NOMENCLATURE

E = activation energy, gram-cal./gram-mole
e = base of natural logarithms
f = combustible concentration exponent
K = water gas equilibrium composition ratio at T
k = rate constant, (liters)$^{n-1}$/(° K.)$^{1/2}$ (gram-moles)$^{n-1}$ (sec.)
m = moles inert gas/mole of oxygen in air
N = air rate, gram-moles/sec.
n = over-all reaction order
P = pressure, atm. abs.
R = gas constant, 1.987 gram-cal./(gram-mole) (° K.) or 0.08206 (liter) (atm.)/(gram-mole) (° K.)
r, $r_{inj.}$, r_0 = radius at probe tip, injector sphere, and reactor wall, respectively, inches
T = reaction temperature, ° K.
T_0 = actual inlet mixture temperature, ° K.
T_{0E} = effective inlet mixture temperature (T_0 corrected for heat loss), ° K.
V = reaction volume, liters
x = mole fraction in combustion gases
y = ϕ for $\phi < 1$; $y = 1$ for $\phi > 1$
ϵ = fractional oxygen consumption efficiency
ϕ = equivalence ratio

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Drying Oil Oxidation Mechanism, Film Formation, and Degradation

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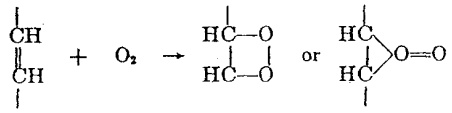
AMONG the more basic phenomena on which present protective coating technology is based is the oxidation of drying oils. One would expect a process so basic to the coatings industry to be the subject of intensive research, as in fact it has been for the past several decades. Nevertheless, as Powers (*18*) has stated in a recent review, the oxidation mechanism of unsaturated oils is still obscure due to the complexity of the oxidation products and the uncertainty of their structure.

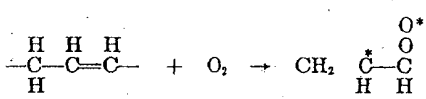
Progress toward an understanding of the oxidation mechanism has been hampered in the past by the inadequacy of the methods of direct chemical analysis. With recent developments of physical methods, however, particularly the techniques of ultraviolet and infrared spectroscopy, the scope of the analytical attack has been broadened considerably; it is by these means, coupled with the information already obtained on chemical structure, that the hope of obtaining more complete information of the autoxidation mechanism seems closer at hand.

PREVIOUS WORK

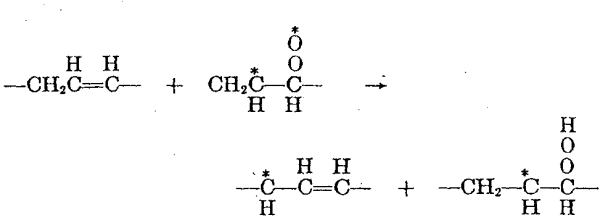
In recent years the older theory (*7, 14, 17*) that the peroxidation mechanism is due to the formation of a peroxide ring



has been challenged by the hydroperoxide theory of Farmer (*8, 9*) who postulates that the autoxidation of drying oils proceeds by a radical chain mechanism which results in the formation of a hydroperoxide group (—OOH) at the α-methylenic group adjacent to the double bond carbon atom. He suggests that the oxygen adds first at the double bond to form a biradical



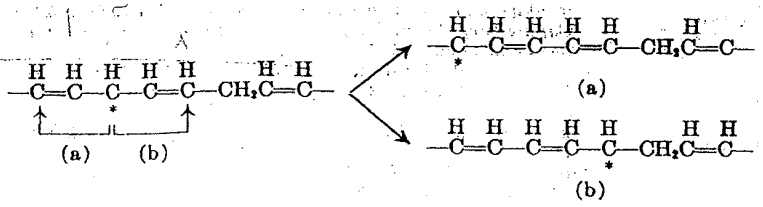
This biradical then combines with another unsaturated group to yield two radicals.

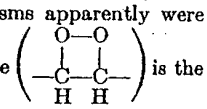


These radicals continue the chain reaction and lead to the formation of α-methylenic hydroperoxides.

As Powers (*18*) has commented, this explanation does not account for the uniform drop in iodine value during oxidation as found by previous workers (*2, 6*) except for the possible formation of conjugated systems which would give a reduced iodine value. However, it is difficult to explain by this means alone the extensive and uniform drop in iodine value which has been observed.

Farmer (*10*) has also advanced good evidence that conjugated systems are formed during the oxidation of fatty acids esters containing unconjugated double bond systems. He postulates that this mechanism is due to the activation of radicals and the methylenic groups which are flanked on either side by a double bond. These radicals presumably undergo the changes that result in increased conjugation



There have been many postulations as to the nature of decomposition products that are formed after the initial stages of autoxidation such as the dehydration of peroxides to form ketone groups (*18*), formation of monoxide groups by loss of oxygen (*3*), rearrangement of cyclic peroxides to form ketones and hydroxyls (*7, 11*), and the breakdown of the carbon chain to form aldehyde groups (*18, 20*). Since all these mechanisms apparently were based on the belief that the cyclic peroxide  is the dominant form of oxidation, they are more or less inconsistent with the later theory of Farmer.

These facts seem to be fairly well established

1. Oxygen is taken up by unsaturated drying oil films in the form of peroxides, most likely hydroperoxides.
2. This uptake of oxygen is accompanied by a drop in iodine value indicating a decrease in the degree or kind of unsaturation.
3. Conjugation of C=C groups occurs in the oxidized films.

With these facts in mind a study was undertaken in an attempt to clarify the autoxidation mechanism of drying oils by means of infrared spectroscopy. Although a number of such studies have been described in the literature, discrepancies in the existing data and their interpretation emphasize the need for additional work. In an initial effort, a preliminary spectroscopic study of the drying process in films of linseed and dehydrated castor oil was conducted. In addition, infrared spectra were obtained on similar films of these same oils that had been allowed to go through the preliminary stages of drying and were subjected to prolonged treatment with intense ultraviolet light; the spectroscopic analysis was made at various intervals of ultraviolet exposure.

EXPERIMENTAL

The infrared absorption spectra were measured with a Perkin-Elmer Model 21 over the wave-length interval 2 to 15 microns. The time required to scan this region was about 15 minutes. The experimental procedure was

1. Liquid films of linseed and dehydrated castor oil, approximately 0.02 mm. thick, were spread on a rock salt plate, and the spectra were observed immediately. The oils contained 0.03% cobalt and 0.3% lead driers based on the weight of the oil. Since the films were held in a vertical position during the scanning period, there were appreciable changes in thickness due to flow. This was especially serious during the first 4 hours of the oxidation process. However, by reversing the orientation of the plates on alternate runs and by using relative absorbance values, the effect of this thickness change was minimized.
2. Between runs the films were stored in a horizontal position under normal conditions of temperature and relative humidity (25° C. and 50%) in an artificially lighted room.
3. The spectra were observed at the time intervals, 0, 2.5, 4.5, 6.5, 7.5, 35, 90, 110, 155, and 200 hours.

The infrared spectra of a film of linseed oil obtained at various stages of the oxidation process are shown in Figure 1. Curve *A* was obtained immediately after spreading the oil over the surface of the plate and approximates the spectrum of nonoxidized linseed oil. Curve *B* shows the spectrum of the same film after drying 7.5 hours and Curve *C* after drying 90 hours. Figure 2 shows the same treatment of the infrared spectra of dehydrated castor oil.

DISCUSSION

The observed data are summarized and compared with the results reported by previous investigators. As a matter of convenience the data are presented according to spectral regions. Unless otherwise stated, the observed results apply both to linseed and dehydrated castor oil films.

2 to 3 μ. Perhaps the most profound spectral change observed occurred in this region; namely, the appearance and rapid development of an absorption band at approximately 2.93 μ. The absorption peak reached its maximum value after drying

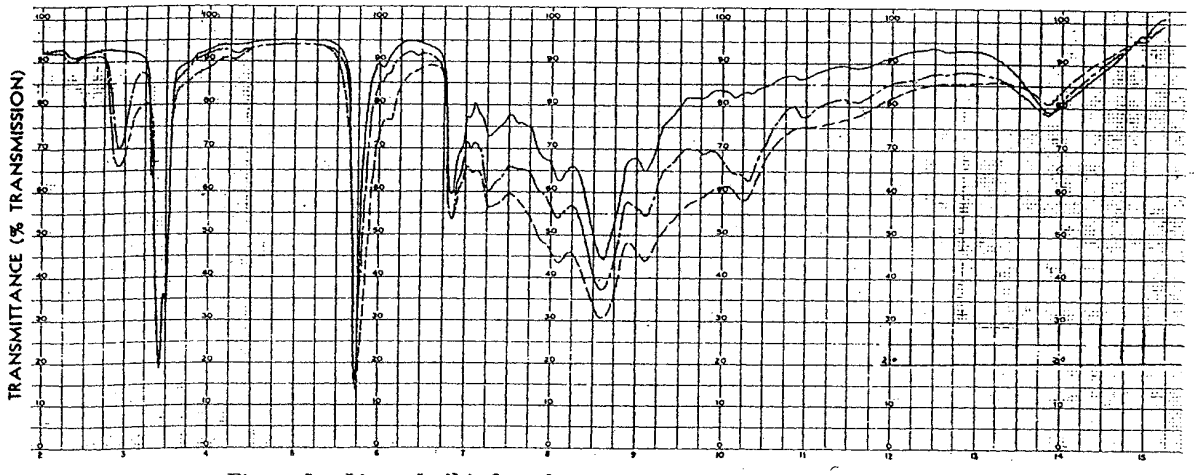


Figure 1. Linseed oil infrared spectra at various autoxidation stages

Sample: Linseed oil
——— 0 Hours (*A*)
—— - - 7.5 Hours (*B*)
— — — 90 Hours (*C*)
Prism: NaCl

Resolution: 927
Response: 2
Gain: 5.5
Speed: 2.2
Suppression: 2

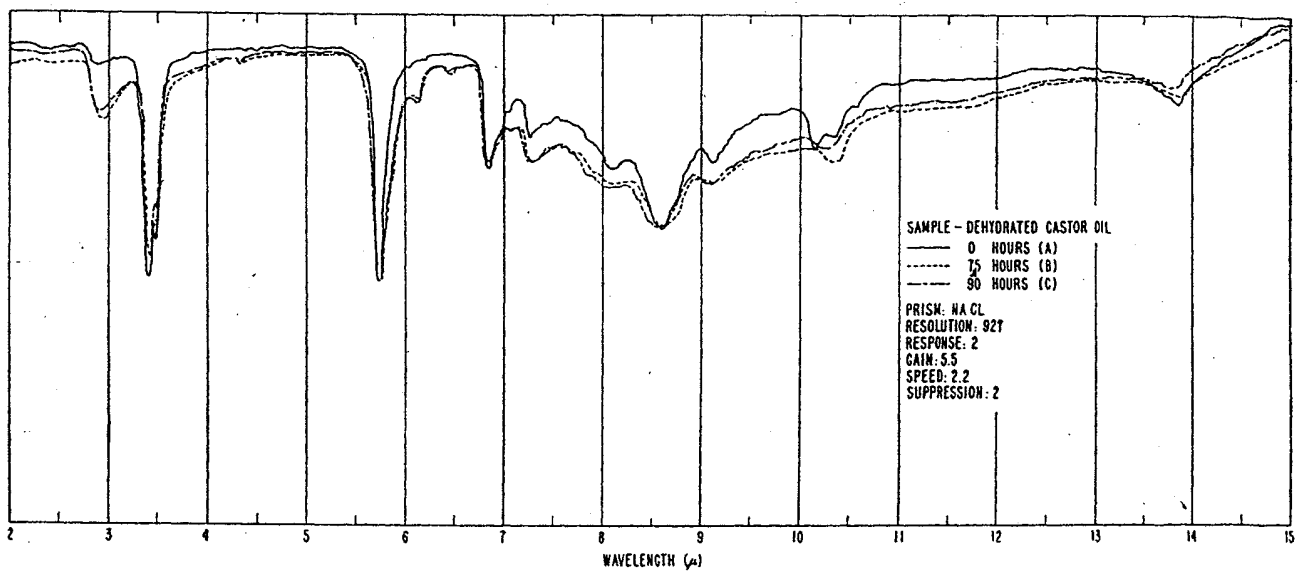


Figure 2. Dehydrated castor oil infrared spectra at various autoxidation stages

10 hours and remained essentially constant during the remaining period (190 hours). Previous investigators have attributed this band to various compounds containing —OH groups, the favorite one being hydroperoxide. Nicholls and Hoffman (*15*), in studying the pentaerythritol esters of linseed oil fatty acids, found a single band at 2.90 μ which they attribute to the hydroxyl groups of alcohols and hydroperoxides. Dugan and coworkers (*4*) observed two distinct bands at 2.91 μ and 2.88 μ in the spectrum of methyl linoleate which they assign to hydroperoxide (R—OOH) and alcohol (—OH), respectively. Adams, Auxier, and Wilson (*1*) have observed the appearance of a single band at 2.78 to 2.83 μ which they feel is due to the formation of hydroperoxides.

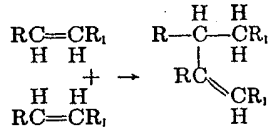
The most intensive investigation of this region to date is probably that of Honn, Bezman, and Daubert (*12*). They examined the autoxidation of linseed oil over a 10-hour period and have interpreted the 2.9 μ band as being a superposition of absorptions due to alcohol (R—OH), hydroperoxide (R—OOH), and carboxyl (R—COOH) groups. In addition, they have proposed a method whereby a quantitative estimate of the relative abundance of these three components is possible. This work is in disagreement, however, with the work of Overholt and Elm (*16*) who found little alcoholic content (about 2%) in oxidized oils. Because of the complexity of the oxidation process and the uncertainty of the reaction products, some of the assumptions of Honn and coworkers appear to be questionable.

Thus it is generally agreed that the appearance of the band at 2.9 μ in oxidized drying oils is due to the formation of some type of OH-group. However, the fundamental question as to the nature of these groups—e.g., alcohol, acid, hydroperoxide, or combinations thereof—does not appear to have a satisfactory answer in the existing spectral and chemical data.

3 to 4 μ. The only spectral change observed in this region was the rapid disappearance of an absorption band at 3.3 μ. Because of the limited resolution of the sodium chloride prism in this region, the band appeared as a shoulder on the strong absorption peak at 3.41 μ. Adams, Auxier, and Wilson (*1*) have reported similar changes in the spectra of some dipentaerythritol esters by means of a double monochromator of high resolution. They interpreted this band (3.27 μ) as being due to the C—H stretching mode of the carbon atom adjacent to the double bond—i.e., the α-methylenic group. This interpretation was apparently based on a paper by Sutherland (*23*) in which he states "in unsaturated hydrocarbons (including aromatics) some of the C—H frequencies, arising from C—H bonds adjacent to the unsaturated bond, occur at a shorter wave length (3.25 μ)."

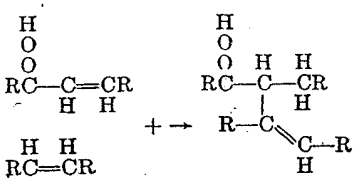
Sheppard (*21*), on the other hand, has interpreted the work of Sutherland and others on olefinic compounds by assigning the band at 3.27 μ to C—H linkages attached directly to the double bonds—e.g., the group R—CH=CH—R_2 has an absorption band at 3.30 μ, whereas, the group R_1R_2 C=CR_3R_4 has no absorption peak in this region. Thus the disappearance of the band under discussion does not substantiate the theory that oxidation occurs at the α-methylene group as concluded by Adams, Auxier, and Wilson (*1*) but rather indicates a reaction involving the double bond.

One view (*19*) that has been advanced is that vinyl polymerization is one of the principal means by which the drying or solidifying of an oil film takes place. If this mechanism occurs, the indicated action would be



Such a reaction mechanism is consistent with the observed decrease in the absorption at 3.27 μ, since it results in fewer CH linkages adjacent to unsaturated bonds. Furthermore, the decrease in C=C linkages also accounts for the drop in iodine value reported in the literature. In addition, it is well known that the presence of peroxide and hydroperoxide groups catalyze vinyl-type polymerizations.

Although the spectral changes discussed do not substantiate the theory of Farmer (*8*) that peroxidation occurs at the α-methylene carbon atom, they do not necessarily conflict with it. Thus the mechanism of Farmer and vinyl polymerization are compatible as this reaction occurs



4 to 6 μ. The outstanding spectral change with oxidation in this region is the broadening of the ester carbonyl band at 5.72 μ

toward longer wave lengths. Such a change would result from the production of carboxylic acids or ketones since both have absorption bands in the region from 5.75 to 5.85 μ. An alternative explanation is that an unresolved C=C band is increasing in intensity. Shreve, Heether, Knight, and Swern (*22*) have observed that peroxidation of unsaturated compounds (cyclohexenes) enhances the intensity of the C=C stretching mode. Nicholls and Hoffman (*15*) and Adams (*1*) have reported increases in carbonyl absorption with drying time.

6 to 7 μ. In previous infrared studies of drying oils no spectral changes were reported in this region for several reasons, the primary one being the presence of atmospheric water vapor absorption bands. Moreover, Shreve (*22*) has pointed out that bands due to C=C stretching vibrations are usually relatively weak. By using the double beam instrument the first of these difficulties was eliminated. The changes observed in this region were

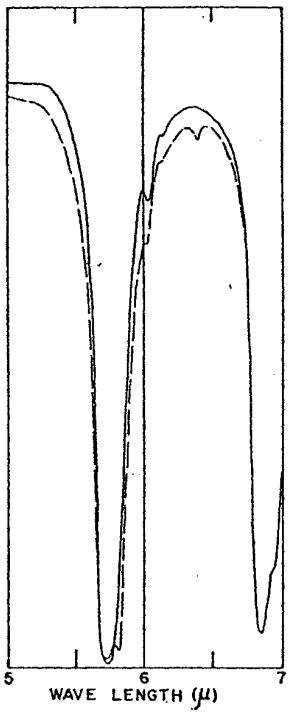


Figure 3. Increased conjugation effect on dehydrated castor oil infrared spectra

——— Untreated dehydrated castor oil
- - - Conjugated dehydrated castor oil

1. The weak band at 6.03 μ rapidly decreases in intensity and disappears after about 6 hours.
2. A band appears at 6.14 μ and increases in intensity; there is indication of a very weak band at this wave length in unoxidized dehydrated castor oil.
3. A weak band appears at 6.45 μ after a period of 2 hours and reaches a maximum value after about 35 hours of exposure. After a period of 200 hours this band was not observed for the linseed oil film and was barely discernible in the case of the dehydrated castor oil film.

Although these observations are preliminary in nature, they tend to show that a rearrangement of the double bonds occurs throughout the course of oxidation and such phenomena as cis-trans isomerization and conjugation are probably involved.

In an attempt to ascertain whether the origin of these bands is due in any way to increased conjugation, a sample of dehydrated castor oil from the same source as that employed was isomerized by a modification of the method of Kass and Burr (*13*) to increase the number of conjugated double bond systems present. This method consists of heating the oil in a medium of glycerol with an excess of potassium hydroxide necessary for saponification, for 24 hours at a temperature of 140° C. The acids are then freed, washed, dried, and re-esterified with glycerol. Diene values using the method of Ellis and Jones (*5*) are then determined for the isomerized product and the original untreated oil. The diene value of the treated product was 30.8 while that of the untreated dehydrated castor oil was 17.8. This indicates a substantial increase in conjugation in the isomerized product. This increase in conjugation resulted in the appearance of a weak band at 6.40 μ as shown in Figure 3 which tends to substantiate the view that the band at 6.45 μ in the oxidized film is also due to conjugation resulting from the autoxidation process.

7 to 10 μ. The spectral changes in this region were rather poorly defined and resulted primarily in a general increase in absorption with a subsequent loss of distinct absorption maxima. Changes in this region have been attributed to numerous functional groups such as esters, epoxides, hydroperoxides, ethers, and secondary alcohols. Because of a vast number of groups exhibiting characteristic absorption frequencies in this range, little if any reliable information appears to be available.

10 to 12 μ. Various investigators have previously reported changes in this region in the absorption spectrum of numerous drying oils. Nicholls and Hoffman (*15*) and Honn (*12*) have attributed the appearance of a band at 10.1 to 10.2 μ to the production of trans-ethylenic linkages. It is generally concluded that the naturally occurring fatty acids contain cis linkages only. Thus, the conclusion is that the geometric structure of the double bond changes on oxidation.

The band at 10.33 μ increases in intensity. Moreover, this increase is accompanied by a decrease in the intensity of the maxima at 10.15 and 10.98 μ. If the correlations that exist in the literature are taken at face value, an increase of 10.3 μ would indeed be indicative of an increase in the number of trans-ethylenic linkages. By the same token the existence of bands at 10.15 and 10.98 μ suggests the presence of an olefinic structure of the type $RCH{=}CH_2$; a conclusion that is inconsistent with the accepted structure of the fatty acid components of linseed oil. Sutherland (*23*) has pointed out that many exceptions to the rule for classifying compounds with ethylenic linkages have been observed. Thus, it is dangerous to form any conclusions concerning

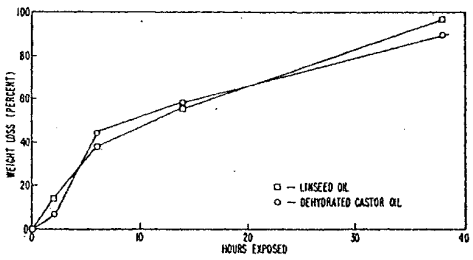


Figure 4. Percentage weight loss on exposure to ultraviolet light

cis-trans structures, particularly in those cases where two or three double bonds are present in a single chain. Additional spectral studies with pure compounds of this type will be necessary before reliable correlations exist between the C—H bending mode frequencies and the isomeric structures involved.

INFRARED STUDY OF OIL FILMS AT VARIOUS PERIODS OF EXPOSURE TO ULTRAVIOLET

Films of linseed and dehydrated castor were applied to potassium bromide plates and allowed to stand for 24 hours in a constant temperature room (24° C. and 50% relative humidity). At the end of this time the films were quite dry, having passed through the usual preliminary period of autoxidation. Prior to application of the films the potassium bromide plates had been weighed. After the 24-hour period the plates were weighed again and by difference the total weight of the dried films was calculated. The infrared spectra were then observed. The films were exposed to ultraviolet light emitted by a 110-volt Mineralight ultraviolet lamp Model No. 343 for intervals of 2, 6, 14, and 38 hours. The distance from the ultraviolet light source to the films was approximately 8 inches. The plates were weighed and the infrared spectra observed after each exposure period.

After each exposure to ultraviolet light a substantial weight loss was noted which increased progressively with exposure time. The results are listed in Table I.

Table I. Effects of Ultraviolet Light Exposure

Oil	Original Wt. after 24-Hr. Drying, Gram	Wt. Loss, Gram	Ultraviolet Exposure Time, Hr.	Original Wt. Loss, %
Linseed	0.0116	0.0016	2	13.8
		0.0044	6	38.0
		0.0064	14	55.0
		0.0112	38	97.0
Dehydrated castor	0.0087	0.0006	2	6.9
		0.0039	6	44.5
		0.0051	14	58.5
		0.0078	38	89.5

Table II. Elimination Rates for OH_2, CH_2, and C=O Groups from Films

Oil	Ultraviolet Exposure, Hr.	Absorbance Values 2.9 μ (OH)	3.42 μ (CH_2)	5.73 μ (C=O)
Linseed	0	0.265	0.900	1.040
	2	0.239	0.760	0.990
	6	0.178	0.630	0.940
	14	0.171	0.451	0.645
	38	0.095	0.169	0.207
Dehydrated castor	0	0.167	0.818	0.910
	2	0.164	0.715	1.040
	6	0.134	0.528	0.780
	14	0.134	0.385	0.615
	38	0.047	0.084	0.188

Figure 4 shows the percentage weight loss plotted against the time of exposure. These curves indicate that rates of weight loss for linseed oil and dehydrated castor when exposed to ultraviolet light are quite similar.

The infrared spectra observed after each period of exposure (Figures 5 and 6 for linseed and dehydrated castor oil, respectively) show a general decrease in absorption indicating a loss in film thickness. These decreases are particularly evident for the strong bands at 2.93, 3.91, and 5.73 μ previously assigned as being due to OH, CH_2, and C=O groups, respectively.

In order to determine the rate at which these various groups were being eliminated from the films, absorbance values were calculated for these bands, and the values are shown in Table II.

Assuming that Beer's law holds for the materials being investigated, the absorbance is directly proportional to the weight or concentration of the group causing the absorption. Therefore, by plotting absorbance percentage loss against ultraviolet exposure time, a curve should be obtained which would show the rate loss of the particular group comparable to weight loss. By this means it is possible to determine the extent to which each particular group contributed to the total weight loss of the films for each period of ultraviolet light exposure.

Figure 7 shows absorbance percentage loss plotted against ultraviolet exposure time in the bands at 2.9, 3.4, and 5.73 μ.

The 2.9 band is indicative of OH groups either as hydroperoxide, alcoholic OH, or the OH of a carboxyl group. The decrease in absorbance indicates the loss of these groups. For the first 6-hour exposure linseed oil shows a rapid decrease in absorbance in this region. For the next 10 hours a plateau is maintained in which no decrease in absorbance takes place. For the next 24 hours a steady diminution of absorbance is noted. The same general trend is observed for the dehydrated castor oil with a slightly lower rate for the first 6 hours.

The same treatment is given to the absorbance data of the band occurring at 3.4 μ—i.e., indicating CH_2 groups. Here a uniform curve is obtained for both oils which begins to level off at longer periods of ultraviolet exposure. This indicates that CH_2 groups are being lost at a gradually diminishing rate throughout the entire exposure. The slopes of the curves are practically parallel.

Absorbance is plotted versus time for the carbonyl band at 5.73 μ. The absorbance of the linseed oil decreases with exposure time in an almost linear manner. For the dehydrated castor absorbance increased slightly at 2 hours, continued to decrease at 6 hours, and then followed a linear decrease parallel to that of the linseed oil. It is hard to account for the increase shown at 2 hours. The instrument may have drifted due to the extremely low intensity at this point.

On comparing these curves (Figure 7) with that of the total weight loss versus exposure time (Figure 4), it is fairly obvious that loss of the groups—e.g., OH, CH_2, and carbonyl—indicated by the diminished absorbance in the bands at 2.9 μ, 3.4 μ, and 5.73 μ, respectively, all contribute to the total weight loss of the films. The more rapid weight loss sustained by the films during the first 6 hours of exposure is probably due for the most part to the more rapid loss of OH groups (probably hydroperoxide) indicated by the steeper slope of the curve at 2.9 μ during this period. The curves at 3.4 μ indicating the loss of CH_2 group are also steeper during this period although to a lesser degree than for 2.9 μ.

These weight losses are quite significant and illustrate the outstanding tendency of ultraviolet light to accelerate the decomposition of oil films in the presence of air. Overholt and Elm

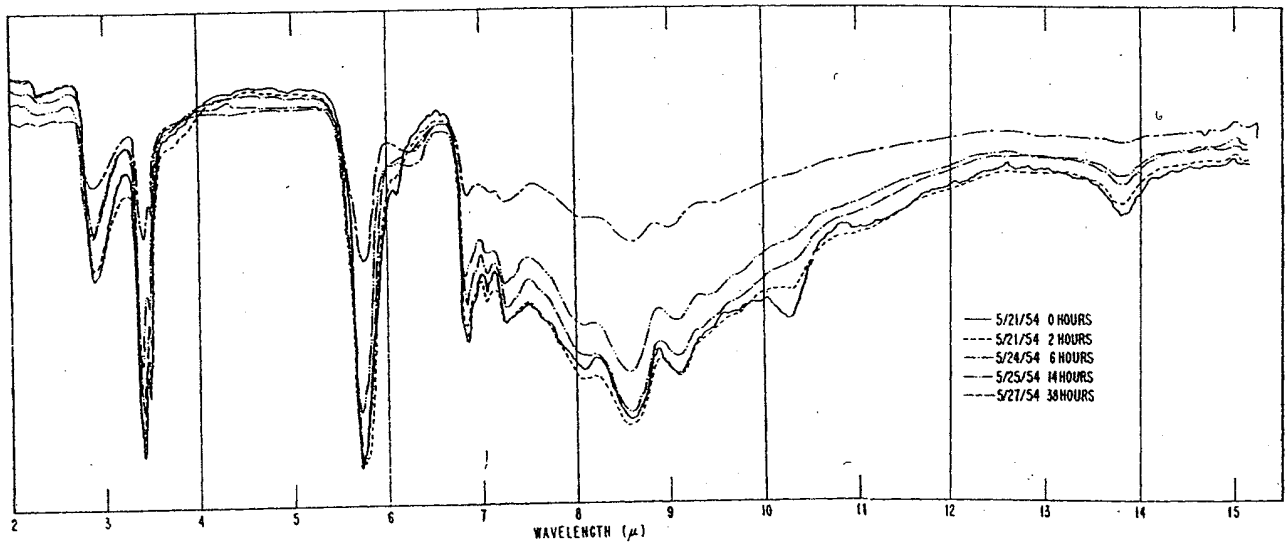


Figure 5. Linseed oil film infrared spectrum at various stages of ultraviolet light exposure

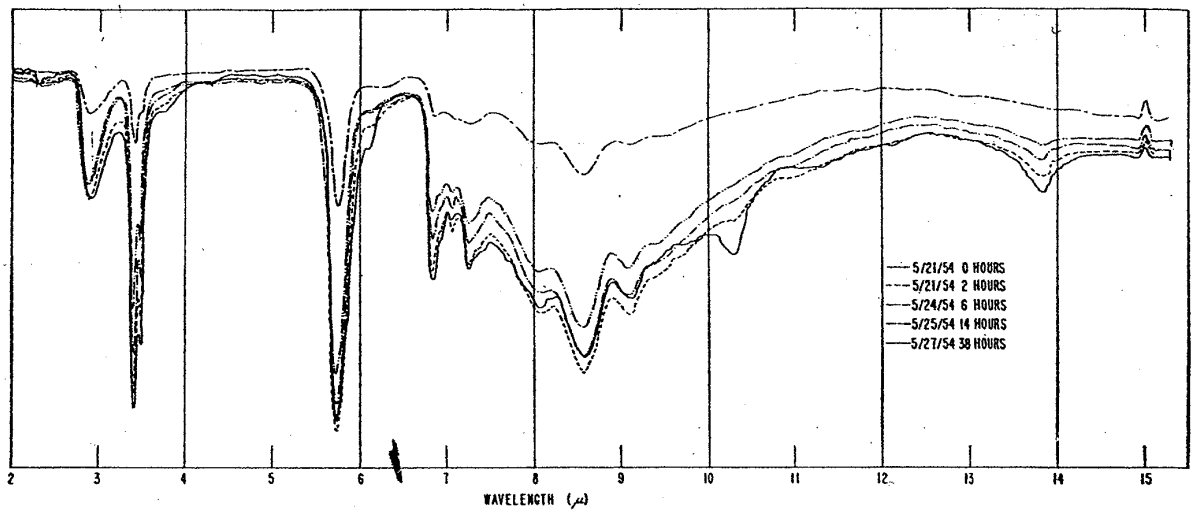


Figure 6. Dehydrated castor oil film infrared spectrum at various stages of ultraviolet light exposure

(*16*) also reported weight losses of oil films on prolonged exposure to ultraviolet light. This decomposition is apparently accomplished at a number of points. The final breakdown products of attack have not as yet been identified, but they are obviously low molecular weight products, possibly CO_2 and water or volatile organic compounds. An attempt to identify these products is planned by submitting similar films to ultraviolet exposure in a closed container in the presence of oxygen and subsequently determining the infrared spectra of the gaseous products evolved.

CONCLUSIONS

The results of this experimental work may be considered in two parts

1. The study of the autoxidation of linseed and dehydrated castor oil films under artificial lighting conditions at normal temperature and humidity by means of infrared spectroscopy.
2. The effect of ultraviolet light on air-dried (24 hours) linseed and dehydrated castor oil films as indicated by weight loss and change in infrared spectra.

With reference to the first part of the study the spectral changes observed during the oxidation of linseed and dehydrated castor oil may be summarized:

1. The appearance and rapid increase in the 2.93 μ region indicates formation of OH either as hydroperoxide or alcoholic hydroxyl together with a slight amount of influence due to carboxyl groups. These observations agree with the findings of earlier investigations. However, earlier studies have been able to determine chemically substantial amounts of peroxide in air-dried films, but there is little evidence from a chemical standpoint for the formation of alcoholic hydroxyls.
2. The disappearance of the band at 3.27 μ would indicate the replacement of hydrogens on the double bond carbon with some other radical, possibly by vinyl polymerization.
3. The broadening of the ester carbonyl 5.72 μ indicates the formation of additional carbonyl groups either carboxyl or ketone.
4. Changes in relative intensities of band 6.0 to 6.5 μ regions indicate changes in the number and arrangement of C=C linkages. The appearance of a band at 6.4 μ is apparently the result of a shift toward conjugation.
5. Increase in absorption at 10.33 μ with corresponding diminution of band at 10.15 and 10.98 μ is also consistent with a rearrangement of C=C linkages, particularly changes involving cis-trans isomerization.

The second part of the study dealing with the effects of exposure to ultraviolet light may be summarized

1. Both linseed and dehydrated castor films lost weight continuously with exposure to ultraviolet light. The rate of weight loss was highest for the first 6 hours of exposure. After 6 hours the loss rate decreased slightly and continued uniformly throughout the remainder of the experiment until ultimately after 34-hour exposure the linseed oil film had lost 97% and the dehydrated castor 89.5% of its total weight.
2. Infrared spectra of the two oil films indicate a continuing decrease in absorbance at 2.91 μ, 3.4 μ, and 5.73 μ for each period of exposure to ultraviolet. This decrease in absorbance was quite comparable for the two oils.
3. The decreasing absorbance at 2.9 μ indicated the loss of OH-groups either as hydroperoxide or alcoholic hydroxyls. The rate of this decrease was quite high for the first 6 hours. After a 6- to 14-hour exposure no decrease was noted. After 14 to 38 hours there was a uniform continuing decrease in absorbance at a somewhat lower rate than occurred during the first 6 hours.
4. The decreasing absorbance at 3.4 μ indicated the loss of CH_2 groups. The decrease in this region was continuous throughout with a gradually lowering in rate for prolonged exposure.

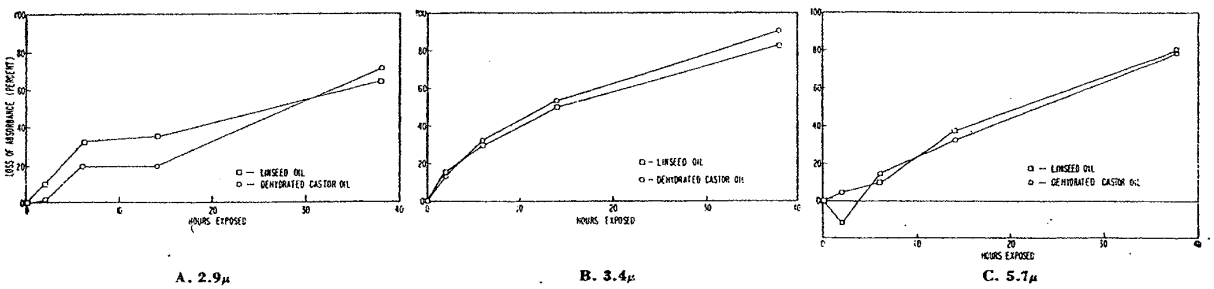


Figure 7. Absorbance percentage loss versus ultraviolet light exposure time

5. The decreasing absorbance at 5.73 μ indicated the loss of carbonyl groups. The rate of decrease in this region was more or less uniform throughout the entire exposure for the linseed oil film. A slight increase in absorbance after a 2-hour exposure was noted for the dehydrated castor oil with a uniformly decreasing rate for the remainder of the exposure.

6. The loss of the individual groups as indicated by the infrared spectra agreed with the total weight loss of both oil films. This loss is apparently sustained by a breakdown of the film at several points—e.g., OH-group, CH_2 groups in the chain, and carbonyl groups—and is greatly accelerated by the ultraviolet light in the presence of oxygen. The breakdown products are apparently highly volatile materials which escape and have not yet been identified.

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Thermodynamic Functions of Carbon Dioxide

ENTHALPY, ENTROPY, AND ISOBARIC HEAT CAPACITY AT 100° TO 1000° C. AND 50 TO 1400 BARS

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AT THE present time, tables of thermodynamic functions based on pressure-volume-temperature (*P-V-T*) measurements of carbon dioxide gas are available in the ranges 25° to 150° C., 1 to 3000 atm. (*6, 7*), and 0° to 600° C., 1 to 50 atm. (*4*). Recently *P-V-T* data have been determined by Kennedy at higher simultaneous temperatures and pressures (*2*). These data have been used in the present work to compute thermodynamic functions in the range 100° to 1000° C., and 50 to 1400 bars.

SMOOTHING OF DATA

The Kennedy *P-V-T* data (*2*) have a precision of 2/1000; these data were obtained by the use of reference values from the 150° C. isotherm determined by Michels and others (*8, 10*) (precision of 1/10,000), and agree to 0.2% or 0.0001 gram per cc. with the data of MacCormack and Schneider (*3*) (precision of 1/10,000). The two sets of data of higher precision agree with each other to about 0.15% in the region of overlap.

Difference tables of Kennedy's data (*2*) indicated that a functional smoothing in two variables should be made. This was done by plotting the compressibility,

$$Z = PV/RT \qquad (1)$$

as a function of density, ρ, to form a mesh of isobars and isotherms. The data of higher precision (*3, 8, 10*) and a temperature extrapolation of the MacCormack and Schneider data (*11*) were used to obtain fixed terminal points. The remaining points, at corners of the mesh, were adjusted so that the smoothed values gave a satisfactory graphical net and also satisfied Equation 1.

Table I contains the smoothed values of the pressure-volume product, PV, as a function of pressure and temperature. The terminal points and their sources are indicated. Most of the changes introduced by the smoothing were well within the precision limit of 0.2%. A few were larger but none exceeded the maximum shift of 0.4% (*2*).

COMPUTATION OF THERMODYNAMIC PROPERTIES

The enthalpy was computed by

$$H(T, P) = H(T, 50.66) + \int_{50.66}^{P} \frac{dP}{P}\left[PV - T\left(\frac{\partial(PV)}{\partial T}\right)_P\right] \qquad (2)$$

and the entropy by

$$S(T, P) = S(T, 50.66) - \int_{50.65}^{P} \frac{dP}{P}\left[\frac{\partial(PV)}{\partial T}\right]_P \qquad (3)$$

where P is in bars, T in ° K., and V in Amagat units. The zero points for both entropy and enthalpy have been chosen at 0° C. and 1 atm. The constants used for this adjustment are those of MacCormack and Schneider (*4*) and are included in the 50.66-bar (50-atm.) starting values.

To obtain the starting values at 50.66 bars, the correction to the value at 1 atm. was plotted against temperature. Values for 75° to 150° C. (*7*) were assumed correct; those for 200° to 500° C. (*4*) and for 600° to 1000° C. (*11*), approximately correct, with greater weight given to the values at higher temperature. The final curve was visually chosen to pass through the first