

Infrared Spectra of Asphalts: Some Aspects of the Changes Caused by Photooxidation

Paul G. Campbell and James R. Wright

(November 29, 1963)

The infrared spectra of coating-grade asphalts to which model organic compounds were added were compared with spectra of the original asphalts and with photooxidized asphalts. By this method, it was shown that the principal oxygen-containing products formed in the asphalt during air- or photooxidation were aldehydes, ketones, and acids. The presence of esters could not be confirmed.

The effects of air-blowing conditions and elevated temperature storage on several asphalts were examined by infrared spectroscopy. Elevated temperature ($\sim 260^\circ\text{C}$) storage of air-oxidized asphalts, under nitrogen, decreased absorbance in the carbonyl band at 1700 cm^{-1} and reduced durability to accelerated weathering.

Photooxidation reactions that occurred at the surface of thick ($625\ \mu$) asphalt films, as detected by infrared spectroscopy, were the same as those which took place in the thin ($25\ \mu$) films. Also, the photooxidation rates were comparable. Only negligible amounts of photooxidation occurred at a depth of $10\ \mu$ beneath the surface.

1. Introduction

The initial application of infrared spectroscopy to the analysis of asphaltene-type materials was made a decade ago by Hadzi [1]¹ who studied qualitatively the infrared spectra of the light-petroleum-solvent-insoluble, benzene-soluble fraction of various materials. Friedel and Queiser [2] made an infrared spectrum of an asphalt film in 1956 and used it to illustrate the similarities to the spectra of coal asphaltenes. Also, in 1956, Knotnerus [3] applied infrared analysis to determine the oxygen-containing functional groups formed during the air blowing of asphaltic bitumens.

Stewart [4] described the infrared spectra of asphalt fractions separated by chromatographic techniques in 1957. In this research, asphalts were separated into four fractions and an infrared spectrum was made of each fraction. Samples of the original asphalts were then exposed for 30 months outdoors, subsequently fractionated, and an infrared spectrum was made from each fraction of the exposed asphalt. Some of the structural changes produced by weathering were elucidated by this method. Stewart worked with solvents, a heated cell, potassium iodide pellets, and mineral oil mulls in obtaining the spectra of various asphalts and asphalt fractions.

In a study of the absorbance of asphaltic materials, Schwyer [5], in 1958, made infrared spectra of asphalt films 0.1 mm thick. For wavelengths below $8\ \mu$, it was necessary to use carbon tetrachloride solutions of the asphalts. Schwyer attempted to explain certain differences in the properties of asphaltic materials on the basis of the ultraviolet and infrared

spectra. Romberg et al. [6], used infrared spectroscopy in the analysis of asphalt components from gel, sol-gel, and sol asphalts in 1959. From the results thus obtained, the percentages of various carbon linkages in each fraction were calculated and compared with other properties such as C/H ratio, elemental analyses, and molecular weight.

Beitchman [7], in 1959, described a method for the preparation, irradiation, and infrared analysis of thin films of air-blown asphalts of about $25\ \mu$ thickness. Beitchman observed that increases in absorbance at 3435 cm^{-1} ($2.91\ \mu$), 1700 cm^{-1} ($5.88\ \mu$), and 1030 cm^{-1} ($9.71\ \mu$), [OH, C=O, C—O groups, respectively], were produced by exposure of unsupported films of asphalt to the radiant energy of a carbon arc. Yen [8], in 1962, published the results of an extensive investigation into the structure of petroleum asphaltenes by infrared analysis.

The research described by Beitchman [7] was the first successful effort to produce infrared spectra of asphalt films without resorting to solvents, mulls, pellets, or salt-crystal supports. The unsupported film was particularly adaptable to research on asphalt photodegradation. The films could be scanned, irradiated, and rescanned without modification to the asphalt other than that caused by photodegradation. Wright, Campbell, and coworkers modified the unsupported film technique [9-11] and used it extensively to determine photooxidation rates of asphalts [10], the effect of temperature and relative humidity on asphalt oxidation [11], and the relationship between carbon-arc intensity and asphalt oxidation [12]. Changes in absorbance at 1700 cm^{-1} , the carbonyl index, were employed to measure photooxidation.

The present paper is an extension of this research with the general objective of interpreting more fully some of the changes observed in the infrared spectra of asphalts due to photooxidation. Specific areas

¹ Figures in brackets indicate the literature references at the end of this paper.

investigated include the nature of the carbonyl compounds with absorbance at 1700 cm^{-1} , spectral changes produced by air oxidation and by elevated temperature storage of asphalts, oxidation rates of thick films, and the depth of the photooxidation reaction in asphalt.

2. Infrared Spectra of Asphalts Containing Model Organic Compounds

Infrared spectroscopy gives evidence of the presence in a material of characteristic groups such as hydroxyl or carbonyl groups. If the material is a pure compound, such information is often definitive. If, on the other hand, the material is a mixture, the interpretation is more complicated as the location of any functional groups, relative to any compound in the mixture, is not normally known.

The complexity of asphalts limits the interpretation of their infrared spectra. Similarly, the changes which occur in the infrared spectrum of an asphalt upon photooxidation are subject to limited interpretation. For example, with respect to absorbance in the carbonyl band at 1700 cm^{-1} , relative changes in the spectra of asphalt films can be measured with considerable accuracy [10]; the source of the carbonyl group, whether it be aldehyde, ketone, acid anhydride, ester, etc., can not be established easily [13].

It is possible, however, to gain some insight as to the identity of these compounds by an indirect approach which consists of adding model organic compounds to an asphalt, scanning a film of the mixture, and observing the changes produced in the infrared spectrum. New absorbance peaks or shoulders are produced if the compound type differs from those in the asphalt. Existing absorbance peaks are reinforced if the model-compound additive corresponds to compounds of the same types already present in the asphalt. The model-compound-additive method was employed in this research to elucidate the types of compounds formed during photooxidation of asphalt with special emphasis on the changes which occur in the absorbance at 1700 cm^{-1} .

2.1. Experimental Procedure

a. Methods

The method for the preparation, irradiation, and infrared analysis of unsupported asphalt films has been described elsewhere [10]. The model organic compounds were incorporated into the asphalt in the following manner: a known amount of a selected asphalt was heated on a hot plate under a blanket of nitrogen until melting occurred. The organic compound was added (1 to 2% by weight) and the resultant mixture stirred until relatively homogeneous. The mixture was then covered and cooled to room temperature. The whole operation required 7 min.

Films ($25\ \mu$ thick) of the additive-treated asphalts were prepared as described in [10]. Infrared scans

were made of these films. For direct comparison, the spectrum of the additive-containing asphalt was made on the chart paper which contained the spectrum of the corresponding untreated asphalt from a film of similar thickness. Perkin-Elmer infrared spectrophotometers (Models 221 and 137) were used in making the infrared scans.

b. Materials

Two air-blown roofing asphalts were used in the present study: One asphalt (No. 16) was of Mid-continent United States origin and had shown a durability to accelerated weathering (ASTM D529-59T) of 93 days using the 51-9C cycle (9 min of cold water spray in each hour). The other asphalt (No. 9) was a California Coastal asphalt fluxed with reclaimed lubricating oil; its durability was 32 days. Properties of these asphalts have been described elsewhere [9].

2.2. Infrared Spectra of Air-Blown Asphalts

a. Asphalts With No Compounds Added

The infrared spectra of a typical air-blown asphalt before and after photooxidation are shown in figure 1. Significant changes in absorbance may be observed at 3436 cm^{-1} , 1700 cm^{-1} , and 1600 cm^{-1} . According to Stewart [4], respective absorbances at these wave numbers are due to: OH stretching, C=O, aromatic and conjugated alkene and OH bonding. Also, absorbance changes at other wave numbers have been reported by Beitchman [7] and Stewart [4].

Of the absorbances mentioned above, relative changes due to photooxidation are best measured at 1700 cm^{-1} since this, the carbonyl band, is relatively free from interference by absorbances of other groups [14] and carbonyl absorbances can be determined with greater accuracy than other groups such as OH and C—O. This band was used extensively by the authors in previous investigations on the photodegradation of asphalts [9-12], but the identification of the types of organic molecules responsible for the absorbance at 1700 cm^{-1} was not made.

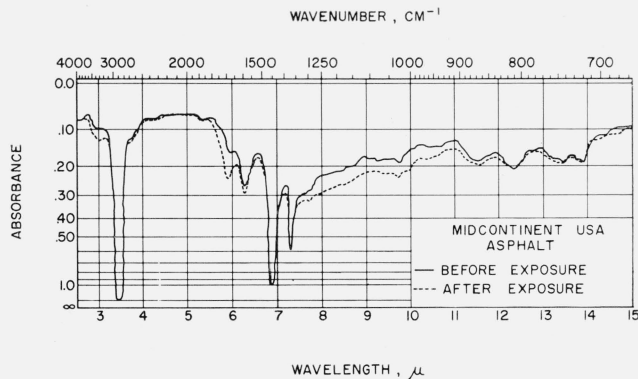


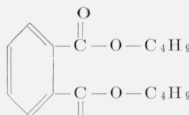
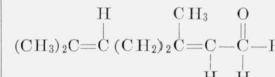
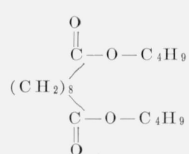
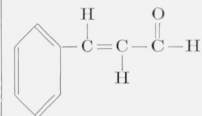
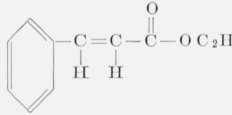
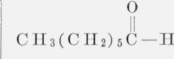
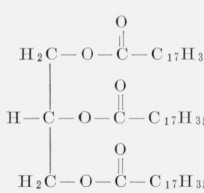
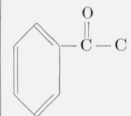
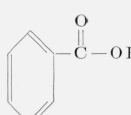
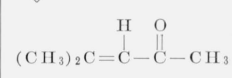
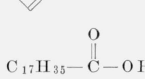
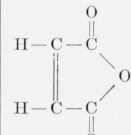
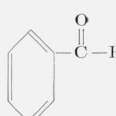
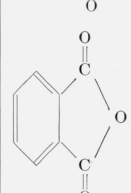
FIGURE 1. Infrared spectra of a midcontinent U.S.A. asphalt before and after carbon-arc irradiation.

b. Asphalts With Organic Compounds Added

The increased carbonyl absorbance observed in asphalt upon photooxidation may be due to any carbonyl-containing organic compounds. To investigate this phenomenon by the method described in section 2a, the asphalts were mixed with esters, aldehydes, ketones, acids, and anhydrides, respectively. A total of 14 different compounds was used. These compounds are listed in table 1 together with their chemical structure, characteristic absorbances, and the absorbances imparted to asphalts containing each compound.

The effects of various organic compounds on the infrared spectra of asphalt No. 16² (with and without organic compounds added) are shown in figures 2 to 7. The changes produced by phthalic anhydride are shown in figure 2. Two carbonyl absorbance bands, characteristic of anhydrides are present at about 1845 and 1775 cm⁻¹. Bellamy [15] reports values of 1845 and 1775 cm⁻¹ for phthalic anhydride. In addition to the carbonyl absorbance, there is evidence of the C—O—C stretching vibration at 1250 cm⁻¹. According to Colthup [16], vibration in the range of 1310–1210 cm⁻¹ is characteristic of cyclic anhydrides.

TABLE 1. Model organic compounds added to asphalts No. 9 and No. 16 and their contribution to the infrared spectra

Compound	Structure	Characteristic absorbance(s) ¹	Absorbance(s) in asphalt ²	Compound	Structure	Characteristic absorbance(s) ¹	Absorbance(s) in asphalt ²
<i>n</i> -Butyl phthalate.		<i>cm</i> ⁻¹ 1730-1717 1310-1250 1150-1100	<i>cm</i> ⁻¹ 1730-1720 1275 (broad) 1115 (broad)	Citral.....		<i>cm</i> ⁻¹ 1705-1685 1440-1325 975-825	<i>cm</i> ⁻¹ 1705 1320 970
<i>n</i> -Butyl sebacate.		1750-1735 1172	1740 1185-1175	Trans-cinnamaldehyde.		1705-1685 1230-1160	1700 1200 (broad)
Ethyl cinnamate.		*1717 1300-1100	1720 (shoulder) 1310 (broad) 1165 (broad)	<i>n</i> -Heptaldehyde.		1740-1720 1440-1325	1710
Tristearin.....		1751-1748 1250 1163 1110	1750 (broad) 1160 1110 (broad)	Acetophenone..		*1686	1690
Benzoic acid.....		*1685 *1290 *714	1690 (shoulder) 1305 1035	Mesityl oxide..		*1690 1325-1215	1700 1275 (broad)
Stearic acid.....		2700-2500 *1708 1350-1180	2600 (broad) 1705 1250 (broad)	Maleic anhydride.		*1848 *1790 1310-1210	1840 1790 1215 (broad)
Benzaldehyde.....		*1704 1300-1260	1705	Phthalic anhydride.		*1845 *1775 1310-1210	1845 1775 1250

¹ Source: L. J. Bellamy, *The infrared spectra of complex molecules*, 2d ed. (John Wiley and Sons, New York, N.Y., 1958). Asterisk (*) indicates value is specific for the compound. Unmarked entries refer to the class of compounds.

² Reference is made to the regions of increased absorbance in the asphalt-additive mixture over that found in the original asphalt.

² Asphalt 16 was selected for this study because it has a high initial absorbance in the carbonyl band and would reflect only large contributions due to additives.

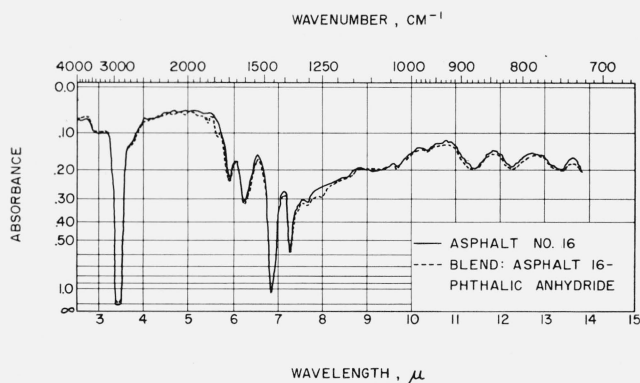


FIGURE 2. Changes in the infrared spectrum of asphalt No. 16 caused by the addition of phthalic anhydride.

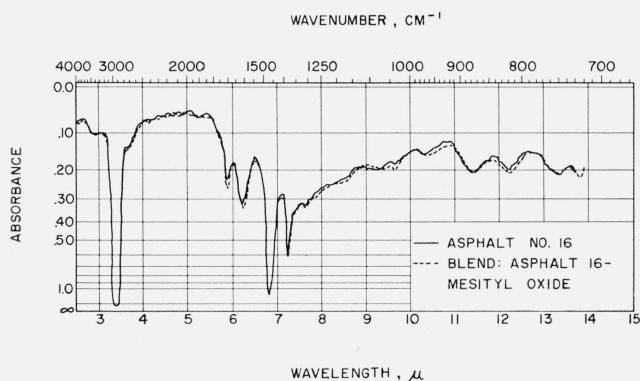


FIGURE 3. Changes in the infrared spectrum of asphalt No. 16 caused by the addition of mesityl oxide.

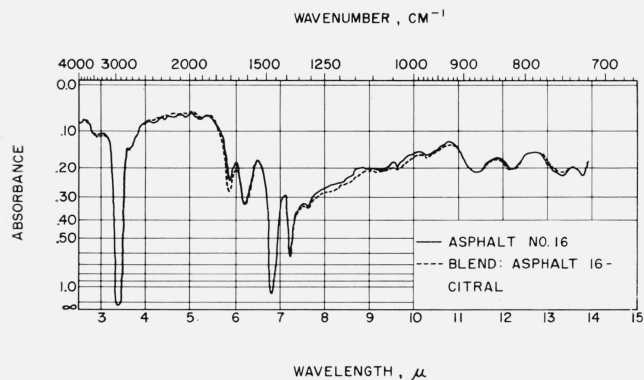


FIGURE 4. Changes in the infrared spectrum of asphalt No. 16 caused by the addition of citral.

The addition of mesityl oxide, an α - β -unsaturated ketone, to asphalt 16 produced increased absorbance at 1700 cm^{-1} and directly reinforced the normal absorbance of the asphalt at this wave number (fig. 3). Thompson and Torkington [17] show the frequency of the stretching vibration of the carbonyl group in mesityl oxide to be about 1690 cm^{-1} .

Similarly, citral, an α - β -unsaturated aldehyde, increased carbonyl absorbance at 1705 cm^{-1} (fig. 4). α - β -Unsaturated aldehydes normally absorb in the range of 1705 – 1685 cm^{-1} [18].

The addition of a fatty acid, stearic acid, to asphalt 16 resulted in spectral changes typical of this class of compounds [19]. Slightly increased absorbance was observed in the 2700 – 2500 cm^{-1} range (bonded OH stretching vibration), at 1705 cm^{-1} ($\text{C}=\text{O}$ vibration), and in the broad region around 1250 cm^{-1} (fig. 5). The increased absorbance in the 1705 cm^{-1} region enhances that of the original asphalt.

The addition of esters to asphalt 16 produced an effect not previously observed with any of the other classes of carbonyl compounds in air-blown asphalts or in photooxidized asphalts. Two absorbance peaks were formed due to $\text{C}=\text{O}$ vibration. This effect is shown graphically in figures 6 and 7 with *n*-butyl sebacate and tristearin, a triglyceride, respectively.

Characteristics $\text{C}=\text{O}$ absorbance for alkyl esters is in the range of 1750 – 1735 cm^{-1} with the *n*-butyrates at the lower end of the range [17]. This absorbance range is notably higher than the carbonyl frequency for alkyl ketones and aldehydes due to the influence of the adjoining oxygen [14]. The $\text{C}=\text{O}$ absorbance for *n*-butyl sebacate in asphalt 16 is 1740 cm^{-1} while the absorbance of the asphalt alone in this region is at 1700 cm^{-1} . Similarly, the respective absorbances for $\text{C}=\text{O}$ in tristearin and asphalt 16 are 1750 cm^{-1} and 1700 cm^{-1} . The triglycerides absorb in the range 1751 – 1748 cm^{-1} [21].

The $\text{C}-\text{O}$ stretching vibrations due to esters (1300 – 1100 cm^{-1}) are found in the asphalt spectra with both *n*-butyl sebacate and tristearin. With the sebacate, an absorbance is found at 1185 – 1175 cm^{-1} . Sebacates absorb at 1172 cm^{-1} [20]. Characteristic $\text{C}-\text{O}$ stretching modes for triglycerides are 1250 , 1163 , and 1110 cm^{-1} [21]. With tristearin, broad absorbance occurred at 1250 , 1160 , and 1110 cm^{-1} . Photooxidized asphalts also exhibit increased absorbance in the 1300 – 1100 cm^{-1} region (see fig. 1). However, with photooxidized asphalts, none of the characteristic bands for $\text{C}-\text{O}$ vibrations in esters can be distinguished.

2.3. Discussion

By adding model organic compounds to an asphalt and observing the changes produced in the infrared spectra, it was shown that ketones, aldehydes, and acids reinforced the absorbance assigned to the $\text{C}=\text{O}$ frequency at 1700 cm^{-1} , while acid anhydrides and esters did not contribute in this wave number region. The anhydrides exhibited two carbonyl absorbance bands at 1845 and 1775 cm^{-1} . The esters developed an absorbance in the 1750 – 1735 cm^{-1} region forming a doublet with the carbonyl absorbance in the asphalt. Thus, it appears that the increased absorbance found in oxidized asphalts is due largely to ketones, aldehydes, and acids with no contribution from anhydrides and little or no contribution from esters. This generalization is applicable to asphalts

oxidized in air, in oxygen, and in oxidants other than oxygen [22] as well as specimens subjected to photo-oxidation.

The insignificant contribution of esters as a source of oxygen in oxidized asphalts is worthy of further comment. In 1955, Goppel and Knotnerus [23] published a paper on the fundamentals of bitumen blowing in which more than 60 percent of the oxygen in the blown bitumen was attributed to ester groups.³ Furthermore, since esters link two different molecules, it was postulated that esters contributed to the formation of higher molecular weight materials. Proof of ester formation, based on saponification values and spectroscopic evidence, was described in a separate paper by Knotnerus [3]. These two papers have been referenced frequently in the subsequent literature dealing with asphalt oxidation under a variety of experimental conditions [24-27].

Since the present work does not support the contention that esters are the predominant oxygen-containing molecules in oxidized asphalt, the discrepancy may be explained as follows: The spectroscopic evidence offered by Knotnerus [3] is based upon the nearly complete disappearance of a strong carbonyl absorption band at 1724 cm^{-1} and the formation of a new band at 1587 cm^{-1} (carboxylic acid salts) when blown bitumens are saponified with excess alkali. (The remaining absorbance at 1724 cm^{-1} was believed due to aldehydes and ketones.) The possibility of high molecular weight acids was ruled out because the hydrogen bridges were not observed between the solvent employed in the spectroscopic method and the potential acids. This evidence, coupled with saponification values, was offered as proof that esters were the predominant molecular type. It is the authors' contention that the presence of "acid-solvent hydrogen bridges" would be extremely difficult to detect by infrared spectroscopy in a solution containing the whole asphalt. And furthermore, that the absence of such bridges under these conditions is rather weak evidence for selecting esters rather than acids as the predominant oxygen-containing molecule.

Saponification values also may be misleading because compounds other than esters may produce positive result. Siggia [28], in discussing the limitations of the saponification equivalent method, pointed out that the presence of reactive compounds would give erroneous results to the method used in ester determination. According to Shriner et al., [29], hot concentrated alkali affects functional groups other than esters. For example, aldehydes with α -hydrogen atoms undergo aldol condensation, aldehydes with no α -hydrogen atoms undergo Cannizzaro's reaction, and β -diketones undergo cleavage under the influence of hot alkali.

To supply further evidence of this fact, saponification equivalents were measured on *n*-heptaldehyde and acetophenone for 4 and 24 hr alkali treatment. The values for the aldehyde were 525 and 253, and for the ketone were 10,020 and 1,469, respectively.

³ Similar effects were postulated for aged bitumens.

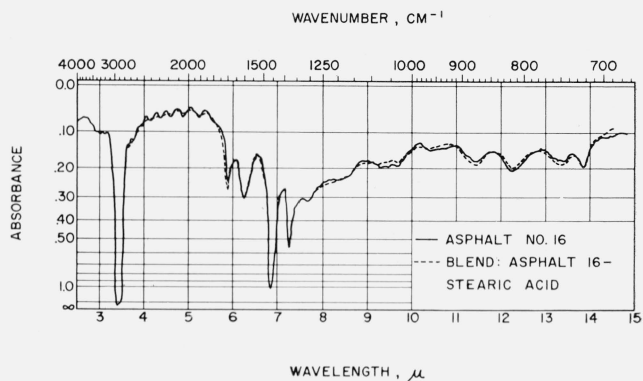


FIGURE 5. Changes in the infrared spectrum of asphalt No. 16 caused by the addition of stearic acid.

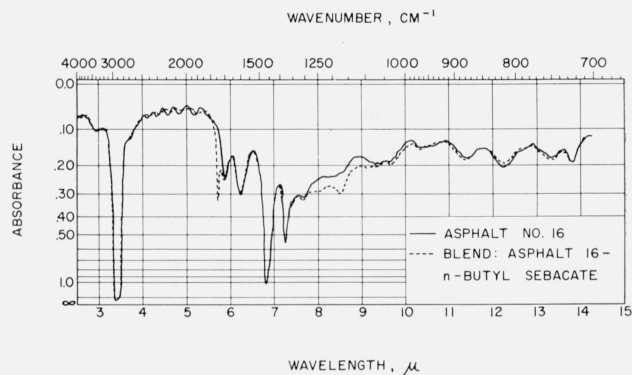


FIGURE 6. Changes in the infrared spectrum of asphalt No. 16 caused by the addition of *n*-butyl sebacate.

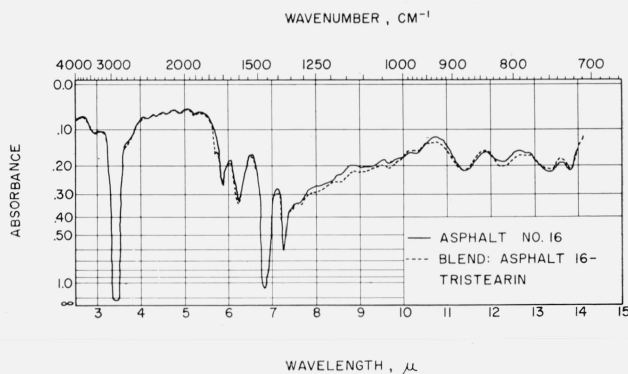


FIGURE 7. Changes in the infrared spectrum of asphalt No. 16 caused by the addition of tristearin.

The present work does not, of course, rule out ester formation entirely. It is well known that α - β -unsaturated esters exhibit carbonyl absorbance in the region of 1720 cm^{-1} . The addition of ethyl cinnamate ($\text{C}=\text{O}$ frequency of 1717 cm^{-1}) to asphalts 16 and 9 broadened the carbonyl absorbance but gave no doublet as was the case with normal saturated esters. Also, in photooxidation of asphalts, poorly defined shoulders are sometimes observed on the main carbonyl absorbance region; these might be attributed to ester formation since asphalts contain both acids and alcohols. It should be noted that esters containing one or more β -hydrogen atoms in the alkyl group may decompose photochemically by an intramolecular rearrangement into an olefin and the corresponding acid [30]. In general, it is concluded that the oxygen in oxidized asphalts is principally in the form of aldehydes, ketones, or acids (the present results do not distinguish among these classes) with a relatively minor part as esters.

3. Spectral Changes Caused By Air-Oxidation and Elevated-Temperature Storage

The changes in the infrared spectra of the asphalts described in section 2 were produced by the addition of model organic compounds to the asphalts. Most hard asphalts, however, are manufactured by air oxidation at temperatures in the order of $260\text{ }^\circ\text{C}$ ($500\text{ }^\circ\text{F}$). Therefore, it was of interest to elucidate the spectral changes produced in asphalt under these conditions as well as those produced by storage of the asphalt at the elevated temperatures used in the air-oxidation process.

Three asphalt fluxes, of Midcontinent United States, Venezuelan, and Southeast United States origin, were used. The designations of these fluxes, some physical properties, the conditions of air oxidation, and the softening points (S.P.) (ASTM D36-26) of the oxidized asphalts are given in table 2. (For more details on these materials, see Greenfield [31].)

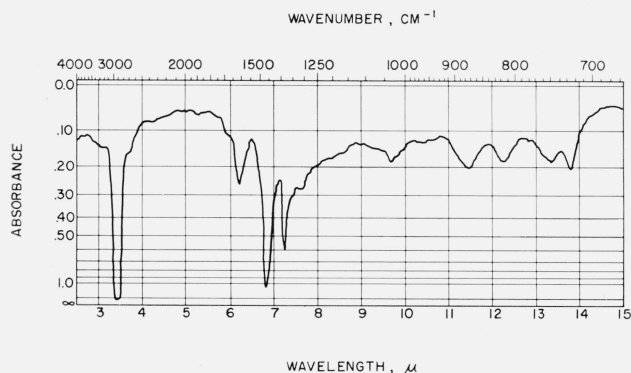


FIGURE 8. Infrared spectrum of Kansas L-22 asphalt flux, softening point, 39° C .

(Film supported on NaCl Plates.)

The infrared spectrum of the Kansas L-22 asphalt flux, before air oxidation, is shown in figure 8.⁴ The area around 1700 cm^{-1} shows practically no absorbance indicating little or no oxygen in the $\text{C}=\text{O}$ form. Upon air oxidation to a softening point of $104\text{ }^\circ\text{C}$ ($219\text{ }^\circ\text{F}$), considerable absorbance was observed in the 1700 cm^{-1} region indicating the formation of $\text{C}=\text{O}$ oxygen (see fig. 9).

Absorbance around 1700 cm^{-1} may be attributed to $\text{C}=\text{O}$ in the form of aldehyde; ketone, and/or acid. The change in absorbance at 1300 cm^{-1} may well represent alkyl ketones and aromatic aldehydes.

Another change appeared in the region⁵ of 760 – 720 cm^{-1} . Well-defined absorbances occurred at 750 cm^{-1} and 725 cm^{-1} in the asphalt flux. In the air-oxidized asphalt, these absorbances were less intense and poorly defined.

The infrared spectrum (not shown) of the air-oxidized but softer asphalt (S.P. = $80\text{ }^\circ\text{C}$) was similar to that of the more highly oxidized asphalt (S.P. = $104\text{ }^\circ\text{C}$). The main difference was one of absorbance intensity in the 1700 cm^{-1} region; the softer product showed less absorbance and, consequently, less carbonyl formation.

Storage of the In-grade⁶ Kansas L-22 asphalt (S.P. = $104\text{ }^\circ\text{C}$) at $243\text{ }^\circ\text{C}$ ($470\text{ }^\circ\text{F}$) for 19 hrs under a nitrogen atmosphere caused a decrease in S.P. to $95\text{ }^\circ\text{C}$. Correspondingly, the absorbance intensity in the 1700 cm^{-1} region decreased, but no shift in the absorbance region was observed. Apparently some thermal degradation of the oxygen-containing molecules took place. The storage temperature of $243\text{ }^\circ\text{C}$ was severe enough to cause decarboxylation of organic acids.

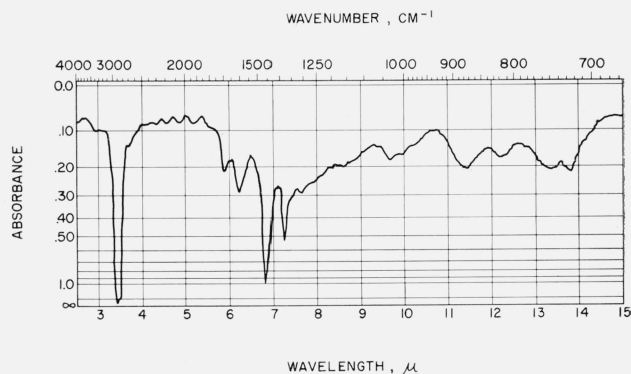


FIGURE 9. Infrared spectrum of coating-grade asphalt (softening point, 104° C .)

(Made from Kansas L-22 flux.)

⁴ The softening point of the L-22 flux was $38\text{ }^\circ\text{C}$ ($101\text{ }^\circ\text{F}$); too low for an unsupported film. For this reason, the asphalt film was prepared between sodium chloride plates.

⁵ Bellamy [32] interprets strong absorbances in this region as due to aromatic substitution. Yen and Erdman [8] assign absorbances for asphaltenes in the 865 – 760 cm^{-1} range as due to aromatic out-of-plane bending frequencies.

⁶ The designation "In-grade" refers to an asphalt which meets the industry's specifications with respect to softening point and penetration.

The relationship between asphalts modified by air-oxidation or elevated-temperature storage and their photooxidation rates was determined. The physical properties of the asphalt fluxes before and after asphalt oxidation are shown in table 2. The

TABLE 2. Physical properties of asphalt fluxes before and after air oxidation

Designation	Before air oxidation		After air oxidation			Air-oxidation conditions ¹		
	Softening point	Penetration at 25 °C	Below grade	In-grade	After storage	Temperature	Time	Air rate
	°C	1/10 mm	Softening point			°C	Min	ml/min
Kansas L-22-----	38	249	80	104	2 95	243	73	9500
Tia Juana 612-----	40	152	99	104	3 97	246	64	4750
Talco 16-RF-2-----	40	190	98	102	4 94	243	81	4750

¹ Conditions given are those used to produce asphalt designated "In grade" [31].
² Stored for 19 hr at 243 °C, under nitrogen.
³ Stored for 21 hr at 246 °C, under nitrogen.
⁴ Stored for 21.5 hr at 243 °C, under nitrogen.

experimental method was that employed by Wright and Campbell [10] in which 25 μ films of each asphalt were exposed to the radiant energy of the carbon arc. Oxidation was measured as a function of exposure by the changes occurring in C=O absorbance at 1700 cm^{-1} . The asphalts exposed and the resultant carbonyl indices are shown in table 3.

Oxidation-rate curves are plotted for Kansas L-22 asphalts in figure 10. The asphalt that was least susceptible to photooxidation was the In-grade asphalt (S.P.=104 °C). Film failure occurred after 16-hr exposure. The Below-grade asphalt (S.P.=80 °C) exhibited a slightly higher photooxidation rate, but film failure did not occur until after 18.5 hr. The least durable asphalt, with a much higher photooxidation rate and a film life of only 12 hr, was the asphalt subjected

TABLE 3. Changes produced in carbonyl indices of various asphalts by irradiation¹

Asphalt-----	Carbonyl index (ΔA at 1700 cm^{-1})								
	Kansas L-22			Tia Juana 612			Talco 16-RF-2		
Softening point, °C-----	80	104	95	99	104	97	98	102	94
Exposure time, hr:									
2-----	0.007			0.014	0.018	0.015	0.013	0.014	0.019
4-----	.009	0.014	0.021	.030	.027	.034	.028	.034	.022
6-----	.033	.027	.034	.050	.040	.056	.040	.054	.051
8-----	.044	.031	.059	.071	.069	.080	⁵ .067	^{4,5} .076	.072
10-----				.114	.115	.135	.098	.110	.126
12-----				.159	.156		.133	.143	.147
13-----		² .072	.112	⁴ .162					
14-----							.165	.157	.180
15-----									.192
16-----	.135	.123					.171	.186	.184
17-----							.179	.186	⁶ .209
18-----	³ .165								

¹ Irradiated in Atlas SMC-R Weather Ometer at 49°C and 40 percent R.H. for time periods indicated.
² Irradiated for 12.5 hr.
³ Irradiated for 18.5 hr.
⁴ One sample only.
⁵ Irradiated for 7.75 hr.
⁶ Irradiated for 17.25 hr.

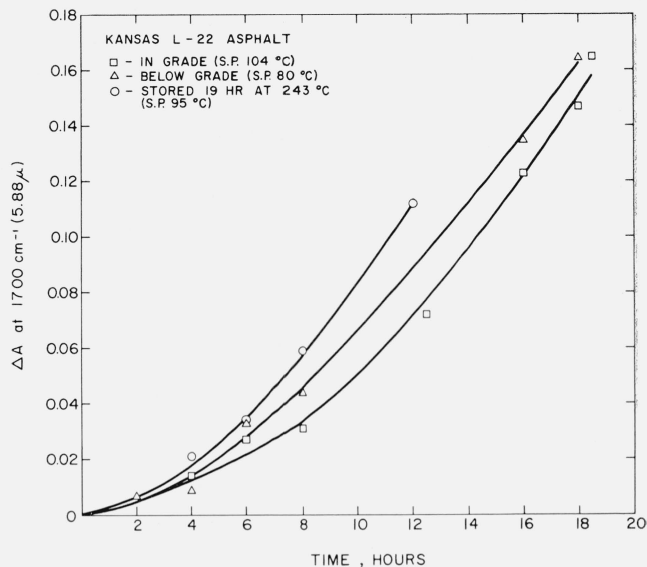


FIGURE 10. Effect of carbon-arc exposure (49 °C., 40 percent R.H.) on the change in infrared absorbance of various Kansas L-22 asphalts at 1700 cm^{-1} .

to elevated temperature storage. It appears that degradation reactions initiated thermally might well have continued under conditions for photo-degradation.

4. Spectral Changes in the Surface of Thick Asphalt Films Upon Photooxidation

4.1. Spectral Changes

The spectral changes in the asphalt described in sections 2 and 3 were determined with thin films of 25 μ (1 mil) thickness. However, the usual methods for the exposure of asphalts to solar or carbon-arc

radiant energy employ asphalt films of $625\ \mu$ (25 mils) thickness [33]. In order to compare by infrared methods the changes observed in the thin films with those which occurred on and near the surface of the thick films upon photooxidation, slices of $25\ \mu$ thickness were removed from the surface of irradiated thick films and their infrared spectra determined.

A Southeast U.S.A. asphalt, No. 6, was used in this study. An asphalt specimen was prepared by pouring the molten asphalt into a small aluminum weighing dish to a depth of about $625\ \mu$. A 3.8-cm diam microtome specimen holder was then embedded into the soft asphalt. Upon cooling, the asphalt was cut to the diameter of the specimen holder and the surface was shaved smooth with a microtome (Spencer, Model 860).

The asphalt samples were exposed to the radiant energy of a carbon arc at $49\ ^\circ\text{C}$ and 40 percent R.H. for the desired time period. The samples were mounted in the same respective positions in the accelerated weathering machine as were previous samples of thin films. After exposure, a $25\ \mu$ slice was removed from the surface, weighed to check thickness, and then pressed between sheets of unlacquered cellophane in a heated press to prepare a specimen suitable for infrared analysis.

The infrared spectrum of a $25\ \mu$ film of asphalt 6, prepared from the irradiated surface of a $625\ \mu$ film is shown with the spectrum of an unexposed thin film asphalt 6 in figure 11. The changes in the infrared spectrum of the asphalt obtained from the surface of the thick film are the same as those produced in the thin films, namely those at $3435\ \text{cm}^{-1}$ (OH), $1700\ \text{cm}^{-1}$ (C=O), and $1030\ \text{cm}^{-1}$ (C—O). The carbonyl absorbance at $1700\ \text{cm}^{-1}$ and the absence of absorbance at $1740\ \text{cm}^{-1}$ indicates that the oxygen is in the form of acids, aldehydes, and ketones. The slight increase in absorbance at $2750\ \text{cm}^{-1}$ suggests the presence of carboxylic acids and that around $1300\ \text{cm}^{-1}$ the presence of alkyl ketones and aromatic aldehydes.

Figure 12 shows the changes which occurred in the infrared spectrum of a thin film of asphalt 6 under the same exposure conditions as those used with the thick films. Significant changes in absorbance occurred at $3435\ \text{cm}^{-1}$, and $1700\ \text{cm}^{-1}$, and increases in general absorbance at $1030\ \text{cm}^{-1}$, as was the case with the thick films. Even the absorbance intensities in these regions were about the same. These results indicate that the photooxidation reactions occurring in the thin films, as determined by infrared spectroscopy, are essentially the same as those which take place at the surface of thicker asphalt films under the exposure conditions used in the present work.

4.2. Photooxidation Rates

A comparison was made of the photooxidation rates of thin films of asphalt 6 and that which occurred on the surface of thick films of the same asphalt. To do this, a series of $625\ \mu$ films were

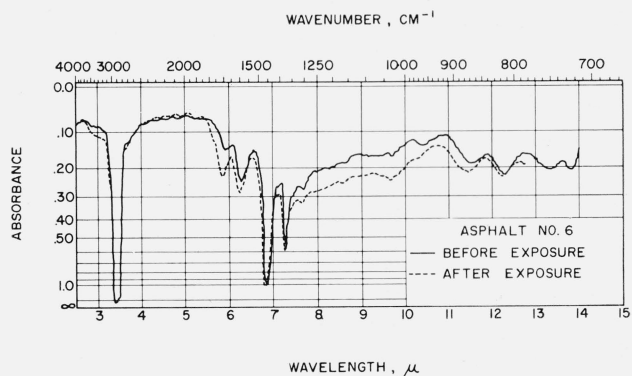


FIGURE 11. Comparison of the infrared spectra of unexposed asphalt No. 6 ($25\ \mu$ -thin film) with that of a film made from the surface ($25\ \mu$ -microtome slice) of the exposed asphalt ($625\ \mu$ thick film).

(Exposure was for 7.5 hr to carbon-arc radiation at $49\ ^\circ\text{C}$ and 40 percent R.H.)

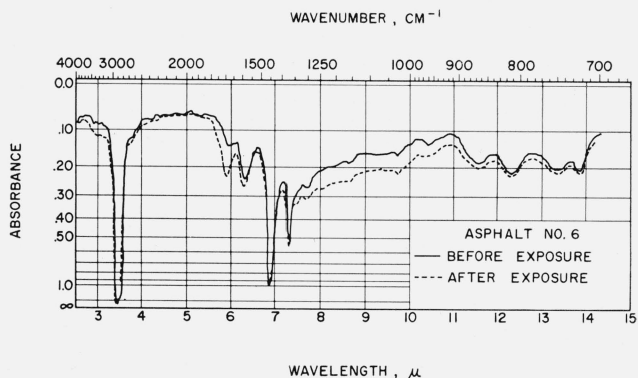


FIGURE 12. Infrared spectra of asphalt No. 6 ($25\ \mu$ thin film) before and after 7.5 hr. exposure to carbon-arc radiation at $49\ ^\circ\text{C}$ and 40 percent R.H.

prepared on microtome holders and exposed for varying durations to carbon-arc radiant energy at $49\ ^\circ\text{C}$ and 40 percent R.H. After selected exposure periods, $25\ \mu$ slices were removed from each film and specimens prepared for infrared analysis as described in 4.1.⁷

A survey of the exposure data (table 4) shows that no significant difference exists in the photooxidation rates of the two films based on carbonyl index for at least the first 10-hr exposure. For greater durations, the surface became hardened, brittle, and uneven. As a result, films of uniform thickness could not be sliced from the asphalt specimen. This was manifested by the large variance of ΔA values obtained beyond the 10-hr exposure period. For this reason, photooxidation rates of $25\ \mu$ and $625\ \mu$ films could not be compared for an exposure period of more than 12 hr.

⁷In order to calculate the carbonyl index (ΔA at $1700\ \text{cm}^{-1}$) [10], the initial carbonyl absorbance of these films was estimated from a graph (previously prepared on thin films of asphalt 6) of film thickness versus initial carbonyl absorbance.

TABLE 4. Changes produced in carbonyl indices of 25 μ films and in 625 μ films of asphalt No. 6 by irradiation¹

Exposure time	Carbonyl index	
	25 μ film	surface of 625 μ film ²
hr		
2	0.011	0.015
4	.024	.022
6	.045	.048
8	.064	.059 ³
10	.101	.096
12	.116	.125 ⁴

¹ Irradiated in Atlas SMC-R Weather-Ometer at 49 °C and 40 percent R.H. for time periods indicated.

² Based on a 25 μ microtome slice from surface of 625 μ asphalt film.

³ Irradiated for 7.5 hr.

⁴ Average of three values, 0.148, 0.085, and 0.132.

4.3. Depth of Photooxidation in Asphalt

In a separate experiment employing the microtome, asphalt specimens were exposed to carbon-arc radiation for 10 hr at 49 °C and 40 percent R.H. A 10 μ slice was removed from the surface and then a second slice of 25 μ thickness removed. The initial carbonyl absorbance (1700 cm^{-1}) of this second film, i.e., 10 to 35 μ below the exposed surface, was not significantly different from films of unexposed asphalt 6 prepared in the usual manner [10]. The implication presented is that photooxidation of asphalt is apparently negligible at depths of >10 μ from the surface. This is in agreement with the conclusions of Dickinson et al., [34].

The authors express their appreciation to S. H. Greenfeld, Research Associate, Asphalt Roofing Industry Bureau, who kindly furnished the asphalt samples and physical property data on the asphalt fluxes.

5. References

[1] D. Hadzi, *Fuel* **32**, 112 (1953).
 [2] R. A. Friedel and J. A. Queiser, *Anal. Chem.* **28**, 22 (1956).
 [3] J. Knotnerus, *J. Inst. Petrol.* **42**, 355 (1956).
 [4] J. E. Stewart, *J. Res. NBS* **58**, 265 (1957) RP2759.
 [5] H. E. Schweyer, *Anal. Chem.* **30**, 205 (1958)

[6] J. W. Romberg, S. D. Nesmith, and R. N. Traxler, *J. Chem. Eng. Data* **4**, 159 (1959).
 [7] B. D. Beitchman, *J. Res. NBS* **63A** (Phys. and Chem.) No. 2, 189 (1959).
 [8] T. F. Yen and J. G. Erdman, *Div. Petroleum Chem. (ACS) Preprint* **7**, 5, March 1962.
 [9] S. H. Greenfeld and J. R. Wright, *Materials Research and Standards* **2**, 738 (1962).
 [10] J. R. Wright and P. G. Campbell, *J. Appl. Chem. (London)* **12**, 256 (1962).
 [11] P. G. Campbell, J. R. Wright, and P. B. Bowman, *Materials Research and Standards* **2**, 988 (1962).
 [12] J. R. Wright, P. G. Campbell, and T. L. Fridinger, *ASTM Preprint No. 88A*, 1963.
 [13] S. Siggia, *Abstracts of Papers, 139th Meeting (ACS), St. Louis, Mo., 24B (Mar. 1961)*.
 [14] L. J. Bellamy, *The infrared spectra of complex molecules*, 2d ed., p. 152 (John Wiley & Sons, Inc., New York, N.Y., 1958).
 [15] *Ibid.*, p. 128.
 [16] N. B. Colthup, *J. Opt. Soc. Am.* **40**, 397 (1950).
 [17] H. W. Thompson and P. Torkington, *J. Chem. Soc.*, 640 (1945).
 [18] E. R. Blout, M. Fields, and R. Karplus, *J. Am. Chem. Soc.* **70**, 194 (1948).
 [19] M. St. C. Flett, *J. Chem. Soc.*, 962 (1951).
 [20] Bellamy, *op. cit.*, p. 191.
 [21] O. D. Shreve, M. R. Heather, H. B. Knight, and D. Swern, *Anal. Chem.* **22**, 1948 (1960).
 [22] J. R. Wright and P. G. Campbell, *Ind. Eng. Chem., Prod. Res. Develop.* (in press).
 [23] J. M. Goppel and J. Knotnerus, *Proc. Fourth World Petrol. Congr., sec. III/G*, 399 (1955).
 [24] S. H. Greenfeld, *J. Res. NBS* **64C** (Engr. and Instr.) No. 4, 287 (1960).
 [25] R. S. Winniford and M. Bersohn, *Div. Fuel Chem. (ACS) preprint*, Sept. 1962.
 [26] R. N. Traxler, *Asphalt, Its Composition, Properties and Uses*, p. 25 (Reinhold Publishing Corporation, New York, N.Y., 1961).
 [27] E. J. Barth, *Asphalt, Science and Technology*, pp. 148-9, 391-2 (Gordon and Breach, Science Publishers, New York, N.Y., 1962).
 [28] S. Siggia, *Quantitative Organic Analysis via Functional Groups*, 2d ed., pp. 46-7 (John Wiley & Sons, Inc., New York, N.Y., 1954).
 [29] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, 4th ed., p. 152 (John Wiley & Sons, Inc., New York, N.Y., 1956).
 [30] P. Ausloos and R. E. Rebbert, *J. Phys. Chem.* **67**, 163 (1963).
 [31] S. H. Greenfeld, *Ind. Eng. Chem., Prod. Res. Develop.* (in press).
 [32] Bellamy, *op. cit.*, p. 8.
 [33] A.S.T.M. Tentative Recommended Practice for Accelerated Weathering of Bituminous Materials (D529-59T), 1961 Book of A.S.T.M. Standards, Part 4, 1233.
 [34] E. J. Dickinson, J. H. Nicholas, and S. Boas-Traute, *J. Appl. Chem. (London)* **8**, 673 (1958).

(Continued on page 68C2-157)