

## THE INFRA-RED SPECTRUM OF ETHYLENE POLYMERS

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Infra-red methods have been devised for the determination in ethylene polymers of methyl group concentration, the type and amount of unsaturation, and the nature and quantity of oxygen containing groups. These determinations are important in considerations of the physical properties, polymerization mechanism and sensitivity to chemical attack of the polymers.

A strong correlation between the extent of chain branching and the degree of crystallinity has been established for higher molecular weight polymers. Unsaturation determinations on a series of fractions covering a wide range of molecular weights show that the total number of double bonds per molecule is of the order of 0.3 to 0.4 both for original polymer and for the fractions. Whilst the  $RR'C=CH_2$  type of unsaturation is most common in direct polymers of ethylene, the  $RCH=CH_2$  type is prominent in low molecular weight pyrolyzed polyethenes and in photo-oxidized polyethylenes. The oxygen containing groups found by infra-red methods in natural or oxidized polyethylene are mainly ketonic or aldehydic, though some hydroxyl exists.

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The wide range of products which can be made by the polymerization of ethylene includes liquids, greases, soft and hard waxes and thermoplastics varying in melting point by as much as 25° C as well as in hardness, softness and tensile strength. To some extent these variations in physical properties can be attributed to changes in average molecular weight and, to a minor extent, in molecular weight distribution, but major differences in physical properties are observed at constant molecular weight and are due to variations in the degree of crystallinity and, in turn, to the variations in the degree to which the molecules have a branched chain structure. The most powerful tool for the determination of the degree of chain branching in ethylene polymers is the infra-red spectrum.<sup>1</sup>

Many ethylene polymers, including normal commercial samples, differ from a simple high molecular weight straight-chain paraffin also in being

<sup>1</sup> (a) Thompson and Torkington, *Trans. Faraday Soc.*, 1945, **41**, 246; (b) Downing, quoted by Bryant, *J. Polymer Sci.*, 1947, **2**, 547.

to some extent unsaturated. The total extent of the unsaturation is known from measurements of iodine number, bromine number and hydrogenation number, but the infra-red spectrum is able to show the extent to which the unsaturation occurs in the various types of olefinic bond such as  $R \cdot CH : CH_2$ ,  $R \cdot CH : CH \cdot R'$  or  $R \cdot R'C : CH_2$ . The double bonds in ethylene polymers are normally present to the extent of, as a maximum, only one per molecule and have little effect on physical properties, but may be, of course, a centre of sensitivity to chemical attack in, for example, oxidative deterioration. The extent of the various types of double bond is also of importance in connection with studies of the mechanism of ethylene polymerization, and measurement of the concentration of the various types by the infra-red method has been used in a recently published study<sup>2</sup> of the mechanism of the thermal degradation of ethylene polymers.

The infra-red spectrum may also be used to detect and estimate quantitatively oxygen-containing groups in ethylene polymers which may occur as a result of an oxygen-containing catalyst or of impurities such as carbon monoxide in the ethylene. They also arise as a result of thermal or photo oxidation. The groups which can be most readily identified and estimated are carbonyl and hydroxyl; unfortunately the peroxide group, which may occur as a result of oxidation is not readily detected by the infra-red spectrum.

**Determination of Chain Branching.**—In the examination of the infra-red spectrum of polyethylene in the  $3 \mu$  region, Fox and Martin<sup>3</sup> observed that the strength of the band at  $3.2 \mu$  indicated that there was an unexpectedly high proportion of the methyl groups in the polymer molecule, and hence the molecule had a branched-chain structure. This is confirmed by examination of the spectrum at around  $7.3 \mu$  and  $11.3 \mu$  where there are also bands which are caused by methyl but not by methylene groups and which can, in principle, be used for the determination of the number of branches in the polymer chain. Considerable caution must, however, be used in obtaining quantitative figures for methyl group contents in ethylene polymers.

The band at  $7.3 \mu$  ( $1378 \text{ cm.}^{-1}$ ) has been used by Thompson<sup>1</sup> to estimate methyl groups. An examination of the extinction coefficient of this band in a number of straight and branched chain paraffins shows that there is a linear relation between the extinction coefficient  $K \left( = \frac{1}{d} \log \frac{I_0}{I} \right)$  at  $1378 \text{ cm.}^{-1}$  and the ratio of the number of methyl groups to the total number of carbon atoms in the molecule ( $[CH_3]/[C]$ ). This is shown in Fig. 1A, based on the spectra from the Naval Research Laboratory given in *American Petroleum Institute Collected Infra-red Spectra*. The following relation is obtained from this graph:

$$[CH_3]/[C] = 1.35 \times 10^{-3} K_{1378}.$$

Extinction coefficients depend to some extent on instrument and technique, and for the Grubb-Parsons instrument used for most of the work on chain branching, the coefficient in the above expression has been found to be  $1.9 \times 10^{-3}$ . When, however, one comes to use this band for the determination of the methyl group concentration in a typical sample of an ethylene polymer, two important points arise. The first is that the  $1378 \text{ cm.}^{-1}$  band lies close to and overlaps a doublet at  $1367$  and  $1355 \text{ cm.}^{-1}$  which appears to be characteristic of methylene groups, and considerable care in graphical resolution is necessary, particularly in polyethylene samples where the amount of branching is small. The second point is that the intensity of the  $1378 \text{ cm.}^{-1}$  band has a different value for solid polyethylene at ordinary temperatures than that for the same polyethylene above its melting point. For a normal sample the intensity in the solid is about

<sup>2</sup> Oakes and Richards, *J. Chem. Soc.*, 1949, 2929.

<sup>3</sup> Fox and Martin, *Proc. Roy. Soc. A*, 1940, **175**, 208.

twice that in the liquid. The expression derived above from the low molecular weight paraffins applies only to liquid polyethylenes and consequently the intensity of the  $1378\text{ cm}^{-1}$  band must be measured in the molten state. Unfortunately the intensity of the  $1367$  and  $1355\text{ cm}^{-1}$  doublet is much greater in the molten state than it is in the solid, and in many polyethylene samples in the molten state the  $1378\text{ cm}^{-1}$  band is only a shoulder on the side of the methylene doublet. Some examples of the spectrum in the  $1350$  to  $1400\text{ cm}^{-1}$  region for ethylene polymers of varying methyl contents are shown in Fig. 2. Nevertheless, provided these points are borne in mind, the  $1378\text{ cm}^{-1}$  band can be used as a measure of the methyl group content and hence the extent of chain branching in ethylene polymers. A sample of commercial polyethylene (Alkathene 20) is found to have one methyl group for every 25-35 carbon atoms.

Another band which may be used in the determination of chain branching lies at  $11.2\text{ }\mu$  or  $891\text{ cm}^{-1}$ . This band, although only one-tenth of the

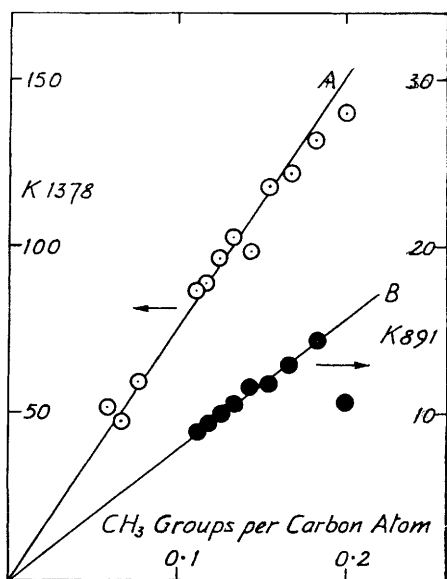


FIG. 1.

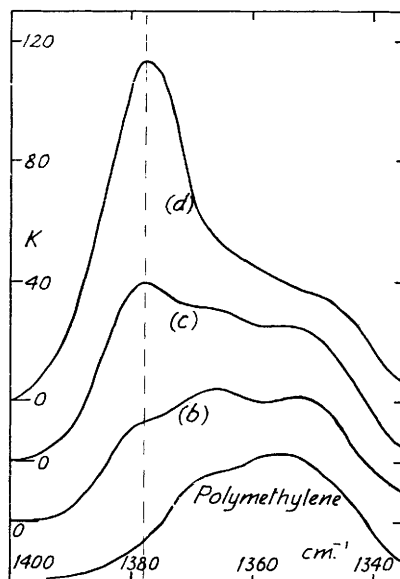


FIG. 2.

intensity, is in some ways more satisfactory than the  $1378\text{ cm}^{-1}$  band as in high molecular weight paraffins it lies well away from other bands and no resolution from near neighbours is required. Fig. 1B, also based on the data from the Naval Research Laboratory given in *A.P.I. Collected Spectra*, shows the linear relation between the extinction coefficient of this band and the methyl content of the hydrocarbon:

$$[\text{CH}_3]/[\text{C}] = 1.25 \times 10^{-2} K_{891}.$$

For the Grubb-Parsons spectrometer, as used in this work, the coefficient is  $2.0 \times 10^{-2}$ . Here again, however, attention must be paid to the effect of phase changes on the intensity of this band. For example, in straight-chain paraffins such as hexatriacontane there is something like a six-fold increase in intensity in passing from the liquid to the solid state, and although the change in ethylene polymers is less marked than this, there may be a 2- or 3-fold variation. Here again, therefore, the intensity of this band must be measured in the molten state if the expression above is to be used for methyl content determination. There is, however, a

second cause of error. It is that there is a band characteristic of one of the types of double bonds which are found in polythene which has an almost identical wave number value ( $888\text{ cm.}^{-1}$ ) and cannot be separated from the methyl group band ( $891\text{ cm.}^{-1}$ ). In a sample of polyethylene of molecular weight about 15,000 (e.g. Alkathene 20) the contribution of the double bond to the band at  $891\text{ cm.}^{-1}$  may be as much as one-third of the total intensity, and in low molecular weight polyethenes, where the double bond concentration is greater, the bulk of the absorption of  $885\text{--}895\text{ cm.}^{-1}$  is due to unsaturation. This is shown by the fact that hydrogenation or bromination reduces the intensity of this band and moves the peak slightly in the direction of increasing wave number, and the absorption at this wave length only gives a true measure of methyl group content if the measurement is done on a polymer sample after all unsaturation has been removed

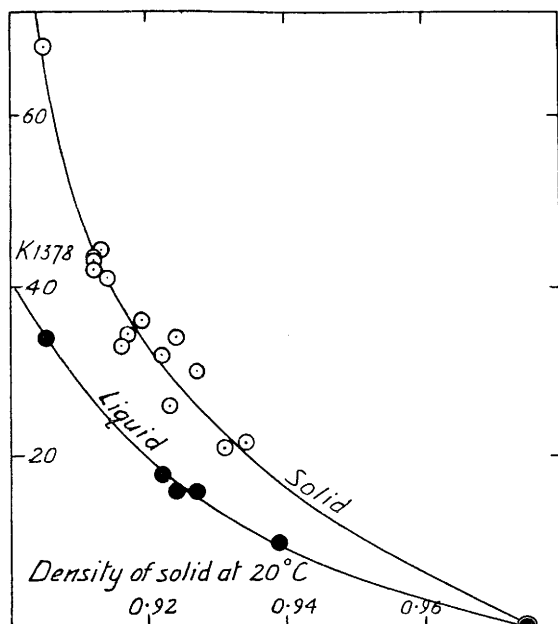


FIG. 3.—Density of solid at  $20^{\circ}\text{C}$ .

by, for example, hydrogenation. When these precautions have been taken the methyl group content determination on a sample of Alkathene 20 from this band is also about one methyl group in 25–35 carbon atoms.

The methyl group concentration determined in either of these ways varies from as much as one in every 15 carbon atoms to as little as one in 200 carbon atoms, and in the higher molecular weight polymers there is a clear cut correlation between the degree of chain branching, as measured by infra-red spectrum, and the degree of crystallinity, as measured by the density, the X-ray absorption, or the intensity of certain infra-red bands which have shown to be characteristic of methylene groups in crystalline or amorphous regions only (Fig. 3). The effect of crystallinity and phase changes on the infra-red spectrum of long-chain paraffins and ethylene polymers is described in a forthcoming paper.

**Determination of Unsaturation.**—Olefinic double bonds lead to absorption in the infra-red at wave lengths of about  $3.3\text{ }\mu$ ,  $5.6\text{ }\mu$ ,  $6.1\text{ }\mu$  and

<sup>4</sup> Thompson, *J. Chem. Soc.*, 1948, 328.

<sup>5</sup> Anderson and Seyfried, *Anal. Chem.*, 1948, **20**, 998.

10-14  $\mu$ .<sup>4,5</sup> For quantitative estimation the last region is most convenient for here each separate type of double bond gives a well-defined intense band at frequencies so far apart that resolution one from the other is simple. The frequencies corresponding to the different types of double bond are listed in Table I.

TABLE I.—INFRA-RED BANDS FOR OLEFINIC UNSATURATION

Double Bond Type	Wave Number cm. <sup>-1</sup>	Molar Extinction Coefficients *
R . CH=CH <sub>2</sub> . . . . .	990	—
	908	121.0
R . CH=CH . R' ( <i>trans.</i> only) . . . .	964	85.4
RR'C=CH <sub>2</sub> . . . . .	888	103.4
RR'C=CHR'' . . . . .	835	34.6
R . CH=CH . R' ( <i>cis</i> ?) . . . . .	705	21.0

$$* \text{ Molar extinction coefficient } \epsilon = \frac{M}{Cd} \log \frac{I_0}{I},$$

where  $M$  = mol. wt. of absorbing group (i.e. 24 for C=C),

$C$  is concentration of the group in g./l.,

$d$  is cell thickness in cm.

Table II also gives average values for the molar extinction coefficients corresponding to each of these bands, based on the extensive work of Anderson and Seyfried<sup>5</sup> on a large number of low molecular weight liquid olefines. If one could be assured that these molar extinction coefficients were valid for solid or semi-solid high molecular weight materials, it would be simple to measure quantitatively the proportion of any type of double bond in polythene. There is, however, a serious complication, account of which must be taken before the infra-red spectrum can be used quantitatively. It is that, as has been shown in the previous section, saturated hydrocarbons also absorb at *ca.* 890 cm.<sup>-1</sup> and that in a normal polyethylene of molecular weight around 15,000 the greater part of the absorption here

TABLE II.—ABSORPTION AT 885-895 cm.<sup>-1</sup> AFTER REMOVAL OF UNSATURATION

Sample	1	2
Molecular Weight	1400	12,000
	$\frac{1}{d} \log \frac{I_0}{I}$ at 885-895 cm. <sup>-1</sup>	
Original sample . . . . .	33.0	6.6
After bromination, i.e. due to methyl . .	5.0	4.7
Difference, i.e. due to RR'C=CH <sub>2</sub> . . .	28.0	1.9
After hydrogenation, i.e. due to methyl.	5.0	4.6
Difference, i.e. due to RR'C=CH <sub>2</sub> . . .	28.0	2.0

is due to methyl groups, rather than to the group RR'C:CH<sub>2</sub>. The absorption spectra of saturated aliphatic hydrocarbons also show a band at 964 cm.<sup>-1</sup>; this is almost exactly superimposed on the band corresponding to R . CH=CH . R'. If, therefore, the proportion of these two types of double bonds in polythene is to be measured, a correction must be applied for a proportion of the absorption at these frequencies due to the

saturated portions of the polymer chain. In low molecular weight ethylene polymers the bulk of absorption at  $885\text{--}895\text{ cm.}^{-1}$  is due to unsaturation, but in high molecular weight materials the bulk is due to chain branching and great care must be taken in separating the contributions caused by the two types of structure. The extent of the separate contributions in high and low molecular weight polythenes is shown in Table II, in which values of  $\frac{1}{d} \log \frac{I_0}{I}$  ( $d$  in cm.) of two samples of ethylene polymers before and after removal of double bonds by hydrogenation or bromination, are listed.

Absorption at  $964\text{ cm.}^{-1}$  remaining after removal of unsaturation is generally small and only in high molecular weight samples is serious error introduced by neglecting this in a determination of  $R \cdot CH : CH \cdot R'$  groups from the infra-red spectrum.

The three types of unsaturation found in ethylene polymers are  $R \cdot CH : CH_2$ ,  $R \cdot CH : CH \cdot R'$  (*trans*) and  $RR'C : CH_2$ . The last is generally the most common in direct polymers of ethylene, whereas the vinyl group is most common in low molecular weight pyrolyzed polythenes. The group  $RR'C : CHR''$  has so far been found only in two polymer samples, and then only in an amount corresponding to less than 10 % of the whole. The band near  $700\text{ cm.}^{-1}$  corresponding to *cis*- $R \cdot CH : CH \cdot R'$  has not yet been detected in an ethylene polymer sample. It is unfortunate that there is not a definite band for the tetra-alkyl ethylene group  $RR'C : C R''R'''$ . Anderson and Seyfried in their work on petroleum derivatives used the difference between the total unsaturation measured by bromine absorption and the sum of the values for the  $R \cdot CH : CH_2$ ,  $R \cdot CH : CH \cdot R'$  (*cis*- and *trans*-)  $RR'C = CHR''$  and  $RR'C : CH_2$  groups as a measure of the proportion of  $RR'C = CR''R'''$ . Fig. 4 shows a plot of the sum of the percentages of the various types of double bonds (calculated from the infra-red spectra with the aid of the coefficients given in Table II) against the iodine number for a number of samples of ethylene polymers ranging from a solid of molecular weight about 15,000 to greases of molecular weight as low as 480 and liquid pyrolysis products of molecular weight as low as 220. The broken line is the total double bond concentration calculated from the iodine number. The samples, in addition to covering a wide range of iodine numbers, molecular weight and physical forms (solids, pastes, greases and liquids), also varied considerably in the proportions of the types of double bonds; they include polymers in which the bulk of the unsaturation is of the type  $RR'C : CH_2$  and samples made by pyrolysis in which the bulk occurs as vinyl groups. It is seen that in Fig. 4 the points representing the sum of the percentage concentrations of  $C=C$  calculations for the infra-red lie close to the line representing the  $C=C$  concentration calculated from the iodine number, but since we cannot assume that the coefficients based on Anderson and Seyfried's work on liquids are valid for solid or semi-solid polymers the presence or absence of the  $RR'C = CR''R'''$  group is still an open question.

As an example of the use of infra-red absorption in the study of unsaturation we may quote the results on a sample of Alkathene 70 and on a series of fractions of number average molecular weight from 1250 to *ca.* 35,000 made from the sample. In all, 53 fractions were produced; the spectra of six have been examined and the values of  $\frac{1}{d} \log \frac{I_0}{I}$  for the bands at  $908$ ,  $964$  and  $888\text{ cm.}^{-1}$  have been measured. When these values are plotted against the reciprocal of the number average molecular weight of the fractions it is found that whereas for the  $908\text{ cm.}^{-1}$  band the points lie reasonably close to straight lines through the origin (as would be found if the number of  $R \cdot CH : CH_2$  groups per molecule were constant), the points for the  $888\text{ cm.}^{-1}$  band are better represented by a line with an intercept (corresponding to infinitely high molecular weight) of about  $3.0$  for  $\frac{1}{d} \log \frac{I_0}{I}$ .

It is suggested that this corresponds to the degree of branching in the polymer chain, and, if this is constant for the various fractions, the difference between the total value of  $\frac{1}{d} \log \frac{I_0}{I}$  and 3.0 is a measure of  $RR'C:CH_2$  unsaturation. The points for the  $964\text{ cm}^{-1}$  band are best represented by a line with a small intercept of about 0.4. Taking account of these intercepts, values are calculated for the concentration of  $C=C$  in the original polymer and in the fractions, and by combining this result with the molecular weights, for the average number of double bonds per molecule.

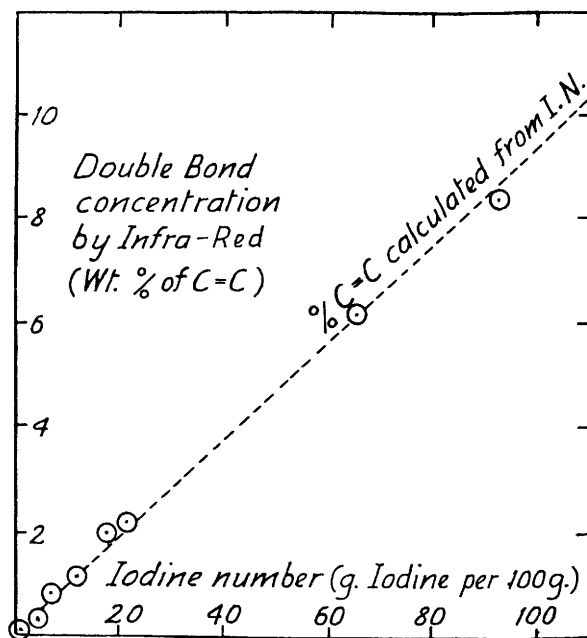


FIG. 4.—Relation between sum of concentration of  $R \cdot CH=CH_2$ ,  $RCH=CHR'$  and  $RR'C=CH_2$  double bonds and iodine number

It is seen that the  $RR'C:CH_2$  group is the most frequent and that the total number of double bonds per molecule is of the order of 0.3-0.4 for all samples. The figures for the high molecular weight fractions and indeed for all polymers of molecular weight above *ca.* 10,000 are of course very approximate as they depend so much on the value assigned to the contribution to absorption at  $888$  and  $964\text{ cm}^{-1}$  due to non-olefinic groups. In other ethylene polymers which have been examined the total double bond concentration is usually within the range 0.3 to 1.0.

**Presence of Oxygen containing Groups in Polyethylenes.**—In the infra-red spectra of some samples of polyethylene, weak absorption bands are found at  $1720$  wave numbers and  $3600$  wave numbers. Absorption bands in these positions are not found in the spectra of paraffins and olefins, and the presence of some other structure is indicated. Since small amounts of free or combined oxygen may be present in the gases used or the catalyst, we have attributed these absorption bands to the presence of carbonyl and hydroxyl groups respectively. This assignment is borne out by the fact that the intensities of these absorption bands vary considerably between different samples.

The frequency of the carbonyl group absorption band ( $1720$  wave



numbers) indicates aldehydic or ketonic groups, but since some long chain aliphatic carboxylic acids have absorption bands in their spectra at 1715 wave numbers, an absorption band due to the carboxyl group might not be resolved if it were present, and the possibility that some of the absorption at 1720 wave numbers is due to the carboxyl group must be considered. However, if carboxyl groups were present, a further band near 1200 wave numbers should occur, due to the C—O vibration within the carboxyl group. Since we have not detected a band in this region which varies in intensity in different samples, the conclusion is that at least the major portion of the absorption at 1720 wave numbers is due to aldehydic or ketonic groups.

From the point of view of the estimation of the oxygen content of polyethylenes by means of the absorption band at 1720 wave numbers, possible interference from the presence of the carboxyl group is an important factor, since the molar extinction coefficient for the carboxyl

TABLE III.—DOUBLE BOND CONCENTRATIONS IN POLYTHENE FRACTIONS

Sample	Mol. wt. (Number average)	Wt. % of C=C			Total	Double Bonds per Molecule
		R. CH=CH <sub>2</sub>	<i>trans</i> - R. CH=CH . R'	RR'C : CH <sub>2</sub>		
Fraction 1 .	1250	0·120	0·095	0·400	0·615	0·32
Fraction 2 .	2300	0·059	0·080	0·169	0·308	0·30
Fraction 3 .	4500	0·042	0·040	0·110	0·192	0·36
Fraction 4 .	7700	0·014	0·022	0·099	0·135	0·43
Original Polymer .	11000	0·019	0·012	0·047	0·078	0·36
Fraction 5 .	15500	0·011	0·011	0·020	0·042	<i>ca.</i> 0·3
Fraction 6 .	35000	0·007	0·004	0·011	0·022	<i>ca.</i> 0·3

group at 1715 wave numbers is about twice that of the ketonic or aldehydic carbonyl group at 1720 wave numbers. To neglect possible interference by the carboxyl group band would therefore involve the possibility of considerable error in oxygen determination.

The absorption band at 3360 wave numbers in some samples indicates the presence of fully associated hydroxyl groups of an alcoholic nature. Absorption in this position also occurs when the polyethylene sample contains a small quantity of water, but if this is removed by vacuum-drying there is often residual weak absorption in this position. In no case have we observed an absorption band at 3600 wave numbers, which would indicate the presence of free hydroxyl groups. However, the molar extinction coefficient of the band at 3360 wave numbers, due to the associated hydroxyl group, is greater than that due to the free hydroxyl group at 3600 wave numbers, and it is therefore possible that a relatively small concentration of free hydroxyl groups might not be detected, in view of comparatively intense absorption of polythene in this region.

Although the spectra of some peroxides and hydroperoxides have been examined, there does not appear to be an absorption band, comparable in intensity with the carbonyl and hydroxyl group absorption bands, which is characteristic of the peroxide or hydro-peroxide group, and the infra-red spectrum cannot therefore be used to detect these groups. This is particularly unfortunate in oxidation studies, when the initial peroxide content might be expected to be an important factor in determining the rate of oxidation.

We have no evidence of the presence of other oxygen containing groups which could be readily detected, such as the ether linkage, in either natural or oxidized polyethylene samples.



**The Study of Heat and Photo Oxidation of Polyethylene.**—The spectrum of a sample of Alkathene 20, before and after heat oxidation for 80 hr. at 105° C is reproduced in Fig. 5A and 5B. The most prominent difference in the spectrum is at 1720 wave numbers, where the very weak absorption band occurring in the original sample has increased markedly in intensity. This difference is attributed to the uptake of oxygen as carbonyl groups.

The evidence is that here also the absorption is almost entirely due to aldehydic or ketonic carbonyl groups. The only additional absorption band which might be attributed to the C—O vibration of a carboxyl group is the weak band which appears at 1170 wave numbers in oxidized samples. The presence of a small concentration of carboxyl groups in a sample of very heavily oxidized polythene was established by boiling a heat oxidized

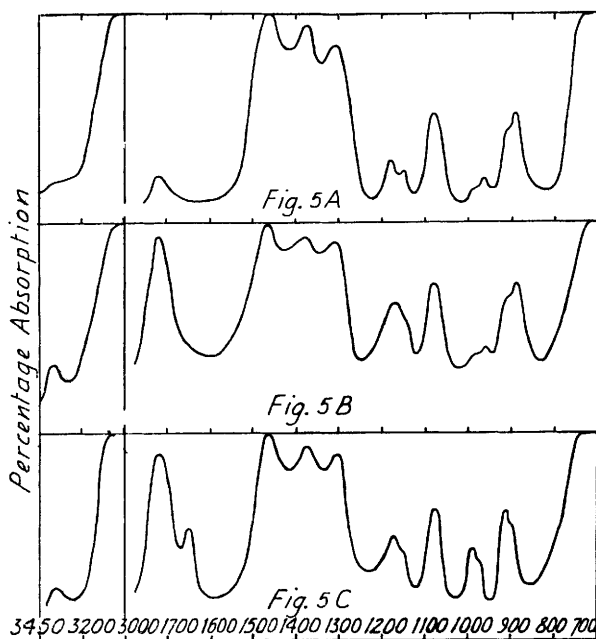


FIG. 5A.—Alkathene, grade 20.

FIG. 5B.—Alkathene, grade 20. Heat oxidized.

FIG. 5C.—Alkathene, grade 20. Photo oxidized.

film in dilute sodium hydroxide solution. The spectrum of the film after this treatment showed an absorption band at 1550 wave numbers (Fig. 6). Absorption in this position is characteristic of the presence of a metallic salt of a carboxylic acid, and it was therefore presumed that the sample contained some carboxyl groups although these could not be quantitatively estimated owing to the difficulty of ensuring complete conversion of the carboxylic acid to the salt. This sample, however, was so heavily oxidized that, as can be seen from Fig. 6, the carbonyl group absorption band was much too intense to measure, and a similar experiment performed with a less oxidized film, in which it was hoped to measure the intensity of the absorption band at 1720 wave numbers before and after this treatment, produced neither a measurable absorption band at 1550 wave numbers nor a measurable decrease in the intensity of the 1720 wave number absorption band. It was concluded from this evidence that the contribution of carboxyl groups to the absorption band at 1720 wave numbers was negligible.

The other major spectral difference is the greatly increased intensity of

the hydroxyl group absorption band at 3360 wave numbers. Even in heavily oxidized samples, containing an appreciable concentration of hydroxyl groups, there was no indication of the presence of an absorption band at 3600 wave numbers due to the free hydroxyl group.

Another effect of oxidation, which was noted by Thompson and Torkington<sup>3</sup> in their examination of heat-oxidized rubber, is a general increase in the intensity of absorption in the region of 800-1700 wave numbers. This effect is partially due to optical scattering by the solid film, since the transmission of an oxidized film increases considerably on melting, but this does not appear to be the complete explanation.

Minor spectral differences occur in the region of 900-1000 wave numbers, which are due to small differences in unsaturation on oxidation, but there does not appear to be a marked difference in any of the three types of unsaturated groups found in polyethylene on heat oxidation.

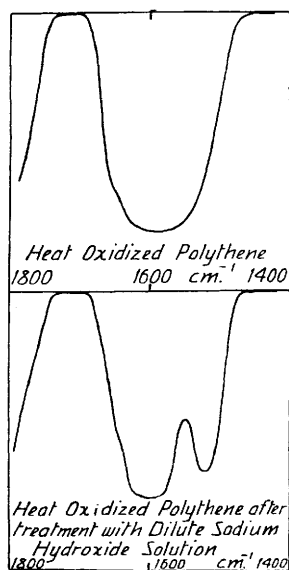
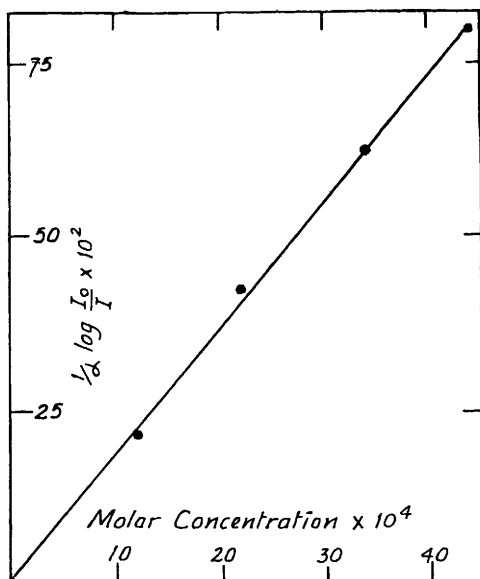


FIG. 6.

FIG. 7.—Determination of the molar extinction coefficient of di-*n*-butyl ketone at 1720 cm.<sup>-1</sup>.

The effect of photo-oxidation has also been studied. The infra-red spectrum of Alkathene 20 after photo-oxidation is given in Fig. 5c. All the effects noted on heat oxidation are apparent in photo-oxidation. There are, in addition, certain other well-defined differences. An absorption at 1645 wave numbers, which is sometimes found as a very weak band in the spectra of thick samples of natural polyethylenes appears as a moderately intense absorption after photo-oxidation. The absorption bands at 909 and 990 wave numbers also increase markedly in intensity.

All these differences may be attributed to a considerable increase in unsaturation of the type  $\text{RCH}=\text{CH}_2$ ; the absorption bands at 909 and 990 wave numbers being the frequencies associated with the deformation of the C—H linkages about the double bond; the absorption at 1645 is the corresponding C=C stretching frequency. The difference at 909 and 990 wave numbers are comparatively more marked, since the molar extinction coefficients for these absorption bands are much greater than that of the 1645 wave number absorption band.

It may be said, therefore, that the major qualitative differences observed in the infra-red spectra of samples of oxidized polyethylenes may

be correlated with the formation of carbonyl and hydroxyl groups ; while in heat oxidation there are no well marked differences in unsaturation there is, in photo-oxidation, a considerable increase in unsaturation of the type  $\text{RCH}=\text{CH}_2$ .

#### The Quantitative Determination of Oxygen containing Groups.—

The estimation of the oxygen present as carbonyl groups is of particular interest, since this accounts for the major proportion of the combined oxygen which can be detected both in normal polyethylenes and in oxidized samples.

The molar extinction coefficient for the absorption band at 1720 wave numbers has been determined on a number of simple aldehydes and ketones. A calibration curve produced from measurements taken on solutions of di-*n*-butyl ketone in cyclohexane is reproduced in Fig. 7 : from the slope of this graph the molar extinction coefficient, as determined on the D209 spectrometer (used as a single beam instrument with dried air-path) is 188. Other comparable ketones and aldehydes give values within 20 % of this figure.

The carbonyl concentration in a sample is found by measuring the value of  $\frac{1}{d} \log \frac{I_0}{I}$  ( $d$  = thickness of sample in cm.) at 1720 wave numbers dividing by the molar extinction coefficient, and calculating from molar concentration to grams per cent. The accuracy attainable may be exemplified by a comparison between chemical determinations and infra-red results obtained on two ethylene-carbon monoxide interpolymers which were measured in chloroform solution.

TABLE IV.—CARBONYL CONTENT OF ETHYLENE-CARBON MONOXIDE INTERPOLYMERS

	Sample 1		Sample 2	
	Chemical	Infra-Red	Chemical	Infra-Red
Carbon . . . . .	75.7 %		82.1 %	
Hydrogen . . . . .	11.2 %		12.8 %	
Carbonyl (by difference) .	22.9 %	26 %	9.0 %	10.1 %

In the measurement of  $I_0$ , it is necessary to apply a correction for general absorption or scattering, otherwise appreciable error may be introduced especially with highly oxidized samples.

The magnitude of the correction is determined by measuring the transmission of the required sample, and that of a similar sample containing no carbonyl groups, at some frequency near 1720 wave numbers at which no specific absorption occurs in either sample. The ratio of the transmissions at this frequency gives a measure of the relative scattering of the two samples. It is assumed that the relative scattering is the same at 1720 wave numbers, which is justified if the comparison position is sufficiently near this frequency. The transmission of the comparison sample at 1720 wave numbers is now measured, and from the determined scattering ratio the transmission  $I_0$  of the required sample at 1720 wave numbers may be calculated.  $I$  is then measured directly, and the oxygen content as carbonyl groups may be calculated.

The concentration of hydroxyl groups in a sample is found in a similar way, using a molar extinction coefficient calculated from measurements on simple alcohols. This molar extinction coefficient is found to be approximately 54 for the D209 spectrometer.

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