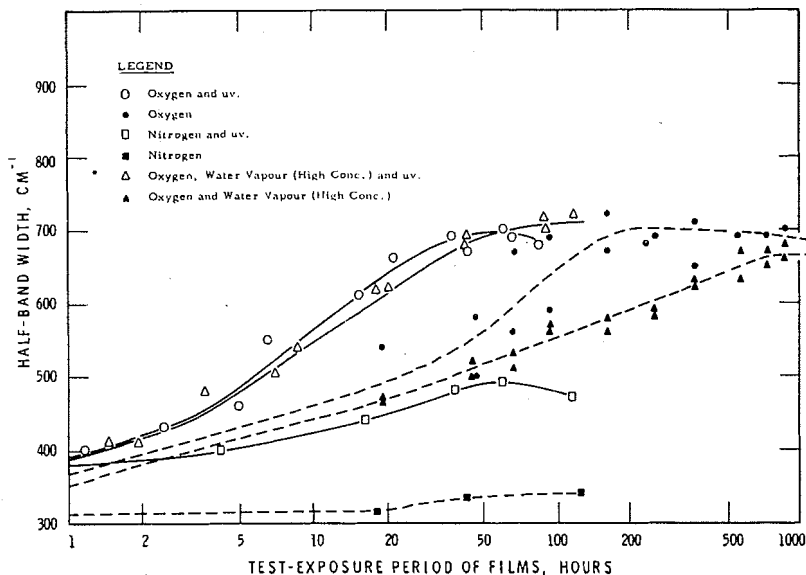
*3400 cm⁻¹ band*—Increase in band intensity and apparent half-band width and the apparent frequency shift of the absorption maximum at 3400 cm⁻¹ were

observed. Corresponding kinetics are illustrated in *Figures* 8 and 9. Shifts were found to be characteristic of the exposure.

The increase in absorption at the initial stages of exposure is probably caused by the formation of more hydroperoxide (3450 cm⁻¹), carboxylic acids and alcohols (*Table* 1). Broadening and shift of the band peak probably resulted from the increase in concentration and hence association of the monomers with polymers by hydrogen bonding.[13] Thus formation of formic and other carboxylic acids brought about increase in band intensity, and as the acid concentration increased the monomer (3500 cm⁻¹) reverted to dimer (3150 cm⁻¹), causing broadening and shift in band peak. The corresponding general increase in carbonyl band absorption at 1200 to 1300 cm⁻¹ tends to confirm this. Formation of monohydric and even dihydric alcohols in any significant amount would also result in monomer hydrogen bonding, with consequent shift in absorption bands as for acids. Here the band peaks are slightly higher, 3635 cm⁻¹ for monomer and 3500 cm⁻¹ for polymer.[13,14,15] The mixture of acid and alcohol hydrogen bondings could then account for the observed peak at 3225 cm⁻¹. For exposures in humid atmosphere some of the water vapor was sorbed by the film so that its infrared band at about 3350 cm⁻¹ [16] interfered with the normal analysis.

*1740 cm⁻¹ band*—The apparent half-band width of this carbonyl band increased on film exposure. The kinetics are given in *Figure* 10. The 1740 cm⁻¹ band is initially produced mostly by the carboxyl group of the ester as for the liquid in *Figure* 7. As the film dries and undergoes deterioration the band peak shifts to 1725 cm⁻¹ and broadens owing to the formation of carboxylic acids (1715-1690 cm⁻¹), ketones (1730-1600 cm⁻¹) (*Table* 1), and aldehydes (1740-1680 cm⁻¹) (*Table* 1). Here again, for exposures in humid atmosphere the infrared band at 1625 cm⁻¹ for water



Figure 8—Increase in apparent half-band width of 3400 cm⁻¹ band for trilinolein films exposed to different degradative agents
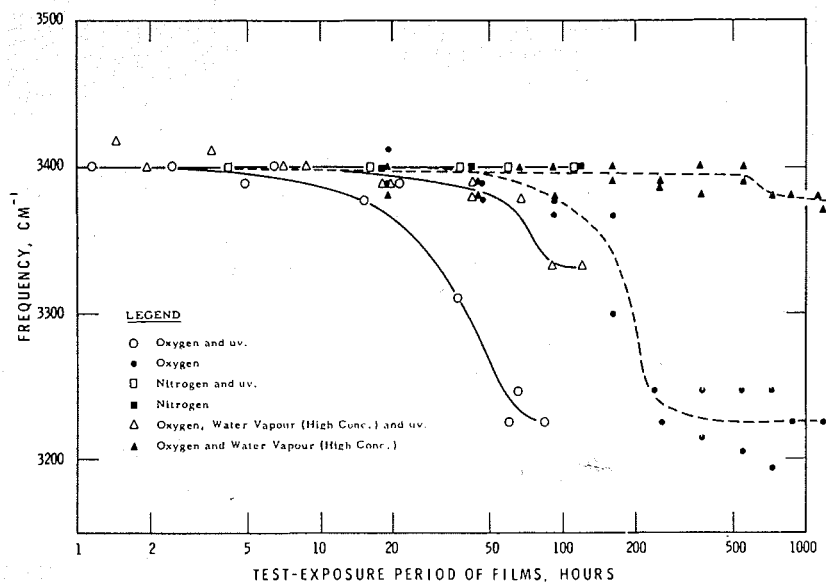
Figure 9—Apparent frequency shift of 3400 cm⁻¹ band peak for trilinolein films exposed to different degradative agents

Figure 10—Increase in apparent half-band width of carbonyl band at 1740 cm⁻¹ for trilinolein films exposed to different degradative agents
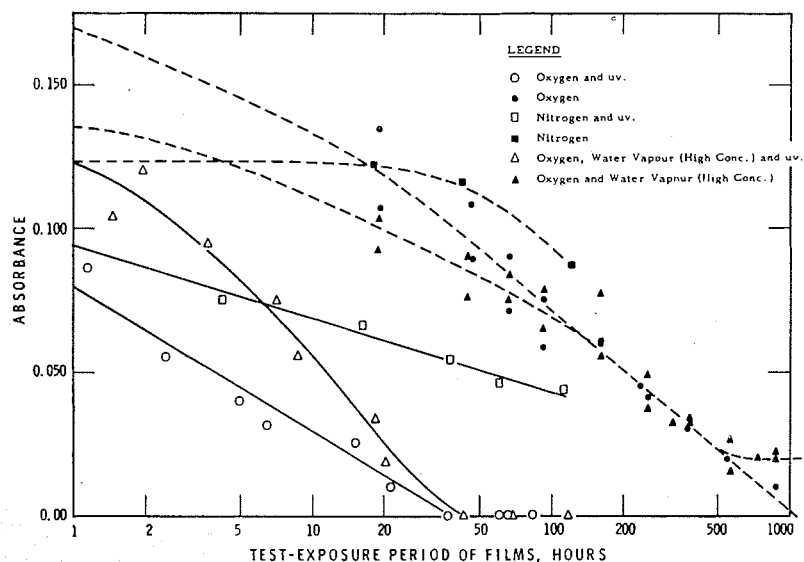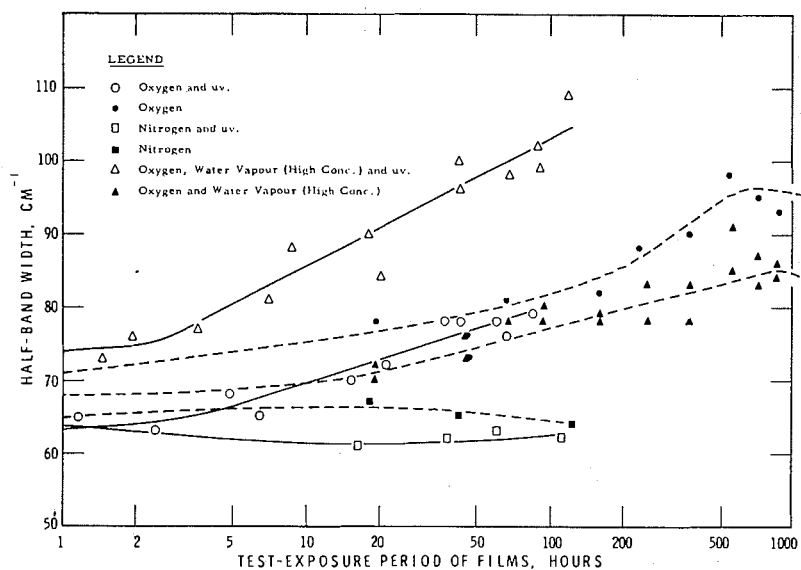
Figure 11—Decrease in intensity of *trans* bonding band at 980 cm⁻¹ for trilinolein films exposed to different degradative agents
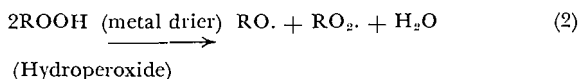
sorbed by the film interfered with the analysis, although to a lesser extent.

*980 cm$^{-1}$ band*—The band decreased in intensity and in some cases disappeared on film exposure. It may be attributed to a mixture of original isolated *trans-trans* (967 cm$^{-1}$) and conjugated *trans-trans* (988 cm$^{-1}$) bonds formed on hydroperoxidation (*Figure* 7); these were gradually destroyed (*Table* 1). The kinetics are illustrated in *Figure* 11.
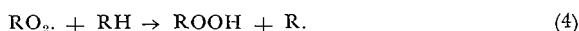
## INTERPRETATION OF RESULTS

In this study interest is centered on the deteriorations reactions. Nevertheless, as other reactions are taking place simultaneously in the film and some are even intimately connected with the degradation processes, the over-all reactions will be studied and interpreted to provide insight into the degradation reactions. Reactions will be classified as film formation, non-film formation and deterioration reactions, and probable mechanisms employing free radicals will be suggested. For convenience, reaction equations are given first. Thus:
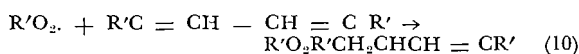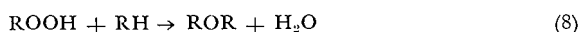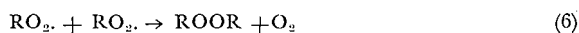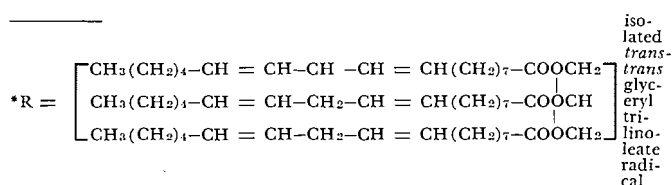
A. Initiation[5]

$$*RH + O_2 \rightarrow \, ^+R. + .OOH \tag{1}$$

$$2ROOH \xrightarrow{\text{(metal drier)}} RO. + RO_2. + H_2O \tag{2}$$

(Hydroperoxide)

B. Propagation[5]

$$R. + O_2 \rightarrow RO_2. \tag{3}$$

$$RO_2. + RH \rightarrow ROOH + R. \tag{4}$$

C. Polymerization and cross-linking[4,17]

$$RO_2. + R. \rightarrow ROOR \tag{5}$$

$$RO_2. + RO_2. \rightarrow ROOR + O_2 \tag{6}$$

$$RO. + R. \rightarrow ROR \tag{7}$$

$$ROOH + RH \rightarrow ROR + H_2O \tag{8}$$

$$\dagger R'OOH + R'H \rightarrow R'OR' + H_2O \tag{9}$$

$$R'O_2. + R'C = CH - CH = C\,R' \rightarrow$$
$$R'O_2R'CH_2CHCH = CR' \tag{10}$$

D. Non-film formation or cleavage[19]

$$\left. \begin{array}{l} ROOH \rightarrow CH_3(CH_2)_4\,CH = CH - CHO \\ \qquad\qquad\qquad \text{(2-octenal)} \\ + CH_3(CH_2)_4\,CHO \;\; \text{(n-hexanal)} \\ + CH_3(CH_2)_4\,CH = CH - CH = \\ \qquad CH - CHO \;\; \text{(2, 4-decadienal)} \end{array} \right\} = S \tag{11}$$

$$*R = \left[ \begin{array}{l} CH_3(CH_2)_4-CH = CH-CH -CH = CH(CH_2)_7-COOCH_2 \\ CH_3(CH_2)_4-CH = CH-CH_2-CH = CH(CH_2)_7-COOCH \\ CH_3(CH_2)_4-CH = CH-CH_2-CH = CH(CH_2)_7-COOCH_2 \end{array} \right] \begin{array}{l} \text{iso-} \\ \text{lated} \\ \textit{trans-} \\ \textit{trans} \\ \text{glyc-} \\ \text{eryl} \\ \text{tri-} \\ \text{lino-} \\ \text{leate} \\ \text{radi-} \\ \text{cal} \end{array}$$

+= free radical
† R' = polymer radical

$$S + O_2 \xrightarrow{h\nu} \underset{\text{(formic acid)}}{HCOOH} + CO_2 + \underset{\text{(acid)}}{RCOOH} + H_2O \tag{12}$$

$$R''CH(OOH) R''' \rightarrow R''COR''' + H_2O \rightarrow R''CO. + R'''. \tag{13}$$

E. Depolymerization[20,21]

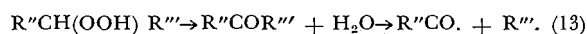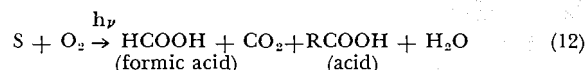$$R'CH_2OOR \rightarrow R'CH_2O. + RO. \tag{14}$$

$$R'CH_2O. + O_2 \rightarrow R'. + HCOOH \tag{15}$$

$$R'CH_2COR \xrightarrow{h\nu} R'COCOR \tag{16}$$

$$R'COCOR \xrightarrow{h\nu} R'CO. + RCO \tag{17}$$

$$R'CO. \rightarrow R'. + CO \tag{18}$$

$$R'CO. + O_2 \rightarrow RO. + CO_2 \tag{19}$$

$$R'CH(OOH)R \longrightarrow \underset{\text{(aldehyde)}}{R'CHO} + \underset{\text{(alcohol)}}{ROH} \tag{20}$$

$$R'CH_2CO. + O_2 \rightarrow HCOOH + CO_2 + H_2O + R. \tag{21}$$

When trilinolein film that has been dried in air for 17 hrs. is placed in an inert oxygen-free atmosphere, principally water vapor is evolved. Rate of evolution falls to zero rather rapidly, however, indicating initiation (equation (2)) and mostly polymerization and cross-linking reactions (equations (8), (9)). Small amounts of formic acid and carbon dioxide are also produced, probably from residue cleavage (equations (11), (12)) and depolymerization reactions (equations (15), (19), (21)). In the film further formation of hydroperoxide (equation (4)), hydroxyl (equation (20)) and carboxyl (equations (12), (15), (21)) products is terminated. *Trans* double-bondings are very slowly lost (equation (10)). In short, on exclusion of gaseous oxygen the reactions in the film, principally free radical formation and probably polymerization and cross-linking, proceeded until the oxygen was exhausted; then they terminated.

On exposure to UV radiation, though still in an inert atmosphere, the film evolved greater quantities of formic acid vapor and carbon dioxide and a small amount of carbon monoxide. These volatiles were probably produced by photolytic decomposition of the carbonyl compounds, ketones and aldehydes (equations (12), (16), (17), (18), (21)), by radiations at 3130 Å and to a lesser extent at 3660 Å. Thus chain-scission increased. In the film there was a slight increase in hydroperoxide and/or hydroxyl products, but none for carbonyl. *Trans* double-bondings were destroyed at a greater rate. Thus, radiation in the absence of oxygen increased deterioration, presumably by depolymerization and cleavage.

On exposure of the film to oxygen (in the absence of test UV radiation) the production of water vapor increased, signifying increased cross-linking reactions (equations (8), (9)). Formic acid and carbon oxides were evolved at a greater rate and quantity, indicating acceleration of chain-scission reactions. In the film

more hydroperoxides and/or hydroxyls and/or carboxylic acids were generated. The 3400 cm⁻¹ band peak shifted to a final position at $3225$ cm⁻¹, signifying increased concentration of carboxylic acids and alcohols, to form hydrogen bonded polymers. Carbonyl concentration increased. *Trans* bondings were more rapidly destroyed. This, coupled with the fact that *cis* bonds were absent, led to the conclusion that all double bonds were lost, so that further film formation through unsaturated hydroperoxide terminated. Thus it is clear that environmental oxygen is required for further polymerization and cross-linking, cleavage, and increased depolymerization of the film after initial drying and solidification of trilinolein.

The presence of UV radiation in addition to dry oxygen encouraged the formation of the products. As trilinolein oil, through drying, assumed a more viscous cross-linked structure, further polymerization reaction, which involves linking of two large molecules, is retarded because of lower mobility of the molecules in favor of cleavage of the molecules. Thus, more carbon oxides (equations (18), (19)) were produced, presumably through the absorption of UV radiation by the carbonyls. Increased formation of water vapor could signify greater depolymerization (equation (21)) and cross-linking (equations (8), (9)) reactions. Increase in changes in the 3400 cm⁻¹ band probably reflects the production of more carboxylic acids (equations (11), (12), (21)). The destruction of *trans* bondings was even more rapid (equation (10)). Thus UV radiation probably accelerated the cleavage, depolymerization and cross-linking reactions. Comparison of the present results with those of Crecelius *et al* with thin linseed oil film $(20\mu)$ [3] shows that carbon dioxide, carbon monoxide and formic acid were evolved in both cases although at different relative rates, but that no volatile carbonyls or formaldehyde were observed here. In the film the concentration of the carbonyl groups and the groups associated with the 3400 cm⁻¹ band as for linseed oil film increased rather than decreased during the exposure period probably because of the absence of short 2600Å radiation and milder intensity of radiation.

The presence of water vapor in high concentration in oxygen decreased the apparent rate of evolution of formic acid and carbon oxides as well as the formation of non-volatiles in the film. The 3400 cm⁻¹ band peak shifted only slightly to 3375 cm⁻¹. The water sorbed by the film produced a strong band at 3355 cm⁻¹ that dominated and masked the other adjacent bands. The film became soft and tacky, presumably through sorption of water vapor. In the process of oxidative polymerization and deterioration of the film, carbonyl and hydroxyl groups are formed. These are polar substances and sorb water vapor from the surroundings. As a result, the film imbibes water and undergoes swelling. In turn, the polar substances dissolve in wa-ter so that the film becomes tacky and weakens mechanically, eventually rupturing. Thus the presence of a high concentration of water vapor retarded the film reactions and mechanically weakened the film so that it ruptured. The results agree with Miller's interpretation[4] that water does not enter chemically into degradation reaction but leaches out solubles and contributes to mechanical stresses in the film.

Exposure of the film to UV radiation in the presence of highly humidified oxygen encouraged the rate of evolution of formic acid and carbon oxides and the formation of non-volatile alcohols, carboxylic acids and other carbonyl compounds. The 3400 cm⁻¹ band peak shifted more, to 3330 cm⁻¹. The rate of formation of the products was generally comparable to or slightly lower than that with UV and dry oxygen. Film became soft and tacky and ruptured after about 100 hrs. of exposure to radiation. Thus, more cleavage and depolymerization reactions probably took place, with possibly more cross-linking than without radiation.

## CONCLUSIONS

Trilinolein film, dried for 17 hrs. and subsequently exposed to oxygen, ultraviolet radiation, and water vapor, underwent chemical changes in the early stages that resulted in formation of hydroperoxides, hydroxyls, carboxylic acids, ketones and probably aldehydes, and destruction of *trans-trans* double-bondings. Volatiles were evolved in the form of formic acid, carbon dioxide, carbon monoxide and water vapor. These products probably formed as a result of reactions involving formation, non-formation and deterioration of polymer film.

With respect to degradation reactions occurring in the film, the increase in apparent half-band width of the carbonyl band gives a measure of the non-volatile ketones, carboxylic acids and probably aldehydes formed when the molecules undergo internal body scissions and break off relatively large molecules. Evolution of the volatile carbon compounds is probably mostly from the chain ends and as such gives the measure of the end chain-scission reactions. The evolution of water vapor may reflect both beneficial and detrimental film reactions. The first two, combined, then give the measure of the deterioration reactions occurring in the film in the early stages of exposure. Comparison of the rates of formation of the above products among different exposure conditions provides an assessment of the degrading quality of the exposure agents and may be listed as follows in descending order;

(a) Oxygen and UV,

(b) Oxygen, water vapor (high conc.) and UV,

(c) Oxygen,

(d) Oxygen and water vapor (high conc.),

(e) Nitrogen and UV,

(f) Nitrogen.

Oxygen is required in the deterioration of the film. Ultraviolet radiation promoted the degradation of the film by cleavage and depolymerization, presumably through absorption of the radiation by the carbonyl compounds. Water vapor slightly decreased the degradation of the film as far as chain scission is concerned. It made the film swell, however, and become tacky and lose its mechanical strength, and caused rupture.

## SUMMARY

In order to obtain better understanding of the degradation process taking place in exterior house paints, a pure constituent of linseed oil, trilinolein, was selected for study. Free films of trilinolein were prepared and subjected to controlled degradation in specially designed exposure-infrared cells. Films were exposed to oxygen, UV radiation and water vapor in various combinations in such a way that the effect of each factor could be studied. The changes in chemical composition of the film and of the volatiles evolved were periodically analyzed by infrared spectrophotometry. The results were interpreted in terms of reactions involving film formation, non-film formation, and deterioration of the polymer film. Finally, conclusions were drawn as to the type of deterioration reaction taking place, the relative effectiveness of the degradative factors and the mode of influence of each factor.

## ACKNOWLEDGMENTS

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