LIX.—*The Composition of Paraffin Wax. Part I.*

By FRANCIS FRANCIS.

THIS investigation was undertaken in the hope that some light might be thrown on the nature of the hydrocarbons contained in paraffin wax. This solid product of the petroleum industry was selected because at temperatures between 130° and 200° it may be more readily oxidised by oxygen-containing gases than the liquid petroleum, and secondly because the process can be carried out, under certain conditions, at a temperature of 100° .

The investigation has now been in progress for some years, and this preliminary account of it describes the first stage of what appears likely to prove a tedious and difficult piece of work.

Since 1918 a series of papers has been published on this subject, but the various authors have only described the results obtained when the oxidation by air or oxygen was carried out at temperatures higher than those I have employed. It is to the use of such temperatures, presumably, that must be ascribed the deep-seated oxidation which takes place, as shown in the number, variety, and relatively low molecular weight of the resulting substances. From such breakdown products, clearly fragments of the original molecular complex, it has not been found possible to obtain any insight into the nature of the hydrocarbons comprising paraffin wax.

I have found, however, that when air oxidation is brought about in the presence of small quantities of turpentine and at temperatures not exceeding 110° , then selective oxidation takes place of one—presumably—class of constituents of the wax, and the resulting derivatives are less numerous than those described by previous observers, and certain members are comparable in molecular magnitude with the hydrocarbons present in the wax. It is believed that these substances are the precursors of the many acids described by other investigators working at higher temperatures.

The part played by turpentine is under investigation, but in the absence of this substance no oxidation has been found to take place with air at 102° in the time occupied by the experiments.

When oxygen is employed instead of air, even at a temperature of 100° , the oxidation appears to proceed further, and among the resulting products, again small in number compared with those described by others, there are present acids of lower molecular magnitude than corresponds with the wax which has been oxidised.

When oxygen is used at the temperature mentioned above, no oxidation takes place until after the lapse of a period in which very considerable change sets in, provided turpentine is present. Oxidation, however, does take place in the absence of this substance, commencing about one month after the wax has been treated continuously with a current of the gas.

A comparison has been made between the oxygen treatment of the wax containing turpentine and the two synthetic normal paraffins—hexadecane, $C_{16}H_{34}$, and dotriacontane, $C_{32}H_{66}$ —in the presence of the same substance, but although all the conditions were strictly comparable with the experiments previously mentioned, it was found that no oxidation of these hydrocarbons takes place.

In all the various oxidations which have been carried out with the wax, there is always a residue of unacted-upon hydrocarbons. These hydrocarbons were isolated and re-treated with oxygen, but the resulting material was never found to contain more than a small fraction of the amount of oxygen present when the original wax was treated in a comparable manner.

These observations, together with the previous fact concerning the synthetic paraffins, lead to the conclusion that the method of oxidation employed may be capable of differentiating between what are, probably, normal paraffins, and other at present unknown constituents of the wax which undergo oxidation. This view has been strengthened by the discovery that it is possible to obtain certain fractions, by distilling the wax in a high vacuum, which, under comparable conditions, are very much more readily oxidised than others.

If the interpretation of this observation proves to be correct, namely, that it is possible to separate, or to separate even partly, the wax into oxidisable and non-oxidisable constituents, then the further investigation of the whole problem will be rendered much easier.

1. The Action of Air and Oxygen on Paraffin Wax.

The material used in this investigation was obtained from the Young Paraffin Light Co., Addiewell, and fused between 55° and 56° . Judging from this, from the analytical data, and from the molecular-weight determination carried out by the ebullioscopic method

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using benzene as solvent—all given in Table I, experiment 1—the substance appeared to consist of hydrocarbons corresponding closely with the average analysis of such paraffin waxes, namely, C = 85.15; H = 14.85 per cent. Our knowledge, however, is insufficient for any statement to be made as regards the nature of these hydrocarbons, although they are generally supposed to be mixtures of normal members of the paraffin series.

When a rapid current of dry air, free from carbon dioxide, was passed through the molten wax at a temperature of 70–80°, no oxidation was found to take place in one hundred and sixty-eight hours, and at 90° there was no change in three hundred and thirty-six hours.

In the next experiments, numbered 2 and 3 in Table I, analytical data are given for the resulting material. These were carried out at higher temperatures than the above, but under precisely the same conditions, in the same thermostat, and at the same time as those to be described later, in which small quantities of turpentine were present in the molten wax.

The results obtained with oxygen, passed through the wax by means of fine jets, are also given in the same table, and these may be compared with the analyses of the resulting material when turpentine is present (see Table II).

TABLE I.

Expt.	M. p.	Mol. wt. Ebullio- scopic method in benzene.	Iodine value.	Temp.	Air current. Dura- tion in hours.	Analysis.		
						C.	H.	O, by differ- ence.
1.	55–56°	363–366	3.9			85.4	14.7	—
2.	55–56	360		101–103°	333	85.4	14.6	—
3.	56–57	—	3.9	110	282	85.3	14.6	—
						Oxygen current.		
4.	55			100	240	85.1	14.8	—
	53–55		3.08	„	696	85.4	14.4	—
	50–54		3.39	„	862	84.9	14.5	0.6
	46–52		3.71	„	956	82.2	14.0	3.8
	36–46		—		1276	74.7	11.6	13.7

The data in Table I show that the wax is not attacked by air during two hundred and eighty hours at 110° or by oxygen during seven hundred hours at 100°.

In the case of oxygen, the sudden increase in the velocity of oxidation after the lapse of so long a period is interesting, and it is highly probable that if the experiments with air had been continued for a sufficient length of time similar results might have been

obtained. Judging from the iodine values, there is no indication of the formation of unsaturated substances previous to the onset of oxidation. Oxidation commences, as it does in all cases investigated, with the simultaneous formation of water, carbon dioxide, and formic acid.

A further communication on what may be termed the latent period in the oxidation will be published shortly. It may be stated here, however, that when paraffin wax is kept in a vacuum at 100° for seven hundred hours, and afterwards treated with a current of oxygen, this period is diminished by about 20 per cent.

That oxidation takes place readily, with varying degrees of velocity, at higher temperatures has been determined by many investigators.

Besides various patents dealing with the oxidation of paraffin wax by air at temperatures between 120° and 150°, of which the first is that taken out by Schaal in 1884, the following are of importance—Bergmann (*Z. angew. Chem.*, 1918, **31**, 69, 115, 148) has used air at 130—135°; Kelber (*Ber.*, 1920, **53**, [B], 66, 1567) at 140—150°, and states that with oxygen the reaction becomes violent if the temperature rises above 200°, but at such temperatures it will be complete in four to five hours. Fischer and Schneider (*Ber.*, 1920, **53**, [B], 922) used temperatures 135—145° and up to 170°, and also carried out the process under pressure. Grün (*Ber.*, 1920, **53**, [B], 987) states that paraffin wax can be oxidised in four to five hours with oxygen at 130—135° and that the composition of the resulting material depends on the temperature employed and on the duration of the experiment. Löffl (*Seifen Z.*, 1920, **27**, 622) also mentions the importance of temperature and states that the best yield of acids is obtained at 115—120° under three atmospheres' pressure. Franck and others have also used oxygen at a temperature of 150°.

It is certain that oxidation with either air or oxygen can be brought about readily at temperatures above 130°, although the experiments described in Table I indicate unquestionably that, at the temperatures described and in the time stated, oxidation either does not take place, or does so with such a small velocity that after the lapse of a considerable period the amount of oxygen in the resulting product is incapable of detection from the results of carbon and hydrogen analyses.

The discussion of the relatively low molecular weight products obtained by the above investigators is left to a future communication.

The very large increase in the velocity of oxidation when the process is carried out in the presence of small quantities of turpentine is described in the next section, and this reaction was

under investigation before any of the papers mentioned above had been published.

II. *The Action of Air and Oxygen on Paraffin Wax containing Turpentine.*

When a small quantity of turpentine is added to the wax and the resulting material treated with a current of air or oxygen under precisely similar conditions to those previously described for the wax alone, then oxidation does take place.

In experiments numbered 2A and 3A, Table II, the current of air passed first through molten paraffin—the analyses of the resulting materials are given in experiments 2 and 3, Table I—then through a layer of cotton wool to retain the wax carried over as vapour by the air current, and amounting to 1.5 per cent. of the whole material in three hundred and thirty-three hours, and finally into another quantity of the wax containing 5 per cent. of turpentine. The analytical data for the resulting material from a series of such experiments with air and oxygen are given in Table II.

In experiments 2A, 3A, 4, and 5, the results of which are summarised in Table II, a considerable amount of turpentine was carried away by the air current. It was collected in tubes filled with cotton wool, and in experiment 4 the amount of unchanged material obtained showed that the oxidation could have been effected with considerably less than the 5 per cent. of turpentine actually employed.

In the case of oxygen, the gas stream carried over but very small quantities of volatile material, which in these cases condensed in the cool part of the reaction vessel.

The results given in Tables I and II illustrate the following deductions:

(1) Paraffin wax treated with dry air at 101–103° for three hundred and thirty-three hours is not affected, whereas in the presence of 5 per cent. of turpentine the resulting material contains 10.8 per cent. of oxygen.

(2) Treated with oxygen at 100° for six hundred and ninety-six hours, paraffin wax is not oxidised; but in the presence of 5 per cent. of turpentine the resulting substance contains 19 per cent. of oxygen.

(3) The velocity of the reaction with oxygen is greater than with air, although the temperature is lower; also the oxidation proceeds further.

(4) In the oxidation with oxygen using turpentine (experiment 6, Table II) the process appears to cease after the lapse of six hundred and ninety-six hours, since the product contains the same percentage

TABLE II.

Expt.	Remarks.	Rapid current of dry air, free from CO ₂ .		M. p.	Analysis.		
		Temp.	Duration in hours.		C.	H.	O, by differ- ence.
2A	400 Grams of paraffin wax and 20 grams of turpentine.	101-103°	333		76.6	12.6	10.8
3A	„ „	110	282		77.7	12.6	9.7
4	1000 Grams of paraffin wax and 50 grams of turpentine.	109-110	646		78.3	12.7	9.0
5	100 Grams of paraffin wax and 5 grams of turpentine.	100	595	46°	78.3	12.8	8.9
Dry oxygen from fine capillaries.							
6	„ „	100	48	52-52	85.2	14.3	0.5
		„	144	47-49	83.7	14.5	1.8
		„	192	47-49	83.0	14.0	3.0
		„	240	44-48	82.3	13.5	4.2
		„	312	44-48	79.9	13.3	6.8
		„	360	43-47	78.7	13.1	8.2
		„	408	40-45	78.8	12.7	8.5
		„	480	37-43	76.1	12.4	11.5
		„	600	34-40	73.4	11.6	15.0
		„	696	35-41	70.2	10.8	19.0
		„	936	39-43	70.3	10.7	19.0
Air saturated with moisture.							
7	„ „	100	501	53-55	84.8	14.5	0.7
Dry oxygen.							
8	Dotriacontane and 5% of turpentine.	100	696		85.0	15.1	
			before treatment		85.0	14.9	
9	Hexadecane and 5% of turpentine.	„	260		84.4	14.7	0.9
			730		84.4	15.3	
			calculated		85.0	15.0	

of oxygen after a further two hundred and thirty hours' treatment with this gas. It will be noticed, however, that the melting point of the resulting material, which falls gradually for the first six hundred hours, commences to rise after that period. It is believed that this has a bearing on the nature of the resulting acids.

(5) Moisture appears to inhibit the oxidation process. After five hundred and ninety-six hours' treatment with dry air the product contains 9 per cent. of oxygen, but in the case of moist air only

0.7 per cent. after five hundred and one hours. Although moisture appears to act in this manner, yet if the reaction has actually commenced it does not hinder its progress.

(6) The two synthetic hydrocarbons, dotriacontane and hexadecane, are not oxidised under the conditions described. As will be seen later, there are constituents of paraffin wax which do not appear to be oxidised by the method employed.

III. Minor Products of the Oxidation, and the Action of Turpentine.

(A) In all cases when oxidation takes place, water, carbon dioxide, and formic acid are evolved. That this is due, in part at least, to the oxidation of turpentine is certain, but that it is not entirely the case is shown by the fact that these substances are also formed after prolonged treatment of paraffin wax with oxygen in the absence of that substance.

In experiment 4, Table II, in which 1 kilo. of wax was oxidised, carbon dioxide was slowly evolved during the process, although it practically ceased forty-eight hours before the air current was stopped. By allowing the air current to pass through a series of wash-bottles containing an excess of barium hydroxide solution, 60 grams of barium carbonate, corresponding with 13.5 grams of carbon dioxide, were collected and the volatile acids were converted into barium salts, of which 50 grams were obtained. An analysis of these salts, and an investigation of the acids obtained from them, showed that they consisted of more than 80 per cent. of formic acid, of which consequently about 17 grams had been formed in the reaction.

These minor products of oxidation may be of significance, but their bearing cannot be discussed until further knowledge of the process shall have been obtained.

(B) In the above experiment, a total amount of 100 grams of turpentine was used, and there was carried over by the air current and collected in the manner described, 102 grams of a liquid consisting of about 40 grams of unchanged turpentine, 45 grams of a liquid of a higher boiling point, which is similar to the material formed when turpentine itself is treated with air, and 9—10 grams of a liquid acid. It is clear that it is possible to account for a very considerable amount of the turpentine used in the process.

Although the acid mentioned above may contain small quantities of substances derived from turpentine, its close analogy with that obtained from the oxidation of paraffin wax in the absence of that

That the velocity of the oxidation of paraffin wax is greatly accelerated in the presence of turpentine is clear, and that this substance itself suffers change during the process has also been established. The action of air and oxygen on turpentine is now being investigated, and the results obtained up to the present with air support the views expressed concerning this substance.

A consideration of the relationship between the amount of oxygen present in the final product (Table II, No. 6) and the duration of the oxygen current, points to the possibility that the process is one of auto-oxidation; but with the information at present at our disposal it is not possible to discuss the part played by turpentine in bringing about the oxidation.

IV. Investigation of the Products of Air Oxidation.

The products of the oxidation fall into two groups :

(A) The small quantities of volatile materials, water, carbon dioxide, and formic acid, carried over by the air current and described in the previous section.

(B) The substances remaining in the reaction flask and composed of :

- i. Small quantities of acidic material of low molecular weight, mentioned in the previous section, and amounting to between 2 and 3 per cent. in all.
- ii. Acidic substances of molecular weight corresponding with that of the paraffin oxidised.
- iii. Non-acidic oxidised material and unacted-upon hydrocarbons.

The oxidised paraffin, when solid, resembles bees'-wax. After many attempts to treat this material in such a manner as to effect a separation of acidic from unchanged wax and non-acidic oxidised material, the most satisfactory method that was found consisted in dissolving 100 grams of the molten product in 400 c.c. of absolute alcohol, adding 10 c.c. of 40 per cent. sodium hydroxide solution to the hot liquid, and then slowly pouring into this solution 200—250 c.c. of hot water. Two layers were formed and could be separated by means of a syphon. The upper layer, solidifying on cooling, consisted of the wax and inert oxidised material; the lower of a solution of alkaline salts, which on acidification gave a dark-coloured oil, solidifying on cooling. The acidic and non-acidic fractions were repeatedly washed with boiling water and dried at 90° in a vacuum before analysis.

Table III gives the analytical data for various preparations of acidic and non-acidic material obtained by employing the above method.

A comparison of the analyses, given in Table III, of the various preparations of acidic and non-acidic materials, shows that the method of separation is better than might have been expected; but it is one that requires some experience in order to avoid the formation of emulsions.

The alkaline salts of the acidic material carry into solution varying amounts of non-acidic substances, and give rise to a slightly opalescent, soapy solution which cannot be extracted by any of the ordinary organic solvents, owing to the formation of emulsions. On acidification, the total material present is thrown out of solution, and the formation of various mixtures of acidic and non-acidic substances accounts for the differences in acid values obtained, and magnifies the yield given in column 5 in a manner that will be discussed later.

Further, the separation is one that does not lend itself to great accuracy, and the numbers in column 5, with the possible exception of experiment 4A, can be regarded only as approximations correct to about 3 per cent.

When the mixture of solid acids described above has been separated by acidification of the aqueous alcoholic solution (and their solubility in this medium was found to be extremely small), the solution still contains small quantities of soluble acids, which amounted to 22 grams in the case of the experiment in which 1 kilo. of paraffin wax was oxidised. These appear to be identical with the material carried over by the air current, amounting to 9 grams and described in section III. This acid gave the following data on analysis : C = 59.86; H = 8.44; O = 31.70 per cent.; the molecular weight by the ebullioscopic method using acetone as solvent was 202, and the acid value 309. For the sake of future reference these acids have been placed in the " γ " group, and they will be discussed later.

Up to this point, taking the data from the experiment carried out with 1 kilo. of paraffin wax, the composition of the material in the reaction flask is 39 per cent. of non-acidic substances composed of unchanged constituents of the wax and oxidised hydrocarbons; 59 per cent. of impure acids containing oxidised hydrocarbons and small amounts of unchanged hydrocarbons; and in all about 3 per cent. of " γ " acids.

TABLE III.

Acidic Material B. ii.

Expt.	Remarks.	Dry air current.		Yield of crude acidic substances per cent.	Mol. wt. Ebullio-scopic method using acetone.	M. p.	Acid value.	Analysis.		
		Temp.	Duration in hours.					C.	H.	O, by difference.
2B	Oxidation of 40 grams.	101-103°	168 333	12 25		42-43°	120	74.1	11.8	14.1
3B	Oxidation of 400 grams.	110	282	56		41-42	112	74.4	11.4	14.2
4A	Oxidation of 1000 grams.	109-110	646	59	440	42-45	75	74.9	11.9	13.2
7		96-98	336	60	446	41-42	123	74.4	11.2	14.4
8		104	168	60	436	40-41	123	73.3	11.5	15.2
9	Residual hydrocarbons from previous oxidations.									
10	800 Grams of material from various preparations, used in the present investigation.	106-110	261	14	—	42-48	88	76.0	12.1	11.9
		—	—	—	442	40-42	82.6	75.2	11.9	12.9

Non-acidic Material B. iii.

Expt.	Remarks.	Dry air current.		Yield of crude acidic substances per cent.	Mol. wt. Ebullio-scopic method using acetone.	M. p.	Acid value.	Analysis.		
		Temp.	Duration in hours.					C.	H.	O, by difference.
4B	Residue from the oxidation of 1 kilo. of paraffin wax (4A above).					47-50	1.2	80.5	13.4	6.1
11	Collection of residues from 2B and 3B above.					45-52	0.8	81.4	13.7	4.9
12	Residue from No. 9 above.					49-53	0.6	81.3	13.6	5.1

Source.

4B Residue from the oxidation of 1 kilo. of paraffin wax (4A above).

11 Collection of residues from 2B and 3B above.

12 Residue from No. 9 above.

V. Investigation of Acidic Substances from Air Oxidations.

[With JOHN CLIFFORD POPE.]

Owing to decomposition it was not found possible to separate the constituents of this mixture by fractional distillation in a vacuum. This, and the impossibility of recrystallising the material, added greatly to the difficulties in the way of, first, separating the acidic from the non-acidic constituent which was known to be present in the material resulting from the preliminary separation, mentioned in section II, and still further of separating the mixture of acidic substances themselves. It was only after a considerable amount of work had been carried out that the former was accomplished. The results of the latter will be communicated at a later date.

(A) The crude acidic material gives sodium or potassium salts from which the inert material present cannot be extracted by the ordinary solvents. The analyses of the acids from different specimens of barium salts washed with light petroleum by different methods are given in Table IV, C, D, I, J.

(B) The analysis of the acid obtained from the most soluble fraction of the magnesium salts in ethyl alcohol is given in Table IV, E.

(C) A more satisfactory method of separating the constituents of the mixture consists in pouring the molten material into ten times its weight of ethyl alcohol containing 8 per cent. of water. The characteristics of the more soluble fraction are given in Table IV, experiment F.

(D) It was only at a later stage of the investigation that it was found possible to separate readily such mixtures of acidic and inert material by dissolving them in a mixture of 50 per cent. of alcohol and 50 per cent. of water containing an excess of sodium hydroxide, and repeatedly extracting the solution with light petroleum. By this method the formation of emulsions is entirely avoided, and a very satisfactory separation into acidic and non-acidic substances soluble in the solvent can be effected.

Various fractions obtained from the original mixture by treatment with alcohol as described in this section (No. C) were subjected to this process of separation, and the analyses of the acids obtained from the more soluble fraction are given in Table IV, experiments G and H.

The acids, freed from inert material by this method, were then converted into barium salts, which were extracted with light petroleum. The analyses of the acids obtained from the insoluble

(experiment K) and soluble barium salts (experiment L) are given in Table IV.

For the sake of reference, we term the substances from the *soluble* barium salt the " α "-acids, those from the *insoluble*, the " β "-acids.

TABLE IV.

Expt.	Source of acid (air oxidation).	Mol. wt. Ebullioscopic method with acetone as solvent.	M. p.	Acid value.	Analysis.		
					C.	H.	O, by difference.
C	Barium salt (Soxhlet) from crude acids.		47-49°	149	73.5	11.6	14.9
D	Barium salt from crude acids.		44-45	131	73.0	11.6	15.4
E	From magnesium salts.	406	37	114	73.6	11.4	15.0
F	Soluble in 92% alco- hol.		35	110	73.8	11.4	14.8
G	Separation by light petroleum; lowest m. p.	410	37.5	137	72.8	11.3	15.9
H	Separation by light petroleum; second fraction.	400	43	138	73.3	11.5	15.2
I	Barium salt insoluble in light petroleum.	410	42	154	74.0	11.9	14.1
J	Barium salt soluble in light petroleum.		9-10	89	73.6	11.0	15.4
K	Barium salt, insoluble in light petroleum, from acids free from inert material.	326	43.5		73.0	12.1	14.9
L	Barium salt, soluble in light petroleum, from acids free from inert material.	452	liquid	141	72.1	11.2	16.7

The method of separation described in this section (No. D) shows that the crude acids (see column 5, Table III) are composed of 54 per cent. of acids and 46 per cent. of non-acidic material.

VI. Non-acidic Substances from Air Oxidation.

(A) The non-acidic substances separated as described in section IV are seen by reference to Table III to contain between 5 and 6 per cent. of oxygen. This mixture of inert oxidised material and unchanged hydrocarbons of the paraffin wax is very difficult to separate by fractional distillation in a high vacuum.

(B) The crude acidic substances are seen by reference to Table III

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to contain an average of about 13·8 per cent. of oxygen, whereas the purer material (see Table IV) contains between 14 and 15 per cent. This is due, as previously indicated, to the fact that the alkaline salts, from which they were obtained, are capable of carrying into aqueous solution a considerable amount of inert oxidised material and what is believed to be smaller quantities of unchanged hydrocarbons.

(1) The complete separation of the oxidised non-acid fraction (see Table III, B iii) from the non-acidic mixture containing hydrocarbons is a difficult matter. The method we have adopted consists in dissolving the mixture in boiling acetone, when, on cooling, the majority of the hydrocarbon crystallises out, but only an impure oxidised material containing 7·8 per cent. of oxygen can be obtained from the solvent.

During this separation a small amount of a substance was isolated practically insoluble in acetone. It showed an extremely high molecular weight, but as it amounted only to about 1·5 per cent. of the whole material, it has not been investigated further.

(2) A much purer specimen of the non-acidic substance can be obtained from the crude acidic material (see table III, B ii) on treatment with alcohol, as described in section V, No. C. When the fractions are further purified as described in section V, No. D, the non-acidic constituent can be isolated from the light petroleum used. The analysis of two specimens, 1 and 2, isolated in this manner from the two most soluble fractions, are given below.

The purest preparations, small in amount but presumably free from hydrocarbons, were obtained in the case of No. 3 from the material extracted by light petroleum from the barium salts (see Table IV, K and L) and in that of No. 4 during the separation of the acids by means of their lead salts.

	M. p.	Mol. wt. Ebullio- scopic method.	Analysis.		
			C.	H.	O, by differ- ence.
1.	Inert oxidised semi-solid	375	77·3	12·5	10·2
2.	" " "	380	77·1	12·7	10·2
3.	" " liquid	—	74·9	11·9	13·2
4.	" " "	—	75·2	12·1	12·7

As far as the investigation has progressed at present we are now in a position to state the approximate composition of the solid material resulting from the passage of air through paraffin wax in the presence of turpentine and under the conditions mentioned. The data are given in Table V.

TABLE V.

	Per cent.
Acids designated α and β , together	32
" " γ , about	2.5
Inert oxidised hydrocarbons, containing 10 per cent. of oxygen ...	10
Hydrocarbons, m. p. 55-64°	19
Material of high molecular weight, about	1.5
Mixture of hydrocarbons and non-acidic oxidised material containing 3-4 per cent. of oxygen	16
Mixture similar to above but containing 7-8 per cent. of oxygen	17

On the supposition that the inert oxidised material contains 13 per cent. of oxygen, the total amount present is 22 per cent., and unchanged hydrocarbons 40 per cent.

VII. Separation of Products of Oxidation with Oxygen in the Presence of Turpentine.

The course of the oxidation can be estimated from the data given in Table II, experiment 6. As in the previous oxidation with air, there was 5 per cent. of turpentine present, and the process was carried out in a steam-bath.

It is unnecessary to give any details of the methods employed to effect the separation of acidic and non-acidic substances; it was readily carried out by extracting the aqueous alcoholic solution of the sodium salts with light petroleum. This process was rendered easier owing to the fact that the oxidations had proceeded further and there were less unacted-upon hydrocarbons present. The data are given in Table VI.

TABLE VI.

Oxidation with Oxygen. Temperature = 100°. Turpentine present.

	Per cent.	M. p.	Acid value.	Mol. wt. Ebullioscopic method with acetone as solvent.	Analysis.		
					C.	H.	O.
Crude material from reaction vessel.		39-43°	149	—	70.3	10.7	19.0
Solid acids β	47	43	188	331	71.5	11.3	17.2
Liquid " γ	7		392	—	61.7	9.0	29.3
" " δ	14		—	—	54.6	7.8	37.6
Non-acidic	25	47	1.1	393	80.7	13.5	5.8
Non-acidic acetone separation { Hydrocarbons oxidised	Estimated %						
	15	57.5	—	—	84.2	14.2	1.6
	10	27	—	—	77.4	12.7	9.9

It appears from the above table that oxygen at 100° brings about a much more profound oxidation than in the case of air at 110°. The β -acids formed, probably containing small quantities of α -acids, amount to 47 per cent. compared with 32 per cent. of α - and β - in the case of air. Further, the γ -acids are formed to the extent of 7 per cent. as compared with between 2 and 3 per cent. in the case of air, and in addition there is also present 14 per cent. of acids with yet smaller carbon content. As regards the inert oxidised material, 10 per cent. is formed compared with 22 per cent. when air is used, and a very much smaller amount of hydrocarbons remains unoxidised.

VIII. Products of Oxidation with Oxygen in the Absence of Turpentine.

As stated in section I, the oxidation of paraffin wax with oxygen appears to set in rapidly after the lapse of about seven hundred hours (see Table I, experiment 4). The resulting oxidised material was separated into acidic and non-acidic constituents by the method previously described. The data are given in Table VII.

TABLE VII.

Oxidation with Oxygen. Temperature = 100°. Turpentine absent.

			Per cent.	M. p.	Acid value.	Mol. wt. Ebullioscopic method with acetone as solvent.	Analysis.		
							C.	H.	O.
Solid	acids	β	38	47°	200	318	71.7	11.9	16.4
Liquid	„	γ	8		367		62.7	9.4	27.9
„	„	δ	9						
Non-acidic			42	49.5	0	390	82.7	14.0	3.3

From the lower oxygen content and higher melting point of the neutral material, it is clear that this fraction contains a higher percentage of hydrocarbons than when turpentine is present during the oxidation.

The amount of solid acids is also lower, and it is presumed that the reaction had not progressed as far as in the previous oxidation (section VII). We point out here that the presence of the acids termed γ and δ indicates that these are derived, certainly in this case, from paraffin wax; but when turpentine is used it is possible that derivatives formed from this substance may also be present in small amounts in those acids.

IX. Classification of Acids formed in Oxidation Processes.

For the sake of future reference we have classified the acids isolated in this investigation into four groups, α to δ . We do not attempt to formulate any of these substances, since it is almost certain that none of them is pure. The data given serve, as they have served throughout this investigation, merely as a guide to the work we are carrying out.

The α - and β -acids are the main acidic products of *air oxidation*, and an inspection of the analytical data in Table IV, experiments D to H, shows that the composition of the mixture varies but little from the mean values C = 73.3; H = 11.4; O = 15.2 per cent. This mixture is very insoluble in water or mixtures of water and alcohol, and shows a mean molecular weight of about 408.

By the method we have described it has been found possible to separate this mixture into an acid (or acids) of low melting point and high molecular magnitude, which we have termed the α -acids, and those generally of higher melting point and smaller molecular weight, termed the β -acids. The solid β - and liquid γ -acids of higher acid value are the main acidic oxidation products when oxygen is employed.

The γ -acids are liquids slightly soluble in aqueous alcohol, and the δ -acids are soluble to a considerable extent in water, but the latter acids, isolated only in small amounts, have so far not been further investigated.

There is no doubt that the α - and β -acids, constituting 32 per cent. of the total oxidation mixture (Table V) when air is used, and the β -acids (with much smaller quantities of α -) forming 47 per cent. when oxygen is employed (Table VI), are the most interesting acidic products of the reaction. It has been found possible to isolate from these mixtures well-defined acids by means of the relative solubility of their lead salts in alcohol. By this means the α -acids have been further purified, and the β -acids have been separated into at least four constituents.

X. Nature of Unoxidised Hydrocarbons.

[With REGINALD HENRY COYSH.]

The inert material which had been twice oxidised and the analyses of which are given in Table III, experiment 11, was separated by solution in acetone, and the resulting hydrocarbon purified by distillation in a vacuum of 0.5 mm. (see section VI, B). This hydrocarbon in the presence of 5 per cent. of turpentine was then treated

as previously described, with a current of oxygen at 100°. After the gas had passed for six hundred and seventy-two hours, the analysis showed the presence of 6.4 per cent. of oxygen. Had the original paraffin wax been employed, the amount of oxygen in the resulting material would have been 18 per cent.

We concluded that the previous treatments with air had freed the paraffin wax from most of its oxidisable constituents, and the resulting hydrocarbons were composed of materials which are either not oxidised by the treatment described or are oxidised only with a very small velocity. We attempted to isolate the oxidisable constituents by a partial fractional distillation of the original paraffin wax in a vacuum of 0.5 mm.; of the fractions obtained four were selected and treated with oxygen in the presence of 5 per cent. of turpentine at 100° under strictly comparable conditions. The data are given in Table VIII, where the percentage of oxygen is determined by difference from carbon and hydrogen analyses.

TABLE VIII.

Oxidation of Certain Fractions, from Paraffin Wax, with Oxygen.
Temperature = 100°.

Fraction.	No. 1.		No. 2.		No. 3.		No. 4.	
B. p. at 0.5 mm.	170–180°		190–200°		205–220°		Residue, above 232°.	
M. p.	41–43		51–52.5		56.9–57.2		64–64.7	
Mol. wt. Ebullo- scopic method using benzene.	292		—		—		423	
Duration of oxygen current in hours.	M. p.	%O.	M. p.	%O.	M. p.	%O.	M. p.	%O.
123	41–43°	0.3	48–51°	0.6	54–57°	2.9	64–64.7°	
268	41–42	1.9	41–45	5.3	46–52	6.0	62–65	1.0
435	41–42	4.0	38–46	12.2	45–52	8.9	61–64	2.6
720	36–40	4.5	38–43	15.2	44–51	12.0	60–63	3.2

It will be seen from the above table that whereas the fractions used in the experiments boiling between 170° and 180°, and that above 232°, contain in the resulting material only between 3 and 4.5 per cent. of oxygen, that boiling between 190° and 200° contains 15 per cent., and that between 205° and 220°, 12 per cent. of oxygen. We have no doubt that there is present in that fraction of wax which we found to distil between 190° and 220° the largest proportion of those constituents of paraffin wax oxidisable by the method employed in this investigation.

We regard these results as so satisfactory that we are now engaged in isolating the oxidisable hydrocarbons by a much more complete

fractional distillation of the paraffin wax in a vacuum of 0.1—0.15 mm. Besides being of great interest in themselves, such substances will serve as a more convenient material for the further investigation of the general problem.

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