OXIDATION OF LUBRICATING OILS

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CONTENTS

Mechanisms are proposed for the oxidation of three types of hydrocarbons—paraffin, naphthene, and aromatic—under conditions comparable to those encountered by lubricating oils in service. The initial oxidation product is postulated to be a hydroperoxide, which decomposes to form acids, ketones, aldehydes, and other intermediate oxidation products. These products may in turn undergo further oxidation or condensation. Condensation products are particularly prevalent in the case of aromatics.

The effect of hydrocarbon structure upon rate of oxidation is discussed. Paraffins and naphthenes oxidize at an intermediate rate. The introduction of olefinic unsaturation or a partially hydrogenated aromatic ring into the molecule increases its rate of oxidation, as does the addition of a benzene ring to the end of a long paraffin molecule. The presence of a naphthalene nucleus has the opposite effect of stabilizing the molecule.

Interaction effects play an important rôle in determining the rate of oxidation of a complex mixture of hydrocarbons, e.g., a lubricating oil. The rate is not, in general, the mean of the rates of the individual components, but is usually quite different. The component which is the most stable when tested alone may be preferentially oxidized in a solution of several components.

The catalytic effect of compounds of copper, lead, and iron is discussed. These compounds, which may be introduced in low concentration into a lubricating oil through contact with the metals, often exert a large accelerating effect upon the over-all rate of oxidation.

I. INTRODUCTION

Modern engines are exacting in their lubrication requirements. An extremely flat viscosity–temperature curve may be needed, or anti-rust characteristics, or good fluid characteristics at low temperatures, or any one or more of numerous other properties. While oils for various applications must meet widely different specifications, they have one requirement in common—they should undergo a minimum of change during use. Changes in properties during operation are due partly to extraneous contamination, but largely to chemical changes in the oil molecules themselves. These chemical reactions are principally those involving oxidation.

Oxidation of a lubricant in some cases benefits certain properties. For example, King (28) found, in a test employing a journal bearing at a pressure of 1000 lb. per square inch of projected area, that preoxidation of a mineral oil reduced its coefficient of friction and increased its "critical seizure temperature" by 145°C. However, the same effect could probably have been realized by the addition of a small amount of polar compound, without the attendant disadvantages of the oxidation treatment. Another example is cited by Baker (1), who reports that the addition of 10 per cent of used turbine oil to a fresh charge imparts rust-preventive properties not present in the fresh oil. This method of rust prevention is not without penalty, however, since other properties of the oil, notably service life and the ability to separate entrained moisture, are drastically damaged. It has accordingly been largely supplanted by the incorporation of a trace of highly effective compound. These additive-type oils are much more effective as rust preventives than the previous blends of new and oxidized oil, and the additive has very little effect upon other properties.

Oxidation of a lubricating oil leads to such difficulties as bearing corrosion, ring sticking, lacquer and sludge formation, and excessive viscosity. It is sometimes possible to overcome the harmful effect of a given class of oxidation products. An example of this approach to the problem is the addition of detergents, which peptize colloidal oxidation products and prevent their deposition as lacquer. Another example is the use of certain sulfur-containing additives which, in addition to performing other functions, passivate bearing surfaces and thus prevent corrosive acids which may be present in the oil from attacking the bearings. While methods such as these are commonly used, the over-all control of oxidation is nevertheless essential, not so much to eliminate the need for specific additives other than antioxidants, but to reduce the burden imposed upon them.

The purpose of the present paper is to review the literature on the subject of oxidation of hydrocarbons and lubricating oils, with the aim of gaining a clearer insight into the mechanisms involved.

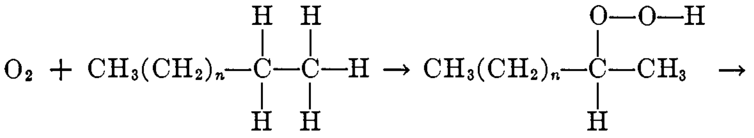
II. OXIDATION PRODUCTS

A. Pure hydrocarbons

Lubricating oils are composed of such a complex mixture of hydrocarbons that it is extremely difficult to identify specific compounds in their oxidation products, except for such degradation products as water, carbon dioxide, and some of the lower carboxylic acids. However, since lubricating oils are composed primarily of hydrocarbons, including three main groups—namely, paraffin, naphthene, and aromatic—it is of interest to examine the literature on the oxidation of pure hydrocarbons of these three types under conditions comparable to those encountered by oils in actual use.

Chavanne and coworkers (4, 5, 17) have studied the oxidation of a few paraffins and naphthenes. They oxidized *n*-decane, *n*-nonane, and *n*-octane with oxygen at atmospheric pressure and a temperature of 120°C. The gaseous oxidation products, which account for 10 per cent or so of the total, were similar in all three cases, and included 30–40 per cent of carbon dioxide, 1–3 per cent of carbon monoxide, 5–7 per cent of hydrogen, and 1–2 per cent of saturated hydrocarbons. The liquid products contained water, succinic acid, and formaldehyde. The three hydrocarbons produced preponderant amounts of methyl octyl, methyl heptyl, and methyl hexyl ketones, respectively, as well as a series of carboxylic acids ranging from formic to C_{n-1}, where n is the number of carbon atoms in the hydrocarbon. *n*-Octane formed, in addition, a small amount of octanol. These data would indicate that attack of a paraffin by oxygen under these conditions is not at the terminal carbon, but at the carbon in the CH_2 group adjacent to the terminal CH_3 group. This is consistent with the views of Burwell (3), who states that, whereas at high temperatures terminal carbons are attacked to produce aldehydes, at lower temperatures (*ca.* 150°C.) the beta carbon is involved primarily, the gamma secondarily, and so on toward the center of the molecule. Thus, formic, acetic, and propionic acids would be expected in order of decreasing concentration. Fenske *et al.* (19, 20) actually found this to be the case in an analysis of the volatile products resulting from the oxidation of a lubricating oil at temperatures of 130–180°C.

George, Rideal, and Robertson (22) found that C_{15} and C_{25} paraffins and alkylbenzenes are oxidized at 100–120°C. to form hydroperoxides, which accounted for 60–80 per cent of the oxygen absorbed by the alkylbenzenes, and which decomposed almost exclusively to give ketones in the case of the paraffins. The presence of peroxides in high concentration in the early stages of oxidation has also been shown by Larsen and coworkers (31). For example, in the oxidation of decalin at 110°C. peroxide is the principal oxidation product until upwards of 5000 cc. of oxygen per 100 g. of hydrocarbon has been absorbed. Balsbaugh and Oncley (2) found that tetralin, decalin, and cetane are oxidized almost exclusively to peroxides in the early stages of the reaction at temperatures ranging from 30° to 100°C. Similar results have been reported by Dornte (14) and by Denison (13) regarding the oxidation of white oils. Several investigators have shown that water is one of the principal oxidation products of lubricating oils (14, 19, 31, 32). Fenske and coworkers (19) report that water can account for as much as 44 to 70 per cent of the oxygen absorbed by an oil. In view of the above, the mechanism of the oxidation of a paraffin at temperatures in the range of 100–200°C. can be postulated as follows:



$$O_2 + CH_3(CH_2)_n\text{—}\underset{\displaystyle H}{\overset{\displaystyle H}{C}}\text{—}\underset{\displaystyle H}{\overset{\displaystyle H}{C}}\text{—}H \rightarrow CH_3(CH_2)_n\text{—}\underset{\displaystyle H}{\overset{\displaystyle O\text{—}O\text{—}H}{C}}\text{—}CH_3 \rightarrow$$

Paraffin Hydroperoxide

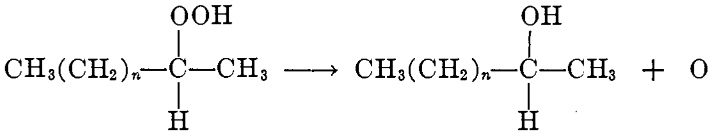
$$CH_3(CH_2)_nCOCH_3 + H_2O$$

Ketone

$$O_2 + CH_3(CH_2)_nCOCH_3 \rightarrow CH_3(CH_2)_nCOOH + HCHO$$

Ketone Carboxylic acid Formaldehyde

In addition, there would be some primary attack on the gamma rather than the beta carbon atom. This would result in the formation of a ketone of the same number of carbon atoms, but with the C═O group shifted one carbon atom toward the center of the molecule. The corresponding carboxylic acid would contain one less carbon atom than shown above, and acetaldehyde, rather than formaldehyde, would be split off. The acids can be oxidized further through attack at other carbon atoms, and the aldehydes are probably oxidized further to the corresponding carboxylic acids and, to some extent, to carbon dioxide and water. The formation of alcohols would require a reducing action on a hydroperoxide, the latter losing one atom of oxygen in acting as an oxidizing agent. Esters could be formed by the condensation of an acid and an alcohol.

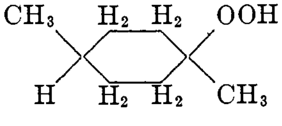


$$CH_3(CH_2)_n\text{—}\underset{\displaystyle H}{\overset{\displaystyle OOH}{C}}\text{—}CH_3 \longrightarrow CH_3(CH_2)_n\text{—}\underset{\displaystyle H}{\overset{\displaystyle OH}{C}}\text{—}CH_3 + O$$

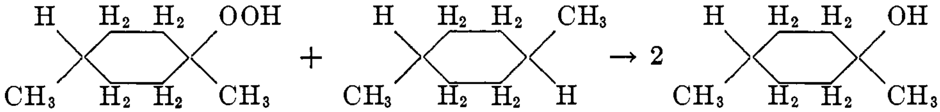
Hydroperoxide Alcohol

Chavanne and Bode (4) have made an extensive study of the oxidation products of 1,4-dimethylcyclohexane. Conditions were the same as in the case of the oxidation of the three paraffins mentioned above, except that the temperature was 100°C. instead of 120°C. They started with 116 g. of hydrocarbon and recovered 21 g. of unreacted material, so that 95 g. was oxidized. The oxygen consumed amounted to 30.7 g., and 123 g. of oxidation products as recovered, as compared with a theoretical of 95 + 30.7, or 125.7 g. The principal oxidation product was 1,4-dimethylcyclohexanol, which was present in sufficient quantity so that 30 g. was recovered in pure form. Other products included water (amount not given), carbon dioxide (5.2 g.), β-methyl-δ-acetylvaleric acid (8–9 g.), acetic acid (4–5 g.), β-methylvaleric acid (2–3 g.), dimethylcyclohexanediol (5.5 g.), and acetonylacetone (0.5 g.). Small amounts of hydrogen, carbon monoxide, methane, ethane, and formic acid were also detected.

The authors postulated the formation of a hydroperoxide,

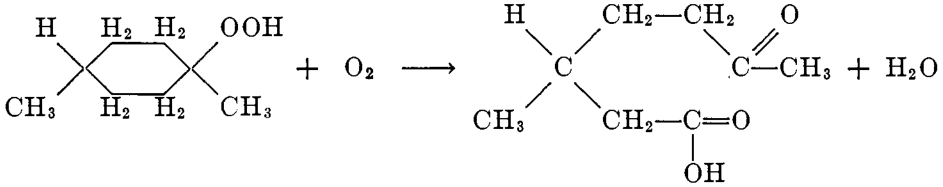


as the first step in the oxidation of 1,4-dimethylcyclohexane. In that respect, the mechanism would be identical with that proposed earlier in this paper for the oxidation of a paraffin, except that a tertiary rather than a secondary carbon atom is the vulnerable point of the molecule. The next step differs somewhat, however. The paraffin peroxide apparently decomposes largely through dehydration to give the corresponding ketone and, to a lesser extent, by reduction to the alcohol. The naphthene peroxide, on the other hand, apparently decomposes largely through reduction to the alcohol. This may be due in part to the fact that the tertiary carbon atoms in this particular hydrocarbon act as reducing agents for the peroxide, according to the following equation:



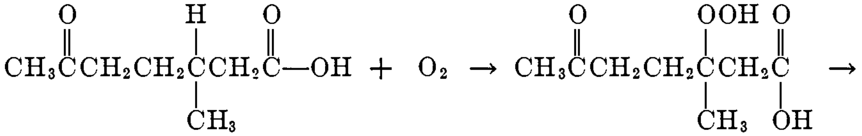
Hydroperoxide of 1,4-dimethylcyclohexane
1,4-Dimethylcyclohexane
1,4-Dimethylcyclohexanol

The formation of the diol can be explained in the same manner. The other oxidation products no doubt form as a result of further oxidation of the hydroperoxide, resulting in rupture of the naphthene ring. This mechanism necessarily differs from that involved in the paraffin in that a ketone cannot be formed, except by rupture of a C—C bond, for a tertiary carbon atom is involved. Thus the peroxide itself, and not the ketone, is oxidized further. Another difference is to be found in the oxidation products. The paraffin oxidizes to give first a peroxide, then a ketone, then an acid plus a "volatile oxidation product," —namely, formaldehyde or acetaldehyde or the corresponding acid. The naphthene peroxide can be oxidized with a rupture of a C—C bond and still form a product containing the original number of carbon atoms, as follows:



Hydroperoxide of 1,4-dimethylcyclohexane
β-Methyl-δ-acetylvaleric acid

Further attack of this molecule at the other tertiary carbon atom would explain the observed formation of acetonylacetone, as indicated by the following mechanism:



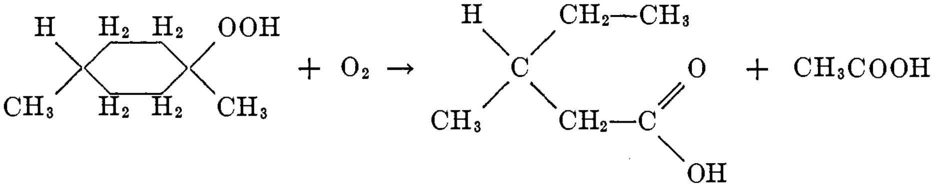
$$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2\underset{CH_3}{\overset{H}{\overset{|}{C}}}CH_2\overset{O}{\overset{\|}{C}}—OH + O_2 \rightarrow CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2\underset{CH_3}{\overset{OOH}{\overset{|}{C}}}CH_2\underset{OH}{\overset{O}{\overset{\|}{C}}} \rightarrow$$

β-Methyl-δ-acetylvaleric acid
Hydroperoxide of β-methyl-δ-acetylvaleric acid

$$CH_3COCH_2CH_2COCH_3 + CH_2OHCOOH$$

Acetonylacetone
Glycolic acid

Glycolic acid was not reported by the authors. It may have been present and escaped detection, or it may have oxidized further to simpler end products like formic acid and carbon dioxide and water. The formation of β-methylvaleric acid can be explained by the further oxidation of the hydroperoxide of the hydrocarbon with two molecules of oxygen, and a split of the naphthene ring on either side of the tertiary carbon. This would result in the formation of one molecule of acetic acid and one of β-methylvaleric acid.



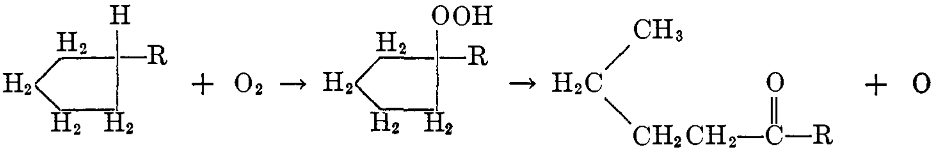
1,4-Dimethylcyclohexane hydroperoxide

β-Methylvaleric acid

Acetic acid

This does not explain the formation of hydrogen, methane, and ethane, which are probably formed through cracking. However, since these substances are formed only in very low concentration in comparison with the other products, their presence does not invalidate the reaction mechanisms as outlined above.

Dupont and Chavanne (17) studied the oxidation of the three cyclopentane derivatives ethyl-, butyl-, and phenyl-cyclopentane, again under conditions of slow oxidation. In every case they obtained a straight-chain ketone containing the original number of carbon atoms. These were ethyl *n*-butyl ketone, an unidentified nine-carbon-atom ketone which we shall assume to be dibutyl ketone, and phenyl butyl ketone, respectively. These three naphthenes probably formed hydroperoxides at the tertiary carbon atom in the same way that dimethylcyclohexane was oxidized; however, the peroxide then decomposed principally by reduction to the aliphatic ketone rather than to the cyclic alcohol as in the case of the cyclohexane derivative.



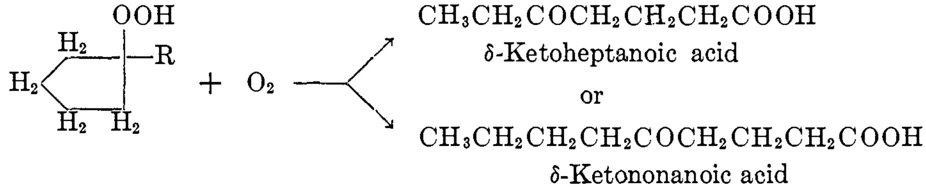
Ethyl-, butyl-, or phenyl-cyclopentane

Hydroperoxide

Ethyl butyl, dibutyl, or phenyl butyl ketone

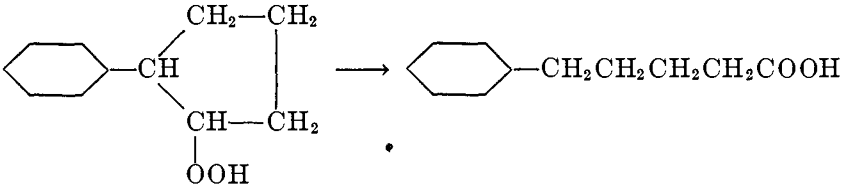
Thus the end product resembles that formed from a paraffin, the only difference being that the paraffin hydroperoxide decomposes to the ketone by dehydration, losing one molecule of water, while the naphthene does so by reduction, losing one atom of active oxygen. The reason for the difference in the behavior of the C_5 and C_6 naphthenes is not clear. It could have been caused by the presence of two tertiary groups in the latter and only one in the former, or by the difference in size of either the ring or the side chains, or possibly to a difference in conditions.

Ethyl- and butyl-cyclopentanes also formed the δ-keto derivatives of heptanoic and nonanoic acids, respectively. These were probably formed by oxidation of the peroxide in the same manner in which β-methyl-δ-acetylvaleric acid was produced from dimethylcyclohexane.



Hydroperoxide of ethyl-
or butyl-cyclopentane

The former cyclopentane derivative also produced formic and propionic acids and the latter, butyric and valeric acids as products of further oxidation. Phenylcyclopentane also produced δ-phenylvaleric acid and benzyl alcohol. The formation of the former is of particular interest. This compound has the same empirical formula as the hydroperoxide of phenylcyclopentane; hence the acid could conceivably be formed from the peroxide by a molecular rearrangement. The peroxide in this case would probably not be the one with oxygen attached to the tertiary atom, but the one with oxygen attached to the naphthene carbon adjacent to it. The rearrangement would then include a break of a C—C bond, the transfer of a hydrogen atom from one carbon to another, and the transfer of an OH group from oxygen to carbon. Benzyl alcohol is possibly a degradation product of this acid.



Hydroperoxide

δ-Phenylvaleric acid

Stevens (41) and Stevens and Roduta (42) have made an interesting study of the slow oxidation of a series of benzene derivatives. They bubbled oxygen through the hydrocarbon for a number of days at temperatures ranging from 80–140°C. and analyzed the products formed. Their data are summarized in table 1. It will be seen that oxidation always centers about a carbon atom attached to the benzene ring. The methylbenzenes all formed aldehydes containing the same number of carbon atoms as the parent molecule, and the substituted benzenes containing larger groups all formed ketones containing a phenyl group plus the other R group originally attached to the benzene ring, or the smaller of the two groups in the case where two groups were present. Acids, resulting from the further oxidation of aldehydes or ketones, were also formed, as well as acids of low molecular weight which formed from the fragments split off in the formation of ketones from secondary compounds. Alcohols were not formed in detectable quantity in any instance.

While Stevens does not report the presence of peroxides, it would appear probable that oxidation in every case was initiated by peroxidation to the hydroperoxide at the carbon adjacent to the benzene ring. This peroxide then decomposes by dehydration to the aldehyde or ketone, respectively, depending upon whether the starting material contained methyl or larger groups, or by the loss of a molecule of alcohol to form a ketone in the case of a tertiary hydrocarbon. The aldehydes may then be further oxidized to acids, and the alcohols to aldehydes and then to acids.. The ketones are oxidized further to benzoic acid, probably by the same mechanism proposed earlier for the oxidation of a paraffin, to the acid of lower number of carbon atoms *via* the hydroperoxide and

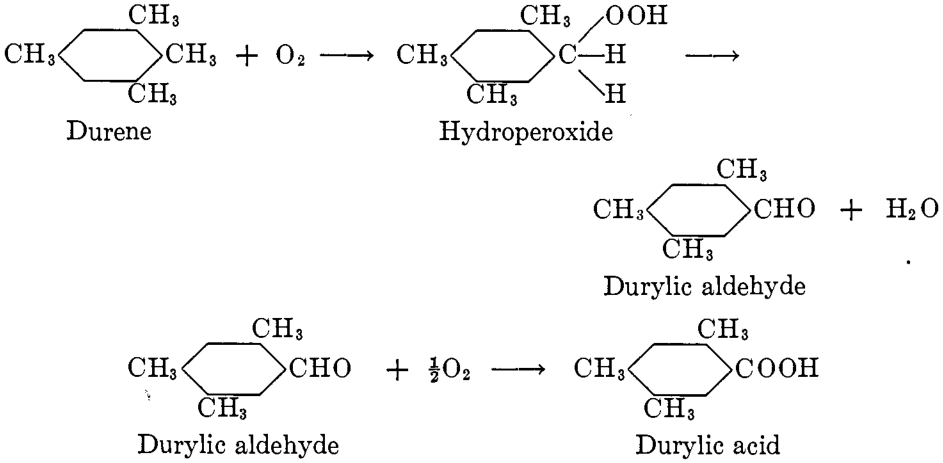
TABLE 1

Oxidation of benzene aromatics

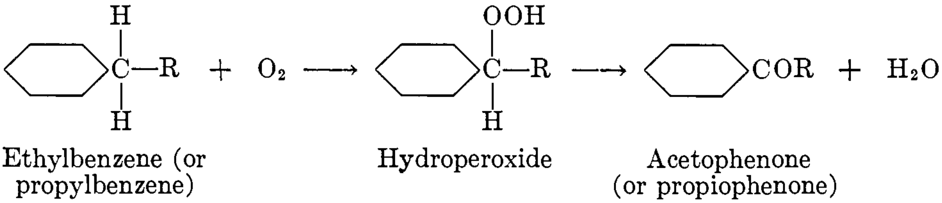
Data from Stevens (41) and Stevens and Roduta (42)

HYDROCARBON	OXIDATION TEMPERATURE	CONDITIONS (TIME)	GRAMS OF PRODUCT PER 100 G. OF HYDROCARBON
	°C.	*hours*	
Toluene	100	48	Trace of aldehyde
m-Xylene	100	30	2.1 g. toluic aldehyde; 1.1 g. toluic acid
Mesitylene (1,3,5-trimethylbenzene)	100	24	2.1 g. 1,3-dimethylbenzaldehyde; 1.4 g. mesitylenic acid
Durene (1,2,4,5-tetramethylbenzene)	100	9	5.8 g. durylic aldehyde; 4.9 g. durylic acid
p-Cymene (1-methyl-4-isopropylbenzene)	85	14	1.2 g. cumic aldehyde; 0.8 g. cumic acid
	102–4	14	Cumic aldehyde; cumic acid; 2 g. *p*-tolyl methyl ketone; formic acid
Ethylbenzene	110–15	24	19 g. acetophenone
n-Propylbenzene	102–4	25	Resin
	78	36	Trace of propiophenone
Cumene (isopropylbenzene)	102–4	23	4 g. acetophenone
	80	32	Formic acid
tert-Butylbenzene	102–4	25	Trace of non-volatile residue
Ethylmethylphenylmethane	119	14–29	2–10 g. acetophenone
	140	90	7.5 g. acetophenone; 4.2 g. benzoic acid
n-Butylmethylphenylmethane	119	14–29	2–10 g. acetophenone; butyric acid identified by odor
Methyldiphenylmethane	119	14–29	2–10 g. benzophenone; formic acid
Triphenylmethane	119	14–29	2–10 g. benzophenone; phenol
Diphenylmethane	119	14–29	2–10 g. benzophenone

ketone. These reactions, which would explain all of the products Stevens reports, are illustrated below:



The reactions of toluene, xylene, mesitylene, and *p*-cymene may be written in exactly the same manner, the products in every case being aldehydes and acids containing the same structure in the carbon skeleton as the original hydrocarbon. The reaction for ethylbenzene (and *n*-propylbenzene) is represented as follows:



$$C_6H_5COR + O_2 \longrightarrow C_6H_5COOH + R'CHO$$

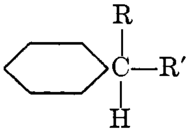
Acetophenone (or propiophenone) — Benzoic acid — Formaldehyde (or acetaldehyde)

$$R'CHO + \tfrac{1}{2}O_2 \longrightarrow R'COOH$$

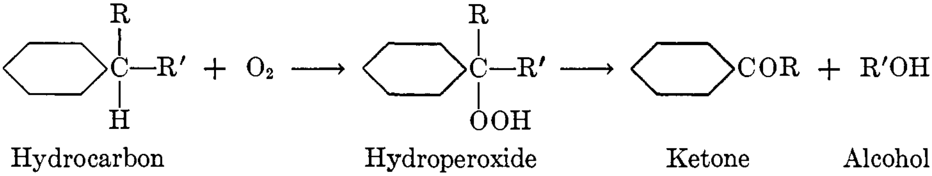
Formaldehyde (or acetaldehyde) — Formic acid (or acetic acid)

Benzophenone could be formed from diphenylmethane by the same mechanism shown for the oxidation of ethylbenzene to acetophenone.

Cumene, ethylmethylphenylmethane, methylphenylpropylmethane, butylmethylphenylmethane, methyldiphenylmethane, and triphenylmethane can all be represented by the structural formula,



where R and R′ are H or alkyl or phenyl groups which may be alike or different. R is the smaller of the two in cases of unequal size. *p*-Cymene may also be thought of as belonging to this group, although it contains an additional methyl group on the benzene ring. These hydrocarbons are probably oxidized according to the following scheme:



$$\underset{\text{Alcohol}}{R'OH} + \tfrac{1}{2}O_2 \longrightarrow \underset{\text{Acid}}{R''COOH}$$

tert-Butylbenzene cannot form a hydroperoxide at the carbon adjacent to the benzene ring, since this is a quaternary carbon. This may account for the fact that very little oxidation of this compound took place under conditions comparable to those for the other hydrocarbons.

Chernozhukov and Krein (8) studied the oxidation products of a number of hydrocarbons, although they did not report the oxidation products in detail as did the previously reported investigators. Their technique differed somewhat in that they used a bomb, and oxygen or air at a pressure of 15 atm. They used temperatures of 110–150°C. for the most part, which are comparable to those used by Chavanne and by Stevens. They found that substituted naphthenes are more unstable than unsubstituted ones, and attribute this to oxidation at the carbon of the ring attached to the alkyl group. They point out that this behavior—namely, the splitting of the ring—is in marked contrast to that of aromatic rings, which remain intact. Both of these observations are in line with the mechanisms proposed above for the initial oxidation of naphthenes and aromatics. They found that aromatics in general tend to give condensation products to a much greater extent than do naphthenes.

Larsen, Thorpe, and Armfield (32) studied the rate of oxygen absorption of a number of hydrocarbons at temperatures of 110–150°C. and at an oxygen pressure of 1 atm. While they did not analyze the products for specific compounds, they did report various functional groups. Thirty-nine compounds were investigated. These are tabulated in the section on "Oxidation rates." The average values for the products of oxidation of five classes of compounds are given in table 2. Conditions of oxidation were 1 atm. of oxygen and 110°C., except in the case of the less reactive naphthalene compounds, in which case the temperature was raised to 150°C. The total amount of oxygen absorbed varied from less than 100 cc. to more than 10,000 cc. per mole. In most cases it was of the order of 5000 cc. per mole.

The figures in table 2 cannot be regarded as absolute, since the total of the various products for a given hydrocarbon varied from 53 to 157 per cent of the total oxygen absorbed. However, in most cases these totals lay between the limits of 80 to 120 per cent, and the data shown in table 2 are probably quite accurate as regards the average distribution of oxygen. Peroxides do not constitute a major oxidation product; however, Larsen *et al.* have shown elsewhere (31) that peroxide content rises sharply in the early stages of oxidation and then falls. The free acid, alcohol, carbonyl, water, and volatile acid can all be explained as decomposition products and further oxidation products of the peroxides, and the combined acids, as determined by saponification value, by condensation reactions.

No value is listed for the average value under "volatile acids" for paraffins, since this value was reported for only one paraffin, hydropolyisobutylene. The value of 6.0 per cent reported is considered significant, in view of the fact that it is so much higher than those for the other hydrocarbons. It will be recalled that earlier in this paper it was pointed out that, according to the proposed theory, a paraffin can be oxidized to an acid only through the splitting off of a C_1, or sometimes C_2, or larger, fragment, which would appear as aldehyde or acid. Polyisobutylene also showed a relatively high percentage of oxygen absorbed as "volatile acid" (6.3 per cent), although the other olefin examined, tetraisobutylene, gave only 0.8 per cent.

TABLE 2

Oxidation products of five classes of hydrocarbons

Data taken from Larsen, Thorpe, and Armfield (32); all values expressed as percentage of total oxygen consumed

CLASS OF HYDROCARBON	FREE ACID	COMBINED ACID (ESTER)	PEROXIDE	ALCOHOL AND PHENOL	CARBONYL	H_2O	CO_2	VOLATILE ACIDS
Paraffin	14.3	16.3	4.1	1.9	46.0	43.9	4.7	
Naphthene and alkylnaphthene	11.2	17.0	13.5	8.9	51.4	21.9	3.8	0.6
Aromatic naphthene	6.1	23.1	4.3	8.5	27.2	16.7	1.2	0.4
Alkylbenzene	9.5	12.7	6.7	3.3	36.3	18.2	6.5	Trace
Naphthalene and alkylnaphthalene	6.9	16.3	1.4	9.4	9.6	51.3	7.8	1.6

Larsen *et al.* (31) found, as did Chernozhukov and Krein, that aromatics give condensation products which darken the oil and precipitate, whereas paraffins and naphthenes remain homogeneous and light in color upon oxidation.

B. *Mixtures and petroleum fractions*

Larsen *et al.* (31) also determined functional groups in the oxidation products of a number of lubricating oils. Oxidation was carried out in the same equipment and under the same conditions used in the study of pure hydrocarbons—namely, 1 atm. of oxygen and 110° or 150°C. The results for nine oils are shown in table 3. The first seven are lubricating oil fractions, while the eighth is a synthetic oil made by polymerization of cracked-wax olefins. The last is a white oil. Both of the last two are aromatic-free. The first six are California furfural raffinates of various stages of extraction, as indicated by the progressively increasing viscosity index (V.I.). It will be observed that as aromatics are removed there is a marked tendency toward a lower asphaltene content in the oxidized oil. This is of course one of the main purposes of solvent extraction, and is consistent with the conclusion based upon work on pure hydrocarbons that aromatics give dark insoluble condensation products. Extraction also results in a higher conversion of oxygen to water, and slightly less to carbon dioxide and to volatile acids. No trends are apparent in the free or combined acids, nor in the alcohols and carbonyl. No peroxides were found in the oxidation products of the California oils, indicating that any peroxides formed were unstable under these conditions, and immediately reacted further. The two aromatic-free oils formed no asphaltenes, and formed less carbon dioxide and water and more intermediate oxidation products. This was particularly true at the lower temperature. Comparison of results on the synthetic oil at the two temperatures shows that the higher temperature favors the decomposition of peroxides and carbonyl, and the formation of carbon dioxide and water.

TABLE 3

Oxidation of lubricating oils

Data from Larsen *et al.* (31); all values expressed as percentage of total oxygen consumed

OIL	TEMPERATURE OF OXIDATION	O_2 ABSORBED	FREE ACID	COMBINED ACID	PEROXIDE	ALCOHOL	CARBONYL	H_2O	CO_2	VOLATILE ACIDS	ASPHALTENE (MG. PER 10 G. OIL)
	°C.	*cc. per 100 g.*									
40 V.I.*California	150	2826	5.0	11		2.9	1.5	36	21	2.4	135
50 V.I. California	150	3010	4.5	10	0	8.9	8.9	51	26	2.0	100
60 V.I. California	150	2853	4.7	12	0	2.5	1.4	56	12	1.7	65
70 V.I. California	150	2800	4.1	9.0	0	.4	1.2	68	9.2	1.6	25
80 V.I. California	150	2803	3.8	10	0	.6		60	16	1.4	6
85 V.I. California	150	2800	4.1	12		1.3	2.5	65	16	1.2	2
Mid-Continent neutral	150	3233	4.5	12	<.1	0.7	5	49		1.1	
Synthetic oil made from cracked wax olefins	150	2532	5.9	16	<1	9	9	34	7	2.4	0
	110	2980	6.6	15	.4	8	19	26	4.9	3.8	0
White oil	110	1571	13	19	5.0	13	44	11		1.3	0

* V.I. refers to viscosity index as defined by Dean and Davis.

A comparison of the data on the lubricating oils as a whole with table 2 reveals that the former correspond most closely to the alkylnaphthalenes in their oxidation products. This would indicate that this class of compounds may be the "front line" which bears the brunt of the attack of a lubricating oil by oxygen. This phase of the subject will be discussed in greater detail in a later section of this paper.

Dornte and coworkers (14, 15, 16) studied the oxygen absorption of a number of oils, and found with a white oil at 135°C. that peroxides were the principal oxidation products. Carbonyl was next in order, with water and acids next. Only a trace of carbon dioxide was found. With lubricating oils Dornte used a temperature of 175°C. and found that about 40 per cent of the oxygen was converted to water, and 8–10 per cent to carbon dioxide.

Fenske *et al.* (14, 20), who used a similar apparatus and technique, found that Pennsylvania lubricating oils are oxidized at 170°C. to give the following distribution·of oxygen in the oxidation products: water, 44–70 per cent; carbon dioxide, 3–9 per cent; carbon monoxide, 0.6–3.2 per cent; volatile acids, 1–7.5 per cent; fixed acids, 2–2.5 per cent; and 2–7 per cent isopentane insolubles, assuming that the latter contain 15 per cent oxygen. They found that the distribution of oxygen is influenced little by temperature over the range of 150–180°C., provided the amount of oxygen consumed is held constant, but that it varies as oxidation proceeds.

Hicks-Bruun, Ritz, Ledley, and Bruun (26) made similar studies. They worked at a temperature of 175°C. and found that 34.5–43.5 per cent of the oxygen could be accounted for as water, and 3.1–7.5 per cent as carbon dioxide. They compared an oil containing 19 per cent aromatic rings by Waterman analysis with one containing 3 per cent, and found that the former produced three to four times as much "soluble sludge" and "insoluble sludge" as the latter. This was of course to be expected, in view of the effect of aromatics as discussed earlier. They also found that the less aromatic oil formed more water and less carbon dioxide than the more aromatic sample. This again is consistent with the trend shown in table 3.

Davis, Lincoln, Byrkit, and Jones (12) studied the oxidation of lubricating oils by measuring the pressure drop in a Sligh flask containing the sample of oil and oxygen, and fitted with a manometer. They showed that the oxidation products remaining in solution, after precipitation of the asphaltenes by the addition of naphtha, can be removed by adsorption, from naphtha solution, on a suitable clay. These oxidation products, which can be desorbed from the clay by means of a polar solvent such as acetone or alcohol, are termed resins. The de-resined oil, after removal of the naphtha, has virtually the physical properties of the original unoxidized oil. This means of separation suggests the use of the resin content of a used oil as a good criterion of extent of oxidation, since it includes a large number of classes of oxidation products. Such an application is, however, complicated by the fact that there is no sharp line of demarcation between oil and resins or between resins and asphaltenes, but a more or less uniform series ranging from the least polar unoxidized hydrocarbon to the most insoluble asphaltene.

The oxidation of paraffin wax and of paraffinic oil fractions has received extensive study, largely by Russian investigators (11, 33, 35–38, 40, 43–45), for the purpose of producing fatty acids from petroleum. While the goal in such work is diametrically opposed to that of lubricating oil problems in that the purpose is to promote rather than stifle oxidation, the conditions used are comparable to those met by lubricating oils, and the products formed are of interest in the present survey.

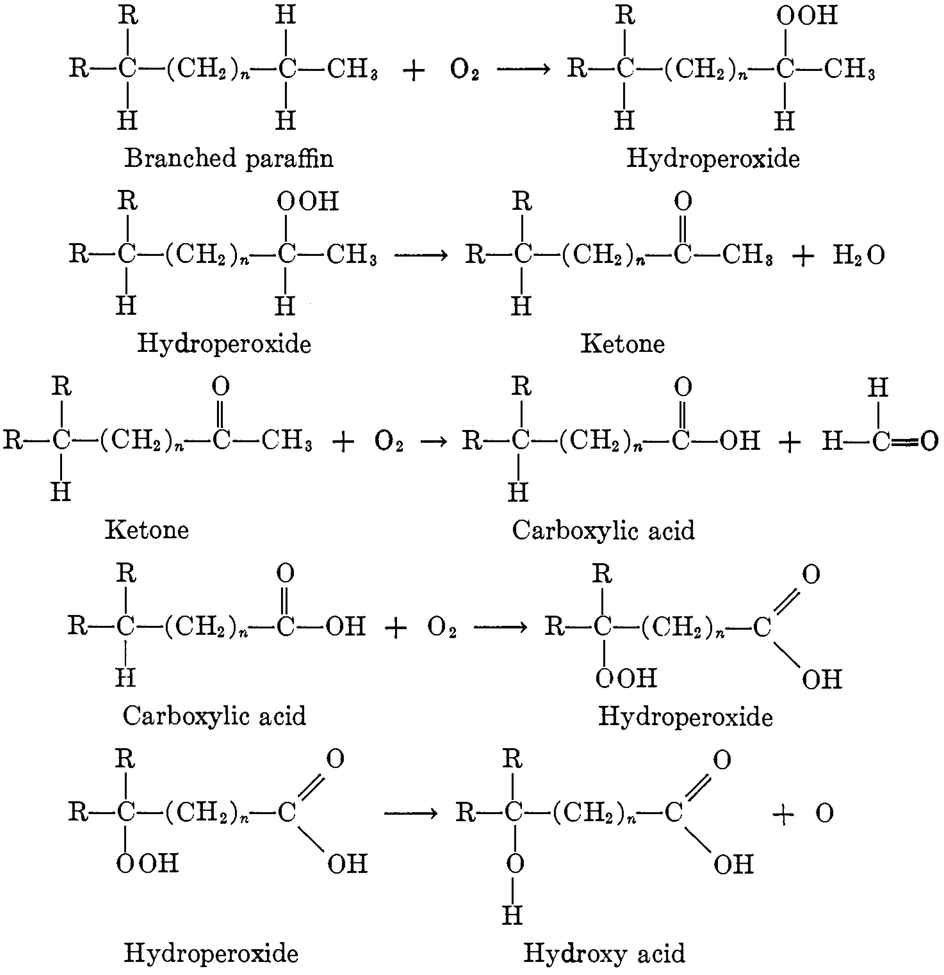
Likhuskin, Masumyan, and Levkupulo (33) state that the oxidation of a wide fraction of fuel oil with air at 130°C. will give yields as high as 41 per cent of acids. Higher yields are accompanied by excessive quantities of hydroxy acids. Sodium naphthenate was used as a catalyst. Danilovich and Dianina (11) prefer oxidation in four to five stages, with calcium naphthenate as catalyst, and report water-white fatty acids as products. Varlamov (43) studied the oxidation of Grozny paraffin at temperatures of 160–180°C. with air at 15–30 atm. pressure. From 20 to 74 per cent of the paraffin reacted, and 70 per cent or more of the oxidation products consisted of fatty acids of varying solubility. He found low-molecular-weight alcohols, aldehydes, and ketones in the volatile oxidation products. He also conducted some experiments in the absence of water, to determine whether this would influence the formation of hydroxy acids. He found, contrary to his expectations, that a high yield of acids could be obtained in the absence of moisture, and that a high percentage of the products consisted of hydroxy acids. He found manganese, copper, calcium, and nickel to be positive catalysts. Velikovskiĭ and Lemer (44) oxidized paraffin and slack wax with air at a temperature of 160°C. both in iron and in aluminum equipment. They found that the former metal favored the formation of insoluble hydroxy acids, particularly in the case of slack wax. With stepwise oxidation they were able to obtain maximum yields of acids, and a minimum of hydroxy acids. Velikovskiĭ and Vasil'eva (45) investigated the oxidation of various crude petroleum fractions, and found that in general reaction cannot be effected without a catalyst, but that oxidation could be accomplished with the aid of catalysts or by pretreatment of the oil with oleum. Calcium oleate was found to be an effective catalyst, and manganese oleate even more so. Petrov (35) describes a commercial process in which a petroleum distillate is sulfonated and the unsulfonated residue oxidized at 96–115°C. in the presence of a calcium or manganese soap until a 20 per cent yield of fatty acid is reached.

Plisov, Galandeev, and Zel'tsburg (37) point out that the petroleum ether-insoluble hydroxy acids, which are generally regarded as undesirable by-products in the manufacture of fatty acids, are valuable as film-forming substances in the lacquer and pigment industries, and as raw materials in the plastics industry. By oxidizing with air at 115–120°C. they were able to obtain yields of 80–86 per cent of hydroxy acids, based upon total acids produced. They regard the product as a mixture of hydroxy acids, lactones, and lactides.

Shoruigin and Kreshkov (40) oxidized paraffin wax with air at 160°C. and found the following products: water, hydroxy acids, lactides, and carboxylic acids and their anhydrides. The following straight- and branched-chain compounds, presumably hydroxy acids, were found: $C_{10}H_{20}O_3$, $C_{13}H_{26}O_3$, $C_{14}H_{28}O_3$, $C_{15}H_{30}O_3$, $C_{17}H_{34}O_3$ (two isomers), $C_{18}H_{36}O_3$, $C_{21}H_{42}O_3$, (two isomers), $C_{22}H_{44}O_3$, $C_{25}H_{50}O_3$, $C_{27}H_{54}O_3$, and $C_{32}H_{64}O_3$. The presence of β-hydroxy acids was indicated.

Plisov (36) reports that Grozny paraffin, having a melting point of 52°C., is oxidized at 140–160°C. to form peroxides which are capable of liberating iodine from potassium iodide and of oxidizing ferrous salts, and which are stable to heat. In addition, they report peroxides which are also stable, but which differ in that they do not respond to the usual tests for peroxides. Both types of peroxide are decomposed by acid or alkali, and they undergo hydrolysis by water. The last-named reaction is catalyzed by calcium and sodium naphthenates.

The production of carboxylic acids from paraffin wax can be explained as outlined earlier in Section II,A: the paraffin is oxidized to the β-hydroperoxide, which decomposes to a methyl ketone, which in turn is oxidized further to formaldehyde plus a carboxylic acid containing one carbon less than the original paraffin. The formation of hydroxy acids may be associated with branched-chain paraffins. Although Shoruigin and Kreshkov found both straight- and branched-chain compounds of the empirical formula $C_nH_{2n}O_3$, the majority of work reported indicates that paraffin wax shows less tendency to undergo oxidation to the hydroxy acid than do oil fractions or slack wax. The oxidation of a branched paraffin to an hydroxy acid could proceed according to the following mechanism:



$$\underset{\text{Branched paraffin}}{\mathrm{R{-}}\overset{\mathrm{R}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{{-}(CH_2)_n{-}}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{{-}CH_3}} + O_2 \longrightarrow \underset{\text{Hydroperoxide}}{\mathrm{R{-}}\overset{\mathrm{R}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{{-}(CH_2)_n{-}}\overset{\mathrm{OOH}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{{-}CH_3}}$$

$$\underset{\text{Hydroperoxide}}{\mathrm{R{-}}\overset{\mathrm{R}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{{-}(CH_2)_n{-}}\overset{\mathrm{OOH}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{{-}CH_3}} \longrightarrow \underset{\text{Ketone}}{\mathrm{R{-}}\overset{\mathrm{R}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{{-}(CH_2)_n{-}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{{-}CH_3}} + H_2O$$

$$\underset{\text{Ketone}}{\mathrm{R{-}}\overset{\mathrm{R}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{{-}(CH_2)_n{-}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{{-}CH_3}} + O_2 \rightarrow \underset{\text{Carboxylic acid}}{\mathrm{R{-}}\overset{\mathrm{R}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{{-}(CH_2)_n{-}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{{-}OH}} + \mathrm{H{-}}\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}\mathrm{{=}O}$$

$$\underset{\text{Carboxylic acid}}{\mathrm{R{-}}\overset{\mathrm{R}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{{-}(CH_2)_n{-}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{{-}OH}} + O_2 \longrightarrow \underset{\text{Hydroperoxide}}{\mathrm{R{-}}\overset{\mathrm{R}}{\underset{\mathrm{OOH}}{\mathrm{C}}}\mathrm{{-}(CH_2)_n{-}C}\genfrac{}{}{0pt}{}{/\!\!/\,\mathrm{O}}{\diagdown\,\mathrm{OH}}}$$

$$\underset{\text{Hydroperoxide}}{\mathrm{R{-}}\overset{\mathrm{R}}{\underset{\mathrm{OOH}}{\mathrm{C}}}\mathrm{{-}(CH_2)_n{-}C}\genfrac{}{}{0pt}{}{/\!\!/\,\mathrm{O}}{\diagdown\,\mathrm{OH}}} \longrightarrow \underset{\text{Hydroxy acid}}{\mathrm{R{-}}\overset{\mathrm{R}}{\underset{\substack{|\\ \mathrm{O}\\ |\\ \mathrm{H}}}{\mathrm{C}}}\mathrm{{-}(CH_2)_n{-}C}\genfrac{}{}{0pt}{}{/\!\!/\,\mathrm{O}}{\diagdown\,\mathrm{OH}}} + O$$

III. OXIDATION RATES

A. Pure hydrocarbons

Larsen, Thorpe, and Armfield (32) have made an extensive study of the oxidation rates of a number of pure hydrocarbons. They measured oxygen absorption at 110°C., except in the case of the more stable compounds, which were oxidized at 150°C. Their results on thirty-nine hydrocarbons, representing paraffins, olefins, naphthenes, benzene and naphthalene aromatics, and combinations of these types in the same molecule, are summarized in table 4. For the sake of brevity the compounds are classified in this tabulation only according to the time required to absorb 2000 cc. of oxygen per gram-mole and according to the type of curve obtained. (It should be understood that the "type of curve" applies only under the given set of conditions. von Fuchs and Diamond (21) have shown that a given oil may exhibit autocatalysis or autoretardation, depending upon the temperature of oxidation.) Two thousand cubic centimeters of oxygen per gram-mole corresponds to the oxidation of approximately 9 per cent of the molecules with one molecule of oxygen per molecule of hydrocarbon, or 4.5 per cent with two molecules of oxygen. It will be recalled that one molecule is required to convert a paraffin to a peroxide or ketone, and an additional molecule to convert the ketone to a carboxylic acid plus low-molecular-weight aldehyde. For a lubricating oil with a molecular weight of 400, the figure of 2000 cc. per gram-mole corresponds to 500 cc. per 100 g. The four types of curve are the autocatalytic, the autoretardant, the linear, and the combination type in which autocatalysis prevails first, then autoretardation. Table 4 lists the hydrocarbons in order of increasing stability. In comparing two compounds oxidized at different temperatures, a factor of 16 was used to convert the rate of oxidation at 110°C. to that at 150°C. This factor is based upon a doubling of reaction rate per 10°C. and is not strictly correct, but sufficiently close for the purpose of comparison.

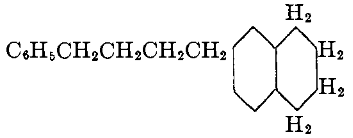
It will be observed that the ten paraffins, naphthenes, and alkylnaphthenes all had "2000 cc. times" between 12 and 47 hr. at 110°C., and all showed the autocatalytic type of curve, at least in the early stages (type 1 or 4). The most rapid oxidation was shown by hydrocarbons containing either a double bond, a partially hydrogenated condensed ring, or a benzene ring with a long paraffinic side chain. Surprisingly, these compounds, eleven in number, which had "2000 cc. times" ranging from 1.5 to 12 hr. at 110°C. do not in general give an autocatalytic type of oxidation curve. Only one gave a type 1 curve, and four a type 4. The other six were equally divided between types 2 and 3. Thus autocatalysis is not a requisite for rapid oxidation. The naphthalene derivatives were as a class the most stable, and most of their oxidation curves were of either the autoretardant or the linear type.

The effect of olefinic unsaturation is brought out by a comparison of items 7 and 13. The latter, hydropolyisobutylene, was obtained by hydrogenation of the former, polyisobutylene, which contained one C—C bond per C_{13} molecule. The paraffin had a 2000 cc. time of 17 hr., which is more than four times that of the olefin.

TABLE 4

Oxidation rates of pure hydrocarbons

Data from Larsen, Thorpe, and Armfield (32)

	HYDROCARBON	OXIDATION TEMPERATURE	TIME TO ABSORB 2000 CC. OF O_2 PER GRAM-MOLE	TYPE OF CURVE (SEE FIGURE 1)
		°C.	*hours*	
1	Tetralin	110	1.5	2
2	Tetraisobutylene	110	2	3
3	Octahydroanthracene	110	2	4
4	9,10-Dihydro-9,10-diisobutylanthracene	110	2.5	2
5	*n*-Octadecylbenzene	110	2.5	3
6	β-*n*-Octadecyltetralin	110	3.5	4
7	Polyisobutylene, $(C_4H_8)_{13}$	110	4	3
8	α-Phenyl-Δ^2-tetralylbutane 	110	7	4
9	9,10-Diisobutylperhydroanthracene	110	7	1
10	5-Isobutylacenaphthene	110	8	2
11	*n*-Hexadecylbenzene	110	12	4
12	Perhydroanthracene	110	12	1
13	Hydropolyisobutylene, $(C_4H_{10})_{13}$	110	17	4
14	Hexaethylbenzene	110	23	1
15	β-*n*-Octadecyldecalin	110	24	1
16	Fluorene	110	26	2
17	Decalin	110	27	1
18	Dicyclohexyl	110	28	1
19	*n*-Amylcylopentane	110	28	1
20	*n*-Amylbenzene	110	28	3
21	1-α-Naphthyl-1-*n*-butylhexadecene	150	2	3
22	*n*-Octadecylcyclohexane	110	37	1
23	*n*-Hexadecylcyclohexane	110	45	1
24	Cetane	110	45	1
25	*n*-Decane	110	47	1
26	*sec*-Amylbenzene	110	68	1
27	*tert*-Amylbenzene	110	85	1
28	Benzylnaphthalene	110	120	3
29	Diphenylmethane	110	>70	2
30	Di-α-naphthylmethane	150	12	1
31	α-*n*-Octadecylnaphthalene	150	33	1
32	Poly-*sec*-amylnaphthalene	150	42	1
33	α-Isoamylnaphthalene	150	55	2
34	α-Methylnaphthalene	150	62	2
35	Di-*sec*-amylnaphthalene	150	72	3
36	β-*sec*-Amylnaphthalene	150	140	1
37	β-Methylnaphthalene	150	>150	3
38	*tert*-Butylnaphthalene	150	>150	3
39	Naphthalene	150	>150	3

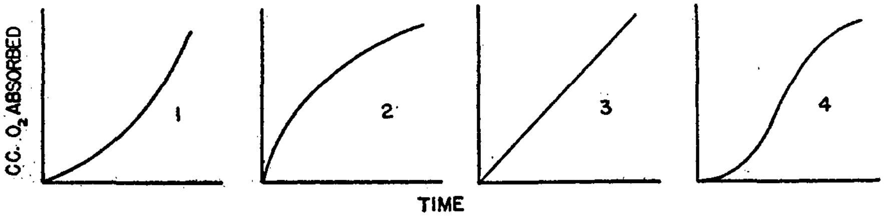


FIG. 1. Types of curve referred to in table 4

Hydrogenation of an alkylbenzene to the corresponding cyclohexane derivative resulted in an increase in stability, as shown by comparing item 5 with 22, and 11 with 23. The effect was to increase the 2000 cc. time by factors of 15 and 4, respectively, which are of the same order as that found in the case of the olefin. Both of these alkylbenzenes had long side chains (C_{16} and C_{18}), and the effect of hydrogenating benzene itself or a low-molecular-weight homolog would probably be quite different.

Hydrogenation of a naphthalene ring, on the other hand, results in a marked loss of stability, particularly if the naphthalene ring is only partially hydrogenated. The most stable hydrocarbon listed in table 4 is naphthalene, with a 2000 cc. time of $>$ 150 hr. at 150°C. or $>$2400 hr. at 110°C., assuming the above-mentioned factor of 16 for the difference in temperature of 40°C. Tetrahydronaphthalene, or tetralin, is on the other hand the least stable compound shown in table 4. It has a 2000 cc. time at 110°C. of only 1.5 hr. Thus the partial hydrogenation of naphthalene reduced its stability by a factor of more than 1600. Complete hydrogenation to decahydronaphthalene, or decalin, brings the 2000 cc. time back to 27 hr., which is 18 times that of tetralin, but still short of that of naphthalene by a factor of $>$ 89. That chain length does affect the influence of hydrogenation of the naphthalene ring is shown by comparing the above results with a comparison of items 31, 15, and 6, which represent the octadecyl derivatives of naphthalene, decalin, and tetralin, respectively, although unfortunately, for purposes of the present comparison, the first is the alpha derivative, and the other two beta. Octadecylnaphthalene had a 2000 cc. time at 150°C. of 33 hr., which would correspond to 530 hr. at 110°C. and the tetralin and decalin derivatives 2.5 and 24 hr., respectively, at 110°C. Thus the factors relating the 2000 cc. times of the naphthalene to that of the tetralin and decalin derivatives are 530/2.5 and 530/24, or 210 and 22, respectively. The differences between these values and the corresponding ones of $>$1600 and $>$ 89 for the unsubstituted homologs are probably due primarily to the effect of the alkyl group rather than the difference in position.

Item 21, 1-α-naphthyl-1-*n*-butylhexadecene, is interesting in that it contains both a naphthalene group, which would classify it with the stable hydrocarbons, and olefinic unsaturation, which would classify it with the unstable compounds. The two effects seem to balance each other, with the result that this compound has an intermediate stability comparable to that of the paraffins and naphthenes.

Comparison of items 20, 26, and 27 is of interest in that these three compounds are primary, secondary, and tertiary amyl derivatives of benzene, respectively, and hence show the influence of the structure of the side chain. According to the mechanism proposed earlier for the oxidation of an alkylbenzene, the first of these three hydrocarbons would form the hydroperoxide at the alkyl carbon attached to the ring. The peroxide would then dehydrate to phenyl butyl ketone. The second would likewise form the peroxide, but, since there was only one hydrogen atom on the carbon in question initially, propyl alcohol, rather than water, would split off, and acetophenone would be the other product. Since this process involves the breaking of a C—C bond, whereas the first does not, it is not surprising that the 2000 cc. time for the primary compound is less than half that for the secondary (28 hr. compared to 68). Furthermore, since the tertiary compound cannot form a hydroperoxide at the carbon attached to the ring, but must oxidize at other positions, it would be expected to be the most stable of the three, and this was again the case, for the 2000 cc. time for *tert*-amylbenzene was 85 hr. A similar trend was noted by Stevens and Roduta (42), who found *tert*-butylbenzene much more resistant to oxidation than any of the other alkylbenzenes which were examined (see table 1). The extreme stability of *tert*-butylnaphthalene as compared to the other naphthalenes (see item 38, table 4) is also in line with this trend.

Larsen, Thorpe, and Armfield (32) attribute the extreme stability of naphthalene aromatics in comparison with benzene homologs to the difference in the effectiveness of their oxidation products as inhibitors (naphthols in the one case *versus* phenols in the other). To support this theory, they oxidized *n*-amylbenzene (item 20, table 4) to which had been added 9.8 per cent of pre-oxidized α-methylnaphthalene. The curve of the mixture was practically coincident with that for α-methylnaphthalene itself (item 34). This represents a thirty-five-fold increase in 2000 cc. time, assuming again a factor of 2 per 10°C. change in temperature.

Chernozhukov and Krein (8) did not determine rates of oxidation, since most of the compounds they studied were oxidized in a bomb for a fixed time. It is possible, however, to compare the behavior of various compounds under identical conditions and thus determine relative stability. They found that naphthalene, anthracene, and biphenyl, after 3 hr. at 150°C. and 15 atm. of oxygen, had zero saponification values, whereas α-methylnaphthalene, β-methylnaphthalene, and propylnaphthalene produced, under these same conditions, saponification values of 12, 16, and 49, respectively. From this the authors conclude that chainless polynuclear aromatics are very stable, that the introduction of side chains, particularly long side chains, decreases stability, and that the beta derivatives of naphthalene are more reactive than the alpha. They also found that the presence of an intermediate link of carbon atoms between two aromatic rings, as in diphenylmethane, lowers stability. All of these conclusions are in agreement with those of Larsen, Thorpe, and Armfield, except that regarding the relative stability of α- and β-methylnaphthalenes. Chernozhukov and Krein found, as did Larsen *et al.* (31), that benzene derivatives are less stable than naphthalene homologs, and that the higher alkyl compounds are less stable than those of lower molecular weight. For example, after oxidation at 110°C. and 15 atm. of oxygen for 3 hr., 1,3,5-trimethylbenzene had a saponification number of 11, whereas propyl-, nonyl-, decyl-, *p*-methyl-, isopropyl-, and *o*-methyl-isopropylbenzenes had saponification numbers ranging from 31 to 48 after oxidation under the same conditions.

Balsbaugh and Oncley (2) studied the oxygen absorption of tetralin, decalin, and cetane at 30°, 75°, and 100°C., respectively, and found these three hydrocarbons to rate in the order of increasing stability in which they are mentioned. This is the same order shown for these compounds in table 4.

Hock and Lang (27) found that cyclopentene is oxidized at a slower rate than cyclohexene, and hydrindene, which can be regarded as tetralin minus one CH_2 group, at a slower rate than tetralin; from these results they conclude that a five-membered ring is less readily oxidized than a six-membered ring. However, their conditions differed from those used by others quoted above in that they used oxygen plus ultraviolet light. Their results cannot, therefore, be compared with the others without reservation.

B. Mixtures and petroleum fractions

When two hydrocarbons of unequal stability are blended, an intermediate stability might be expected, with the component of lower stability being oxidized preferentially. Actually a blend may possess a stability considerably greater than that of either component, and the least stable component is not necessarily oxidized in preference to the more stable one. Thus the stability of a blend of a few hydrocarbons or a mixture of several is probably determined to a large extent by interaction phenomena among various molecules or radicals. This, of course, greatly complicates the problem.

It has been pointed out earlier in this paper that the oxidation products of a lubricating oil resemble those of substituted naphthalenes, and that this class of hydrocarbons may, therefore, be oxidized preferentially in a blend, even though by themselves such compounds are exceedingly stable. This point is brought out in greater detail in table 5, which shows the effect of the addition of diamylnaphthalene to a white oil upon the distribution of oxidation products. The average data for naphthenes and alkylnaphthenes, to which class a white oil would belong, and for naphthalene derivatives, including diamylnaphthalene, are repeated from table 2 for comparison.

Of the six oxidation products listed, three—namely, free acid, peroxide, and carbonyl—show appreciably lower values for the napththalene than for the naphthene, and one, water, behaves in the opposite manner. Alcohols and combined acids or esters are produced to about the same extent in both classes of compounds. It is significant that as the percentage of diamylnaphthalene in white oil is increased from 0 to 50 per cent the percentage of oxygen appearing as free acid, peroxide, and carbonyl decreases progressively, and the percentage appearing as water increases accordingly. It would appear that in blends of 25–50 per cent of diamylnaphthalene in white oil, the former is oxidized preferentially, even though white oil has a *2000 cc. time* at 130°C. of about 5 hr., compared with 72 hr. at 150°C. for diamylnaphthalene, or 288 hr. at 130°C., which means that by itself, the white oil is fifty-eight times as reactive as diamylnaphthalene.

That a blend of two components may be more stable than either by itself is brought out clearly in an example cited by von Fuchs and Diamond (21), who measured the time required for the absorption of 1800 cc. of oxygen per 100 g. of oil for a motor oil containing varying quantities of bright stock aromatics. Oxidation was effected in the presence of iron as a catalyst. They found that the curve relating absorption time to concentration of added aromatics passed through a distinct maximum in the vicinity of 5 per cent, dropping off to absorption times less than half of the maximum at 0 and 10 per cent. Thus this blend has a definite "optimum aromaticity." The concept of optimum aromaticity is of great practical importance; it, along with the more conventional critieria of viscosity index and yield, determines the proper degree of solvent extraction to which a given stock should be subjected.

That lubricating oils possess an optimum aromaticity with respect to stability was also found by Fenske *et al.* (19), who separated a Pennsylvania oil, containing 9 per cent of aromatic rings, into 124 fractions by a combination of vacuum distillation and solvent extraction. They studied the rate of oxidation of seven of the fractions, ranging in aromaticity from 0 to 2 per cent and from 15 to 40 per cent aromatic rings, along with the original material. They used a temperature of 140°C. in a conventional oxygen-absorption apparatus, and found that none of the fractions examined was as stable as the original oil. Two fractions of zero aromaticity were the least stable, with one containing 2 per cent aromatic rings next, two of 37 and 40 per cent next, and two of 15 and 25 per cent the most stable, except for the original oil. That this was not caused by damage inflicted in the processing was proved by an oxidation test on a blend of all 124 fractions in the original proportions, which checked the run on the original sample.

TABLE 5

Effect of the addition of diamylnaphthalene to a white oil upon the distribution of oxidation products

Data from Larsen *et al.* (31); all figures expressed as percentage of total oxygen consumed

	FREE ACID	COMBINED ACID (ESTER)	PEROXIDE	ALCOHOL	CARBONYL	H_2O
Average naphthene or alkylnaphthene.....	11	17	14	8.9	51	22
White oil (mol. wt. = 387)................	13	20	5	13	44	17
White oil + 12.5% diamylnaphthalene.....	16	22	2.6	5.1	33	21
White oil + 25% diamylnaphthalene.......	9	23	0.2	6.4	14	24
White oil + 50% diamylnaphthalene.......	5.7	28	0.3	8.0		57
Average naphthalene derivative...........	7	16	1.4	9.0	10	51

An optimum aromaticity for insulating oils is indicated in the work of Clark (9), who studied the dielectric stability (which is known to be closely related to oxidation stability) of a series of oils with varying olefinic and aromatic unsaturation. Olefinic unsaturation was determined by absorption in sulfuric and boric acids, and aromatic plus olefinic unsaturation by absorption in sulfuric acid and phosphorus pentoxide, both according to Kattwinkel. Clark found a sharp and progressive decrease in dielectric stability with increasing olefinic unsaturation over the range of 0–6 per cent; however, variation in aromatic unsaturation from 0–12 per cent showed a maximum stability in the vicinity of 6 per cent.

von Fuchs and Diamond (21) found that the shape of the rate curve can be drastically altered by the concentration of added aromatics and by temperature. This necessitated a revision of the theory proposed by Dornte *et al.* (14, 15, 16), who classified oils into three groups: those whose oxidation products were (*1*) positive catalysts, (*2*) negative catalysts, or (*3*) without any catalytic effect. von Fuchs and Diamond concluded that aromatics can possibly "act in a two-fold capacity—i.e. both as inhibitors and retardants; either several compounds present may be acting differently or the same compound may be playing a dual rôle. At low concentrations conventional inhibitor action outweighs the other and an induction period is observed; at higher concentrations this effect is obscured by the additional quantity of aromatics, and autoretardation predominates. At intermediate concentrations the opposing tendencies of autocatalysis and autoretardation are balanced against each other more evenly so that the rate curve may possess an intermediate curvature or even be linear."

Larsen, Thorpe, and Armfield (32) studied the effect of adding naphthalene derivatives to other substances, and found a stabilizing effect. A much greater effect was, however, obtained when the napthalene compound was preoxidized in the absence of the other component. They attribute these results to the fact that in the former case oxidation of the naphthalene compound and oxidation of the second component are competitive, whereas in the latter the oxidation products of the alkylnaphthalene, probably naphthols, are present as antioxidants throughout the oxidation of the blend.

The effect of added aromatics upon the oxidation of paraffins and naphthenes has also been investigated by Chernozhukov (6) and by Chernozhukov and Krein (7, 8), who regard the stability of mineral oils to be determined essentially by the character and quantity of the aromatics present. They found, for example, that the addition of 1–10 per cent of naphthalene, phenanthrene, or anthracene to a vaseline oil resulted in a marked improvement in stability, according to their oxygen bomb test. They show this to be due to a preferential oxidation of the aromatics, with the oxidation products acting as antioxidants. They obtained similar results, though to a lesser degree, with substituted aromatics. This order of effectiveness of the substituted and unsubstituted aromatics in increasing the stability of a blend is the opposite of that found by Larsen, Thorpe, and Armfield (32), who found naphthalene ineffective in altering the oxidation curve of decalin, whereas substituted naphthalenes are effective. It must be remembered, however, that the conditions used in the two laboratories were different.

Denison (13) does not concur with Chernozhukov and others in their views on the importance of aromatics in determining the stability of a mineral oil. He considers natural sulfur compounds, rather than the hydrocarbon composition, to be the important factor. His conclusions are based on oxygen-absorption measurements on three oils before and after desulfurization, which was effected by treatment with metallic sodium in the presence of hydrogen at a pressure of 200 psi and at a temperature of 500°F. His results are summarized in table 6.

Denison reasons that since desulfurization resulted in little change in the hydrocarbon content of the oil, as shown by specific dispersion and Waterman analysis, and by the fact that no olefinic unsaturation was indicated by bromine number determinations, the decrease in stability was due solely to the removal of sulfur, and that "natural sulfur compounds seem to be the agents responsible for the stability of straight mineral oils." However, a glance at table 6 shows that, if this is the case, the relationship between stability and sulfur content is not a simple function, for the Pennsylvania oil, which was lowest of the three in sulfur both before and after treatment, was in both cases intermediate in stability, while the California naphthenic, which was highest in sulfur, was the least stable of the three before treatment, and the most stable after. Furthermore, the process of desulfurization necessarily alters the hydrocarbon structure. The sulfur was presumably removed by decomposition, with the rest of the molecule remaining in the oil. Since 2–20 per cent of the original oil consisted of sulfur compounds, it is scarcely conceivable that the changes in hydrocarbon structure do not affect stability. It is possible that a small amount of olefinic unsaturation escaped detection in the bromine number determination, since this analytical method is known to be less reliable for complex molecules as found in a lubricating oil than for the simpler olefins for which the method was devised. There is, moreover, a possibility that some reaction between sodium and aromatic rings took place, with the subsequent formation of tetralin-type compounds. Gilman, in his *Organic Chemistry*, reports that naphthalene can be reduced to tetralin by the action of sodium in liquid ammonia solution. It is conceivable that a similar reaction occurred under the conditions used by Denison. While the extent of such reactions could not have been great, since specific dispersion was not affected appreciably, the presence of a small amount of tetralin or related compound would be expected to have a profound influence on stability. It will

TABLE 6

Effect of desulfurization upon stability and properties

Data from Denison (13)

OIL	TIME TO ABSORB 100 CC. O_2 PER 100 G.	SULFUR	SPECIFIC DISPERSION	PER CENT AROMATIC RINGS (WATERMAN)
	hours	*per cent*		
California naphthenic SAE 30	0.7	0.53	120	15
California naphthenic SAE 30, desulfurized	0.2	0.07	121	14
California paraffinic 400 neutralized	5.0	0.22	106	1
California paraffinic 400 neutralized, desulfurized	<0.1	0.06		1
Pennsylvania SAE 30	2.5	0.10	111	7
Pennsylvania SAE 30, desulfurized	0.1	0.01	110	4

be recalled from the discussion of table 4 that tetralin is more than 1600 times as reactive as naphthalene. Furthermore, tetralin forms copious quantities of peroxides (2) which probably act as proöxidants, whereas naphthalene forms naphthols which act as antioxidants (21).

In view of this analysis of the problem, it would appear that the relative importance of aromatics and sulfur compounds in determining the rate of oxidation of straight mineral oils cannot be stated definitely without further experimentation. Both are probably involved, rather than either one alone. In addition, compounds containing other elements, notably oxygen and nitrogen, and which occur naturally in the lubricating oil fraction of petroleum, undoubtedly play a rôle in determining the stability of an oil.

C. Effect of catalysts and inhibitors

All of the oxidation studies discussed thus far in this paper, with the exception of a few cases where catalysts were specifically mentioned, have been in the absence of added catalyst or antioxidant. In actual practice either of these classes of material can, and usually does, have a profound effect upon the rate of oxidation of a lubricating oil.

Catalysts for the oxidation of lubricating oil include a wide variety of compounds. Hanson and Egerton (24) report that nitrogen dioxide, in concentrations comparable to that present in engine cylinders, greatly influences the rate of oxygen absorption of an oil at 220°C., the effect being that of shortening the induction period. Oxidation products, notably peroxides, may themselves be catalysts, as evidenced by the concave-upward, or autocatalytic, type of oxygen-absorption curve exhibited by certain oils under certain conditions. However, these do not constitute the most serious source of catalysis of deterioration encountered by lubricating oils. Metal catalysis, principally by compounds of metals which can readily change valence and specifically by compounds of copper, lead, and iron, is always to be reckoned with. These three metals are probably no worse in their effect than several others which could act as catalysts, such as manganese, chromium, or vanadium, but they play a more important rôle because of their much greater prevalence: copper in the form of oil lines, brass fittings, and bearing metal; lead as bearing metal and as a constituent of the decomposition products of tetraethyllead; and iron as the major constituent of the engine itself.

Davis, Lincoln, Byrkit, and Jones (12) showed that the napthenates of iron, lead, copper, cadmium, and silver all act as catalysts for the oxidation of lubricating oil, the effect varying with concentration. They found that in general an oil can "tolerate" a certain amount of catalyst without any appreciable effect upon rate of oxidation, but that an increase in concentration beyond this threshold value results in a marked decrease in induction period. As the concentration is increased further, a point is eventually reached where the system is again insensitive to further change in concentration. For example, a Mid-Continent, vacuum-distilled, solvent-refined oil had an induction period of 80 min. at 175°C. The addition of iron naphthenate up to 0.006 per cent as Fe_2O_3 had no effect, but further addition to 0.1 per cent resulted in a linear decrease in induction period, on a log-log plot, to less than 20 min. Further addition of iron naphthenate was without noticeable effect. All of this work was done in a static system, and measurements were limited to the initial phases of oxidation, so that the conclusions reached need not necessarily apply under conditions of agitation of the oil and oxidation to a greater extent. It would appear, however, that oils contain natural "anticatalysts" which are capable of nullifying the effect of a certain amount of added catalyst, and that at high concentrations of metal soap the system reaches a state of catalytic saturation.

Fenske *et al.* (19), who used a conventional circulatory oxygen-absorption apparatus, studied the effect of copper, iron, and lead, both in metallic and in soluble naphthenate form. They found copper naphthenate to be the most potent of the three soaps, and lead the least. This same order prevailed for the bulk metals in the early stages of oxidation, but in the later stages, lead became the most potent of the three. This was attributed to the greater solubility of lead compounds in the oil, as compared with those of iron and copper. Fenske also found that catalysis by these metals has little effect in altering the distribution of oxidation products, the main effect being that of increasing the over-all rate of oxidation rather than that of any one specific reaction.

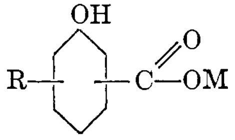
Larsen and Armfield (30) studied these same three catalysts, both in soluble and in bulk metal form, in three different oils, and at varying concentrations of soluble naphthenate and ratios of surface of metal to volume of oil. Their results with an extracted Mid-Continent oil were essentially in agreement with those reported by Fenske. Five and one-tenth square centimeters of copper per gram had approximately the same catalytic effect as 14.1 sq. cm. of iron per gram, indicating the former metal to be the more active of the two on a basis of equal areas per gram of oil. Three square centimeters per gram of lead was much less active than either copper or lead in the early stages, but became equal to them when 800 cc. of oxygen per 100 g. of oil had been absorbed. From there on it was the most active of the three metals. They found 100 p.p.m. of copper, 500 p.p.m. of lead, and 1000 p.p.m. of iron, all in the form of naphthenate, to have about the same catalytic effect. This order differs from that reported by Fenske in that the positions of lead and iron naphthenates are reversed.

In their study of the effect of surface area of metal and concentration of soluble metal, Larsen and Armfield found that curves of varying forms were obtained, depending upon the catalyst and upon the oil. They showed, for example, that three oils, a California extracted, a Mid-Continent extracted, and a Pennsylvania, could be rated in all six of the possible orders of stability at a given temperature (150°C.) and with a given catalyst (copper naphthenate), merely by altering the concentration of dissolved copper. Thus, if an oxidation test is to have significance in terms of correlation with engine behavior, the choice of catalyst, with respect to both kind and amount, must be judicious.

Larsen and Armfield studied catalysis in engines by withdrawing oil samples and determining their rate of oxidation in glass without any other added catalyst. They found that an oil loses stability very rapidly, particularly if the engine is operating without a filter. They found that a used oil could be considerably improved with respect to stability simply by filtration. Removal of fuel dilution by steam distillation had little further effect, but removal of soluble metals by washing with dilute hydrochloric acid and percolation through clay restored the oil practically to its original stability. They show that the oil insolubles, or "crankcase catalyst," constitute a potent catalyst, particularly when obtained from an engine which operated on a leaded gasoline. The copper and lead contents of crankcase catalyst are too low to account for its activity, which the authors believe is due to the presence of iron halides, derived from engine metals and the halogen compounds present in tetraethyllead fluid.

While heavy petroleum fractions have been in the past, and still are to a certain extent, used as such, the trend is toward the incorporation of additives for various specific purposes. These include the following: pour-point depressors, viscosity-index improvers, detergents, metal passivators and deactivators, and conventional antioxidants. The last-named class is, of course, of the greatest concern here, but the others cannot be ignored in oxidation studies, for they may have a profound, though indirect, effect upon rate of oxidation. Detergents, for example, peptize certain oxidation products and keep them colloidally dispersed, thus preventing their deposition as lacquer. In this manner they keep the metal surfaces of an engine clean, but vulnerable to attack by acidic oxidation products of the oil. The dissolved metals then act as catalysts for further oxidation. Passivators, on the other hand, protect metal surfaces from attack by forming a protective film on their surface, and thus prevent metal catalysis as well. Deactivators nullify the catalytic effect of dissolved metals by reacting with them and forming a non-active, or sometimes an insoluble, combination. Thus, detergents, passivators, and deactivators, none of which need have any effect upon oxidation rate in glass and in the absence of catalysts, may have a large effect in engines.

A single compound may serve in more than one capacity. Reiff (39) has shown that metal salts of phenolic acids of the following general structure have multifunctional properties. M is a metal and R an alkyl group. Compounds of this class act as pour-point depressors and viscosity-index improvers as well as inhibitors, as shown by the fact that viscosity increase, naphtha insolubles, and neutralization number are maintained at a low value in engine tests as compared to a blank run on the oil without additive.



Since the pioneer work of Moureu and Dufraisse (34), antioxidants have been investigated for stabilizing a number of products, including rubber, fats, chemicals, and gasoline as well as lubricating oil. A complete review of this field is beyond the scope of this paper, and only a few references will be cited.

The mechanism of the action of antioxidants is generally considered to be that of chain breaking, the antioxidant reacting with a "hot" molecule and thus being itself oxidized. In this process the antioxidant molecule is destroyed, but with a dissipation of the energy possessed by the "hot" molecule, so that the chain is broken. Thus the oxidation of hundreds or thousands of molecules of hydrocarbon has been prevented, since this energy is passed on from one molecule to the next in the normal chain reaction.

One of the earliest studies of antioxidants in mineral oil was reported by Haslam and Frolich (25) in 1927. They tested a number of compounds, most of which contained nitrogen, in 0.01 per cent concentration in a medicinal oil by bubbling dry oxygen through the oil at a temperature of 130°C., and followed the course of oxidation by measurements of neutralization number. The following compounds, listed in order of increasing potency, were found to be effective: diphenylguanidine, β-naphthylamine, ethyl-α-naphthylamine, *p*-aminophenol, diphenylamine, phenyl-α-naphthylamine, and unsymmetrical diphenylhydrazine.

Fenske *et al.* (19) classify antioxidants as: (*a*) hydroxy compounds (phenols, naphthols), (*b*) nitrogen compounds (amines, etc.), (*c*) sulfur compounds (disulfides, thioethers, etc.), (*d*) organometallic compounds, (*e*) halogen compounds, (*f*) compounds containing higher members of the oxygen and nitrogen groups in the Periodic Chart, such as phosphorus, arsenic, antimony, selenium, and tellurium.

Dornte (14) showed that the addition of 0.01 per cent of phenyl-α-naphthylamine to a white oil increased its induction period from practically zero to about 20 hr., after which the oxidation curve was practically parallel to the curve for the original oil. von Fuchs and Diamond (21) found that a turbine oil base stock, which approached white oils in degree of refining, responded to the addition of phenyl-α-naphthylamine in a similar fashion. On the other hand, less severely treated oils, e.g., solvent-extracted neutrals, display a far inferior susceptibility to this inhibitor. Thus the addition of antioxidant, at least of the phenyl-α-naphthylamine type, to an oil is by no means a universal "cure-all." The base stock to which it is added must be carefully refined, not for maximum stability, but for maximum inhibitor susceptibility.

Chernozhukov and Krein (8) investigated several compounds as antioxidants in their bomb test, and found catechol, hydroquinone, resorcinol, pyrogallol, quinone, aniline, and β-naphthylamine to be effective. Resins obtained from petroleum fractions by extraction with acetone were also effective. These were probably similar in character to the bright stock aromatics previously mentioned as reported by von Fuchs and Diamond (21) as increasing the stability of a motor oil when added in low concentration. Chernozhukov and Krein also report favorable preliminary results on several organic sulfur compounds, but do not list the compounds tested.

IV. CONCLUSIONS

The oxidation of a paraffin, under conditions comparable to those encountered by lubricating oils in service, tends to initiate at a beta carbon atom; that of an alkylnaphthene at a carbon in the ring to which an alkyl group is attached; and that of an alkyl aromatic at a carbon in an alkyl group adjacent to the ring. Thus, the two types of ring compounds differ in their course of oxidation in that the aromatic ring tends to remain intact, whereas the naphthene ring is ruptured at an early stage of oxidation. Branched paraffins probably oxidize at the point of branching as well as at a beta carbon. The complex molecules comprising lubricating oils probably have several carbon atoms possessing varying degrees of vulnerability. For example, a naphthene or aromatic with a long alkyl side chain would probably be oxidized at the carbon adjacent to the terminal methyl group, as governed by the rule for paraffins, as well as at the carbon in or adjacent to the ring, as influenced by the naphthene or aromatic ring, respectively.

The initial oxidation product is in every case postulated to be a hydroperoxide, which decomposes in one of three manners: by dehydration, with the liberation of a molecule of water; by reduction, with the liberation of an atom of active oxygen; or by further oxidation, with the splitting of at least one C—C bond. Aldehydes, ketones, and acids are among the principal products formed from peroxides. These can in turn undergo further oxidation or condensation. When an aromatic is oxidized, the condensation products are particularly conspicious, for they are dark in color and usually insoluble.

Paraffins and naphthenes oxidize at comparable rates. The introduction of a benzene ring at the end of a paraffin molecule causes an increase in rate, as does the introduction of olefinic unsaturation. The presence of a partially hydrogenated ring, e.g., tetralin, has a particularly great effect in increasing oxidation rate. The presence of a naphthalene nucleus, on the other hand, stabilizes the molecule to a remarkable extent. This is probably caused by an inhibitory effect by oxidation products of the naphthalene derivative (naphthols).

Mixtures of hydrocarbons do not in general oxidize as might be expected, i.e., with the least stable component reacting to the greatest extent. On the contrary, the naphthalene derivatives, which by themselves are the most stable, seem to be oxidized preferentially in mixtures. Thus, interaction effects play an important role in determining the oxidation rate of a lubricating oil.

Oxidation rate may be markedly increased by the addition of compounds of copper, lead, and iron. The effect of these catalysts is largely on the over-all rate and not upon the formation of specific products, since the distribution of oxidation products remains sensibly constant. Catalyzed oxidation may be retarded by the use of passivators or deactivators, which may both be regarded as anticatalysts in that one prevents the solution of metals, and the other reacts with soluble compounds to render them catalytically inactive. Oxidation can also be retarded by the incorporation of antioxidants, which act as chain breakers in the oxidation process.

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