tained when γ is considered constant at an average of the values at the inlet and outlet conditions.

The use of Equation 6 with γ values from Figure 2 is a step in the right direction but does not correct for the fact that Equation 6 is based on perfect gas law behavior. However, the effect of deviation from ideal gas law behavior on Equation 6 is not so important as the effect on γ; therefore the use of Figure 2 should greatly improve the accuracy of such computations.

In engineering work the compression and expansion of mixtures is frequently encountered. γ for mixtures may be determined by computing the molal average of γ values of the individual components, the γ for each component being determined for the temperature and total pressure involved.

Acknowledgment

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Infrared Absorption Spectra of Drying Oils

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The application of the methods of infrared absorption spectra in the study of the drying oils is described. The discussion includes the following items: the spectra of the drying oils and the effect of pigmentation on the spectra, the absorption spectra of the pure esters of the drying oil fatty acids, the effect of conjugation on the absorption, changes in the infrared absorption spectra caused by exposure of the esters to ultraviolet light and oxygen, and the effect of polymerization on the spectra.

THE economic importance of the physical and chemical changes which take place during the formation and decomposition of films of the drying oils is such that these reactions have been the subject of constant investigation for a number of years. The purpose of this paper is to present results indicative of the possibilities of the method of infrared absorption spectra as applied to this general problem.

The peculiar efficacy of the infrared absorption technique lies in the fact that it is a physical method with no chemical effect on the paint film; therefore, it permits repeated examination of the specimen in which progressive changes are taking place. Since many pigments are transparent in the infrared, the measurements are unaffected by the presence of pigments, and thus the method offers the possibility of studying the effects of pigments on the changes occurring in the vehicle during drying and aging. Excellent discussions of the theory and interpretation of infrared absorption spectra as applied to organic compounds will be found in the literature (*1*, *5*).

Apparatus and Procedure

The apparatus described in the previous paper (*2*) was modified somewhat for this work:

A Nichrome glower was used as the source of radiation although it is weak at wave lengths beyond 10.0 microns; filters (7) were used to remove contaminating radiation. Since glass is opaque in the infrared beyond 6.0 microns, samples are examined in rock salt cells, as films on rock salt plates, or often without any backing. Thick cells may be made with rings of known thickness as separators, while for thin cells thin tinfoil is a suitable material. The cell is held together with clips or with any adhesive that is not attacked by the sample. Pigmented films may contain from 20 to 40 per cent by weight of pigment and are usually prepared for examination by brushing out the paint on a plate of polished rock salt. The absorption spectra of such a film may be measured wet or dry or after any desired period of exposure; the same film is used throughout, and the absorption spectra are determined at various stages in its life. Films may be prepared on amalgamated panels, and sections may be removed as desired and mounted directly without any backing. The thickness of the films should be carefully controlled. The best way to do this is by measurement of the transmission through the film at some wave length where there is a minimum of absorption.

As an indication of the sensitivity of the spectrometer, Figure 1 (left) shows the absorption spectrum of linseed oil compared with the published curve of Stair and Coblentz (*3*) and with the results obtained with a grating spectrometer which was set up to study the region between 5.0 and 8.0 microns more closely. The agreement between the two prism spectrometers is good, or at least the difference between the two is insignificant in view of the difference between either one and the grating spectrometer.

Absorption Spectra of China Wood and Linseed Oils

Figure 1 (right) shows the absorption spectra of linseed oil, China wood oil, and oiticica oil from 2 to 12 microns. Absorption bands are found in the first at 3.4, 5.8, 6.9, and 8.4, and 11.5 microns and in addition at 10.0 microns in the China wood and oiticica oils. The bands at 3.4 and 6.9 microns are due to the C—H vibration and that at 5.8 to the C=O; the band at 8.4 microns has been variously ascribed to C=O (*9*), C—C (*3*), and (OH) (*4*). Lecompte (*5*) lists this as a characteristic absorption of esters which varies somewhat with the composition of the ester: "Our personal opinion is that these changes are attributable to the acid radical which serves to form the ester, rather than to the alcohol radical." For the purpose of this paper it is enough to ascribe it to the presence

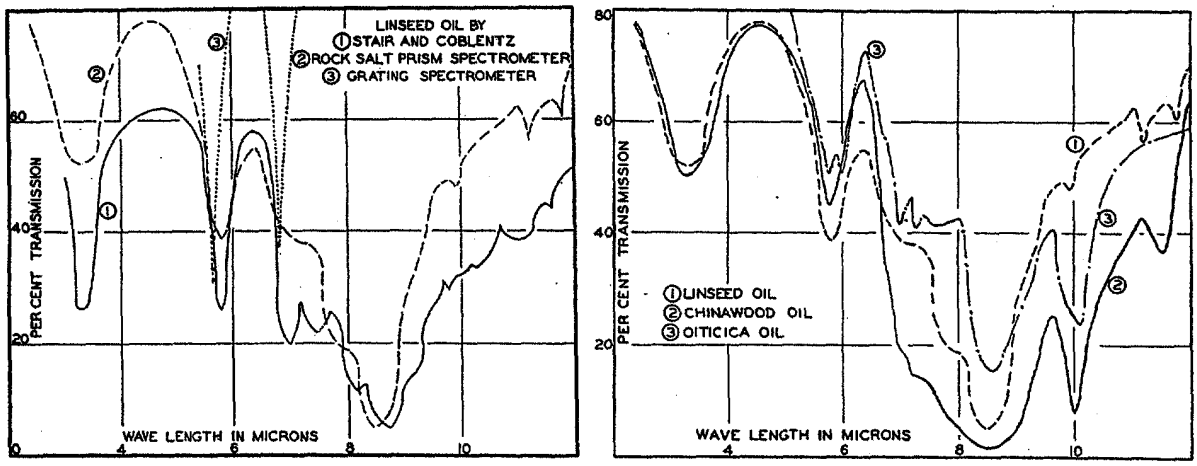

FIGURE 1. ABSORPTION SPECTRA OF NATURAL DRYING OILS

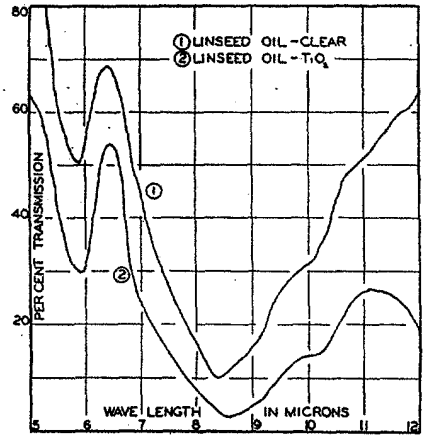

FIGURE 2. OPTICAL EFFECT OF PIGMENTATION

of oxygen in the molecule in some form. The 10.0-micron band in China wood oil and oiticica oil arises from the conjugation of the C=C bonds in these oils and will be discussed later.

Optical Effects of Pigmentation

The optical effect of pigmentation on the vehicle absorption spectrum of a pigmented film of linseed oil is shown in Figure 2. These curves are run from 5 to 12 microns, since at shorter wave lengths scattering by the pigment frequently tends to obscure the absorption spectra of the oil. Certain of the pigments have no effect on the absorption spectra of the oil in this wave-length region. The pigmented film shown here, however, contains titanium dioxide and exhibits an absorption band at 12 microns not appearing in the clear oil. This is due to an absorption band in the pigment itself and is one point that must be watched in work with pigmented films. For example, silicates such as mica and asbestine have strong absorption beyond 7.0 microns, and sulfates have a strong absorption band at 9 microns which will be superimposed on the absorption spectrum of the vehicle when these materials are present.

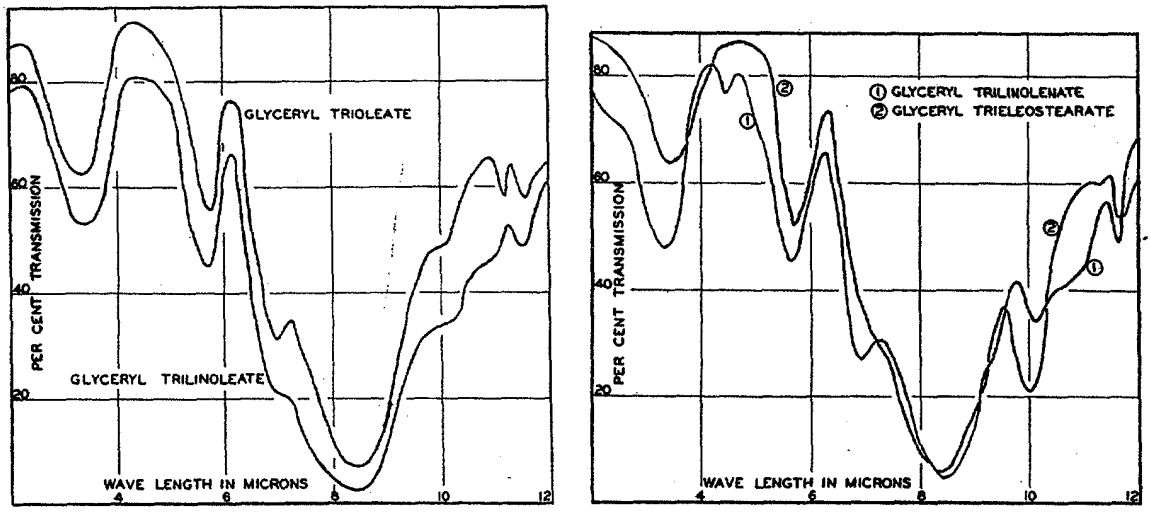

FIGURE 3. ABSORPTION SPECTRA OF GLYCERYL ESTERS

Single Esters of Drying-Oil Fatty Acids

The complex nature of the drying oils was the principal cause of difficulty in interpreting many of the spectra which were obtained after aging of the films. J. G. Smull of Lehigh University kindly prepared the pure methyl, glycol, and glyceryl esters of oleic, linoleic, linolenic, and eleostearic acids. These are 18-carbon-atom fatty acids with, respectively, 1, 2, and 3 double bonds, and 3 conjugated double bonds. The study of these single esters has made it possible to distinguish a number of effects which were obscure in the natural oils.

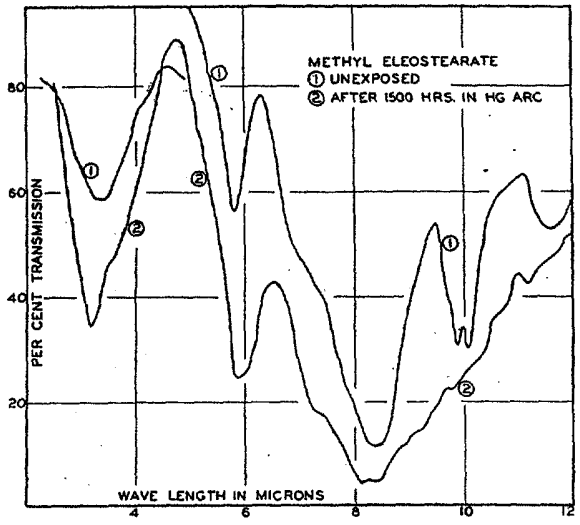

FIGURE 4. EFFECT OF 1500-HOUR ULTRAVIOLET EXPOSURE ON THE CLEAR METHYL ELEOSTEARATE

Figure 3 shows the absorption spectra of the four glyceryl esters. The same absorption bands are found in these esters as were noted in the natural drying oils of Figure 1 (lower portion). The eleostearate shows strong absorption at 10.0 microns which is very feeble in the other esters, although stronger in the linolenate than in the oleate or linoleate. Since the difference between the linolenate and eleostearate is the conjugation of the double bonds in the latter, this 10.0-micron absorption band is ascribed to that conjugation. The spectra of the methyl and glycol esters correspond closely with the glyceryl esters for the same fatty acid, although the intensity of the 8.4-micron absorption increases in the order methyl < glycol < glyceryl. This is the same order as the increase of oxygen atoms in the molecule and is in line with the previous discussion assigning the 8.4-micron absorption to an oxygen linkage. Both methyl eleostearate and glycol dieleostearate show strong absorption at 10.0 microns which is not found in the other esters.

Effect of Ultraviolet Exposure

Figure 4 shows the effect of 1500 hours of exposure to ultraviolet light on the clear methyl eleostearate. All exposures for this work were made with the films held at a distance of 14 inches from an 8-inch quartz mercury arc operating at 4.5 amperes and 110 volts. This experiment was made by holding the ester in a Petri dish during the exposure to the radiation of the mercury arc and determining the spectrum of a film of the residue spread out on a rock salt plate. After the exposure, instead of the absorption band at 3.4 microns in the unexposed ester, intense absorption was found centering at 3.1 microns. Similar changes in the spectra of other compounds have been ascribed to a modification of the carbon-hydrogen linkage by hydroxyl groups since a strong O—H absorption band is found at 2.9 microns. In other words, after exposure of the ester to ultraviolet radiation, absorption occurs at 3.4 microns as in the original ester and at 2.9 microns due to the introduction of OH groups. The spectrometer fails to resolve these bands completely but records an absorption band intermediate between the two. The 10.0-micron absorption band of the eleostearate has disappeared completely as a result of the exposure. This was shown to take place early in the exposure in agreement with the theory that the double bonds of glyceryl trieleostearate are rearranged as a first step in the drying of China wood oil (*6*). The discontinuity in the curve for the unexposed ester at 5.0 microns is due to a change in film thickness. No explanation has been found for the increase in opacity at 5.8 microns as a result of the exposure of the ester to ultraviolet radiation.

Figure 5 (left) shows the effect of 50 hours of ultraviolet light exposure on a pigmented film of methyl oleate. The absorption spectra of the unexposed film is similar to that for the clear methyl oleate, but after the exposure much of the character of the absorption has disappeared. All the absorption bands have decreased in intensity, and the transmission has approached a constant value independent of the wave length which is similar to the transmission of a film of dry pigment in this spectral range. The experimental results indicate that a considerable proportion of the oxidation products of this ester are volatile and leave the film. The change in the visual appearance of the film confirms this disappearance of binder during the mercury arc exposure. Similar experiments with the other esters show that with each fatty acid the stability of the esters increases in the order methyl <glycol < glyceryl. Of the twelve esters studied in these experiments, glyceryl trilinolenate was unique in its stability under the conditions of exposure to the mercury arc.

The absorption spectra in Figure 5 (right) illustrate results obtained with glyceryl trieleostearate. The upper curve is

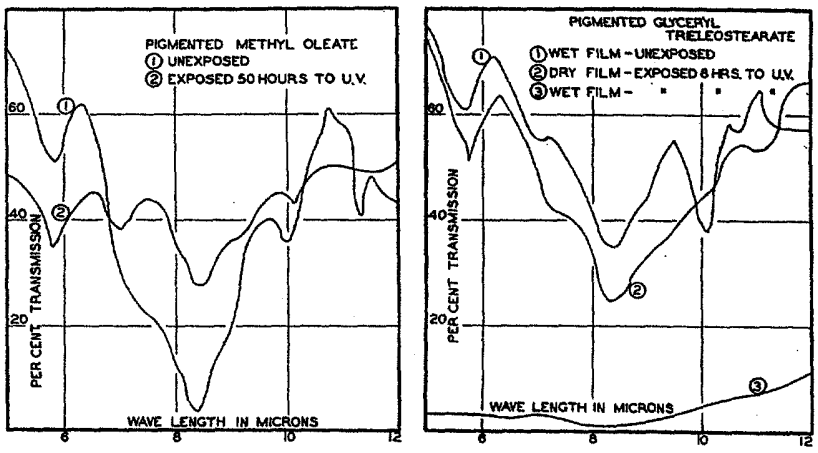

FIGURE 5. EFFECT OF ULTRAVIOLET EXPOSURE ON METHYL OLEATE AND GLYCERYL TRIELEOSTEARATE

for the unexposed ester and the line across the bottom of the chart represents the transmission after 8-hour exposure of the wet film to the radiation of the mercury arc. If the film is permitted to dry in air before the mercury arc exposure, the absorption spectrum is little different from that of the unexposed film, with the exception of the disappearance of the conjugation band at 10.0 microns and broadening of the 8.4-micron band. The development of high opacity when the film is exposed to the mercury arc radiation before drying is believed to be due to polymerization of the ester to large molecular aggregates which effectively scatter the infrared radiation. Normal air drying modifies this polymerization, either because of the general rigidity developed in the molecule or through deactivation of the atomic groups which function in the polymerization reaction. Similar results are obtained when wet films of the glyceryl eleostearate are baked and compared with normal air-dried films. This polymerization effect on baking or mercury-arc exposure of the wet films is shown by glyceryl trilinolenate and glycol dieleostearate as well as by glyceryl trieleostearate, but by none of the other esters. It thus appears that a high degree of functionality in the molecule is necessary in order to obtain it.

Acknowledgment

The authors' thanks are due to J. G. Smull of Lehigh University for the preparation of the esters of the four drying oil fatty acids and to John Fleming who determined all the infrared absorption spectra.

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Formation and Deterioration of Paint Films

Changes in Films of Methyl Esters of Several Unsaturated Fatty Acids under Exposure to Ultraviolet Light

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SEVERAL years ago one of the authors (*2*) described the results obtained in an investigation of the changes taking place in films of trilinolenic glyceride during exposure to room conditions. This investigation had been undertaken in the hope that a study of a simple unsaturated glyceride might yield information which would prove helpful in the explanation of the formation and deterioration of the more complex drying oil systems and the effect exerted upon them by pigments, especially zinc oxide. One of the more important results of the investigation was the realization that compounds less complicated than trilinolenic glyceride would have to be studied if the basic reactions involved in the drying process were to be uncovered and explained. The methods of chemical analysis commonly employed in the examination of drying oils had been used to follow the changes in the trilinolenic glyceride films. Since then it has become increasingly apparent that considerable uncertainty was attached to some of the more important experimental results and that, therefore, conclusions based on them might be seriously in error. There is always the question as to whether the compounds or groups indicated by the chemical analysis were actually present in the film or whether they were formed in the course of the analysis under the influence of the reagents used. Physical methods of testing offer a possibility of answering this question. Of the physical methods available, infrared absorption spectra seem to offer the most promise. Therefore when it became possible to resume this work, it was decided to investigate by infrared absorption as well as by chemical and other physical methods the changes taking place during exposure in simple unsaturated fatty ester films. The present program includes a study of the methanol, glycol, and glycerol esters of oleic, linoleic, linolenic, and eleostearic acids. The use of infrared absorption spectra in the study of these compounds is described in this issue by Gamble and Barnett (*3*).

Experimental Procedure

The oleates and eleostearates used in this investigation were prepared from vacuum-distilled methyl esters which had been obtained by esterifying recrystallized fatty acids. The linoleates and eleostearates were obtained from debrominated methyltetra- and methylhexabromides which had been purified by repeated recrystallization. The constants of the esters given below indicate that they were of satisfactory purity and had not been bodied appreciably in the course of preparation:

Ester	Acid No.	Wijs Iodine Value	Saponification No.	Viscosity, Poises
Methyl oleate	3.9	81.5	...	0.08
Methyl linoleate	2.0	173.2	...	0.05
Methyl linolenate	None	258.3	198.2	0.02
Methyl eleostearate	2.7	163.3	191.9	0.2