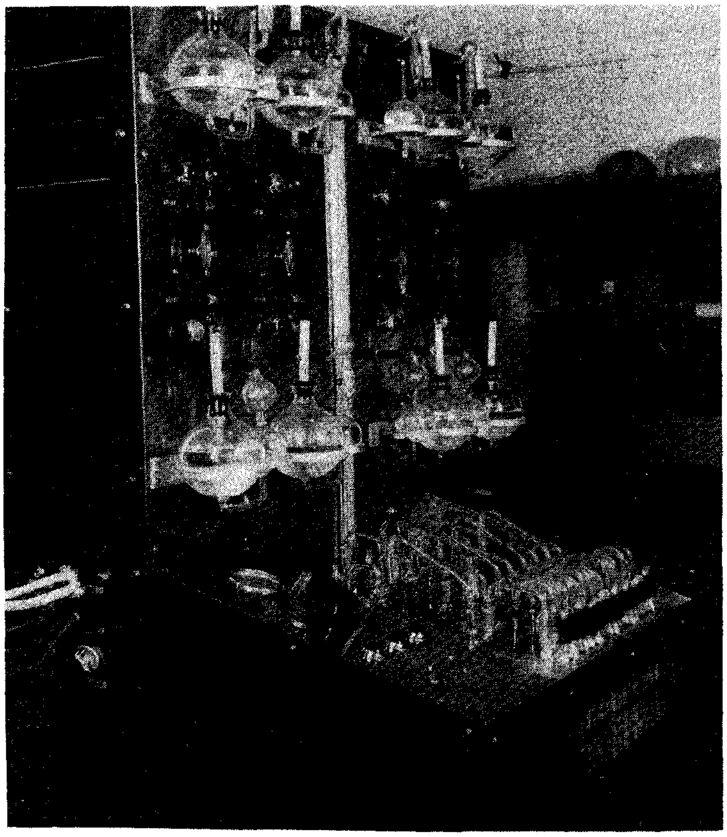

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AUTOMATIC OXIDATION APPARATUS FOR LUBRICATING OIL

Oxidation Characteristics of Pure Hydrocarbons

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From a study of the oxidation characteristics of pure hydrocarbons, useful information has been obtained relative to the effects of structural factors upon oxidation stability. Thus it was found that all saturated hydrocarbons, paraffinic or cycloparaffinic, behave similarly and are quite reactive. The aromatics containing a benzene ring attached to a saturated side chain or hydroaromatic ring are still more reactive, as a result of the activating influence of the aromatic ring. In contrast, naphthalene and other polynuclear aromatics are very stable, apparently as a result of the formation of effective inhibitors upon oxidation.

It is concluded that stability of a lubricating oil results, not from stability of the basic hydrocarbons, but from content of natural inhibitors.

MOST problems arising from the use of mineral oils in service are fundamentally related to oxidation of the oil. This is especially true for modern high-output engines where the demand on fuels and lubricants is becoming more critical. Fresh mineral oil consists essentially of hydrocarbons capable of furnishing satisfactory lubrication to moving parts. Under conditions of use, however, these hydrocarbons are converted to oxygenated products, properties of which we do not understand and the formation of which we can control only within limits. These products lead to lacquering, ring sticking, corrosion, sludging, and other problems of engines.

The importance of the deterioration of lubricating oils in service is well recognized, and the susceptibility of an oil to this type of deterioration is measured by tests such as the Indiana or Sligh oxidation tests. Such conventional tests have been accepted, although somewhat reluctantly, as control tests for refining oils with regard to their oxidation stability.

There is increasing indication from experimental and service observations that attempts to refine oils drastically—for example, to obtain extremely favorable viscosity-temperature characteristics—have in some cases resulted in overrefining with respect to stability. In view of our limited knowledge of oil composition, it seems important that a clearer picture of overrefining be obtained. For years, refining as a process of lubricating oil manufacture has been directed toward the removal of "aromatics", paraffin wax, and asphalts. Since it is not known what products are actually being removed, one is inclined to focus attention on what should remain to constitute a stable oil. For example, should aromatics be entirely absent? Apparently not, for aromatic-free medicinal white oil is extremely unstable. A need for a fundamental knowledge of the oxidation characteristics or various types of hydrocarbons thus becomes apparent. Certainly the long standing conceptions of stability need to be finally placed on a scientific basis. By establishing such a basis, a great gap in our knowledge of oil oxidation will have been filled.

Table I. Preparation and Purification of Hydrocarbons

		Combustion Analysis			
		Carbon, %		Hydrogen, %	
Hydrocarbon	Source and Method of Purification[a]	Found	Theory	Found	Theory
Aliphatics					
n-Decane	Reaction of Na with *n*-amyl bromide, distd. over Na	...	...	...	...
Cetane	Du Pont; distn., 158.7–160° C. (10 mm.) fraction crystd. from acetone	...	...	...	...
Tetraisobutylene	Distn. of acetone-sol. portion of crude polyisobutylene	...	...	...	...
Polyisobutylene	Distn. residue from acetone-sol. portion of polyisobutylene	...	...	...	...
Hydropolyisobutylene	Catalytic hydrogenation of above	...	...	...	...
Naphthenes					
Decalin	Eastman Kodak; treatment with H_2SO_4, distn.	...	...	...	...
Dicyclohexyl	Eastman Kodak; distn.	...	...	...	...
n-Amylcyclopentane	Reaction of cyclopentanone with *n*-amyl magnesium bromide, dehydration of alcohol, catalytic hydrogenation	85.51	85.63	14.37	14.37
n-Hexadecylcyclohexane	Hydrogenation of *n*-hexadecylbenzene	85.58	85.63	14.39	14.37
n-Octadecylcyclohexane	Hydrogenation of *n*-octadecylbenzene	85.59	85.63	14.37	14.37
n-Octadecyl Decalin	Hydrogenation of *n*-octadecyl Tetralin	86.11	86.07	13.96	13.93
Perhydroanthracene	Hydrogenation of anthracene, m. p. 216–216.5° C.; liquid and solid isomers are formed	87.39	87.42	12.59	12.58
9,10-Diisobutylperhydroanthracene	Hydrogenation of 9,10-diisobutyl-9,10-dihydroanthracene (complete hydrogenation difficult)	87.00	86.76	12.94	13.24
Aromatic naphthenes					
Tetralin	Eastman Kodak; distn.	...	...	...	...
Octahydroanthracene	Condensation of Tetralin using $AlCl_3$, purification by distn. and crystn.	90.31	90.26	9.78	9.74
9,10-Diisobutyl-9,10-dihydroanthracene	Reaction of Na addition product of anthracene (m. p. 216.4° C.) with isobutyl chloride	90.43	90.35	9.62	9.65
9,9,10,10-Tetraisobutylanthracene	Reaction of isobutyl chloride with Na addition product of 9,10-diisobutylanthracene	88.99	89.04	10.98	10.96
β-*n*-Octadecyl Tetralin	Reduction of *n*-heptadecyltetralone; oxidation (HNO_3) yields trimellitic acid	87.43	87.42	12.59	12.58
α-Phenyl-Δ^2-tetralylbutane	Condensation of Tetralin using $AlCl_3$; separated from other products by distn.	90.86	90.85	9.17	9.15
5-Isobutylacenaphthene	Clemensen reduction of 5-isobutyrylacenaphthene	91.34	91.37	8.70	8.63
Benzene aromatics					
n-Amylbenzene	Reaction of *n*-amyl iodide with bromobenzene	89.10	89.12	10.92	10.88
tert-Amylbenzene	Eastman Kodak; purified by distn.	...	...	...	...
Hexaethylbenzene	Reaction of benzene with ethylene; purification by distn. and crystn. of acetone	...	...	...	...
n-Hexadecylbenzene	Reduction of pentadecylphenone	87.42	87.34	12.73	12.66
n-Octadecylbenzene	Reduction of stearophenone	87.12	87.19	12.68	12.81
Diphenylmethane	Eastman Kodak; purified by distn.	...	...	...	...
Fluorene	Eastman Kodak; distn. and fractional crystn. from ethanol	...	...	...	...
Polynuclear aromatics					
Naphthalene	Eastman Kodak; purified by fractional crystn. from ethanol	...	...	...	
α-Methylnaphthalene	Eastman Kodak; purified by distn.	...	...	...	...
β-Methylnaphthalene	Eastman Kodak; distn. and fractional crystn. from ethanol	...	...	...	...
α-Isoamylnaphthalene	Reaction of isoamyl bromide and α-bromonaphthalene; purified by distn.	...	...	...	...
β-*sec*-Amylnaphthalene	Sharples Solvent Corp.[b]; purified by distn.	...	...	...	...
tert-Butylnaphthalene	Reaction of diisobutylene with naphthalene; $AlCl_3$ catalyst	...	...	...	...
Diamylnaphthalene	Sharples Solvent Corp., "white" grade	...	...	...	...
Polyamylnaphthalene	Sharples Solvent Corp., clay-filtered (mol. wt. 340)	...	...	...	...
α-*n*-Octadecylnaphthalene	Reduction of α-naphthyl-*n*-heptadecyl ketone	88.28	88.35	11.81	11.65
Benzylnaphthalene	Reaction of benzyl chloride with naphthalene in presence of $AlCl_3$	93.60	93.54	6.52	6.46
5-α-Naphthyl-5-*n*-eicosene	Dehydration of alcohol resulting from reaction of pentadecyl-α-naphthyl ketone with *n*-butyl magnesium bromide; purified by distn.	88.88	88.60	11.12	11.40
Di-α-naphthylmethane	Condensation of methylal with naphthalene in presence of H_2SO_4	93.74	93.99	6.06	6.01
9,10-Diisobutylanthracene	Oxidation of 9,10-dihydro-9,10-diisobutylanthracene with quinone	90.96	90.97	9.03	9.03
Phenanthrene	Selective oxidation of impurities distn. followed by crystn. from ethanol, methyl ethyl ketone, methanol	94.12	94.34	5.67	5.66

[a] When a product was purified by distillation at atmospheric pressure, a 10-plate column was used. Those made under vacuum were through a column, 1 meter long, packed with glass cylinders.

[b] The amylnaphthalenes of Sharples Solvent Corp. were predominantly secondary, but possibly some tertiary groups are also present.

Method of Study

Since deterioration by oxidation is essentially a reaction between organic materials and oxygen, the most general and simplest method of study is to determine the volume of oxygen consumed in the process. Such a study will give an unambiguous measure of the over-all rate and extent of oxidation, regardless of the quantities of secondary oxidation products which appear.

While inherent oxidation is important, nevertheless, if the oxidation products formed do not deposit in the engine, corrode bearings, or interfere with lubrication, then oxidation becomes a minor problem. While the ideal solution is to produce hydrocarbons resistant to attack, it may be that some oxidation is inevitable especially as some thermal decomposition is unavoidable. The ideal, then, should be to strive for high resistance to attack and to limit deterioration to the production of harmless types of oxidation products. In practice the latter may even be more important than the former.

To study this phase of the problem, complete analyses for functional groups were made—acidic groups, esters (including saponifiable groups such as lactones, anhydrides, etc.), carbonyl and hydroxyl groups, and peroxides. In addition, water and carbon dioxide were determined. The methods of analyses were chosen not only for their suitability in the present investigation but also because of their usefulness with oxidized lubricating oils which are, in the main, quite dark and make exact determination of end points by colorimetric methods impossible. Hence, for those analyses in which difficulty might be experienced, correct end points were determined by potentiometric methods employing a glass electrode in combination with a Beckman pH meter (*1*).

Acidity was determined by potentiometric titration with a solution of potassium hydroxide in anhydrous isopropyl alcohol. The oxidized hydrocarbon was dissolved in a solution of benzene and isopropyl alcohol before titration.

The amount of saponifiable material formed was determined by refluxing the oxidized hydrocarbon in benzene–isopropyl alcohol solution with potassium hydroxide and titrating potentiometrically with hydrochloric acid in isopropyl alcohol solution.

Carbonyl values were obtained by reacting the aldehydes and ketones with hydroxylamine hydrochloride to produce an oxime and an acid which was titrated potentiometrically with potassium hydroxide in isopropyl alcohol solution.

Alcohol was determined by acetylation with acetyl chloride in the presence of pyridine followed by titration with aqueous sodium hydroxide solution.

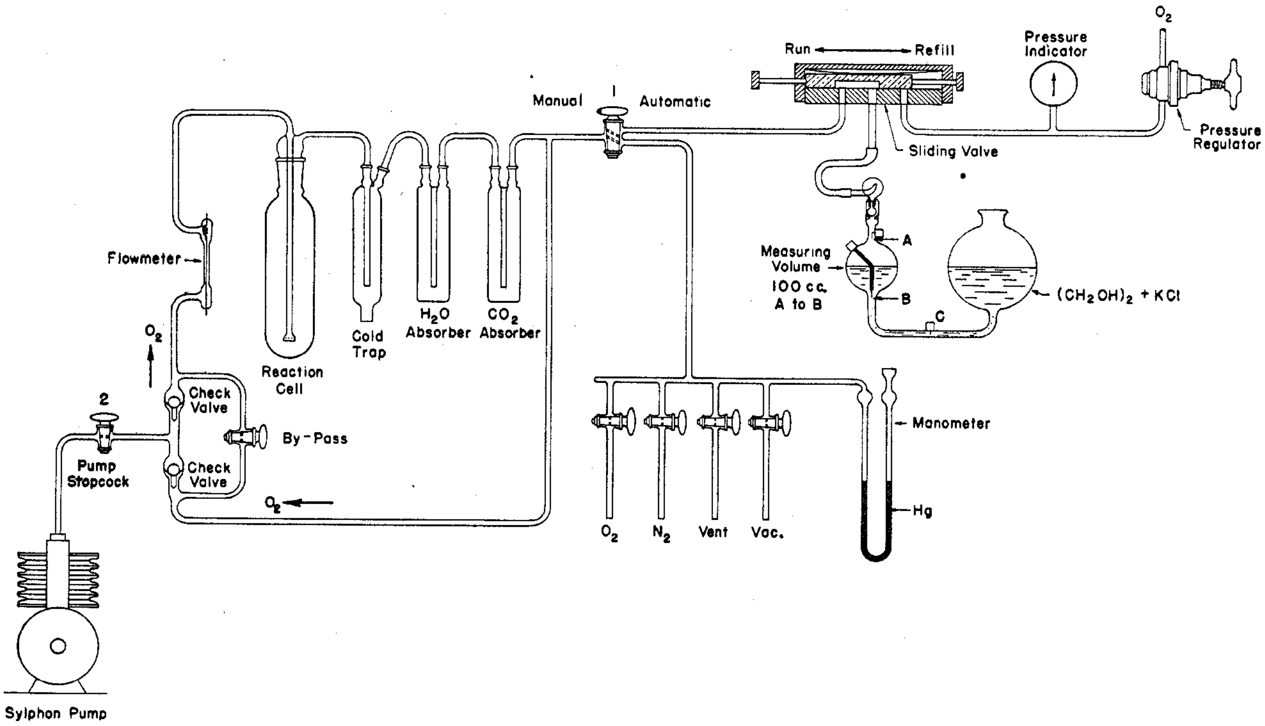


FIGURE 1. FLOW DIAGRAM OF OIL OXIDATION SYSTEM

Peroxides were determined by the ferrous sulfate–titanous chloride method.

The amount of carbon dioxide formed was determined from the increase in weight of the carbon dioxide absorption tube which contained ascarite, while the amount of water formed was measured by the increase in weight of the water absorption tube (containing anhydrous calcium sulfate) and the weight of water retained in the cold trap. Volatile acid formation was determined by colorimetric titration of the trap contents with sodium hydroxide solution.

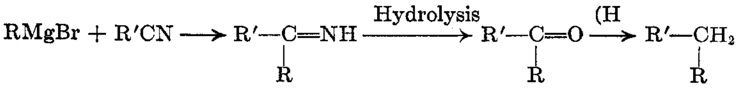
Any analysis for a single functional group in oxidized material, as encountered in this work, must be a compromise, since few of the analyses are unaffected by other oxidation products; hence, in some instances the amount of oxygen involved as measured by oxidation products is greater than that actually consumed. In the case of some rapidly oxidizing hydrocarbons, the amount is less, as a result mainly of incomplete removal of water from the oxidation cell to the cold trap and drying tube.

Some work on the liquid-phase oxidation of pure hydrocarbons has been published in the literature. Thus Stephens and Rodata (*4*) described the effect of various substituents on the autoxidation of alkyl benzenes. Chernozhukov and Krein (*2*) studied the oxidation characteristics of a wide variety of hydrocarbons as well as petroleum fractions. In both cases the extent of oxidation was judged by the analysis of the oxidized mixture, which is believed to be less precise than the oxygen absorption methods. In several respects these investigators arrived at conclusions similar to those of the present work.

Hydrocarbons Studied

The hydrocarbons were selected to be representative of possible types present in a mineral oil, but were not limited solely to those of high molecular weight since frequently it was desirable to study the effect of increasing the number of rings in the cyclics or the number of carbon atoms in a chain.

PREPARATION AND PROPERTIES. In preparing many of the hydrocarbons the methods described by Mikeska (*3*) were used; they involve reduction of an aromatic ketone to the corresponding hydrocarbon by a modified Clemensen method. We preferred, however, to prepare the ketones by the reaction of the aromatic organomagnesium complex with the side-chain nitriles rather than by reaction of the acyl halide with the aromatic nucleus:



$$\mathrm{RMgBr + R'CN} \longrightarrow \mathrm{R'{-}}\underset{\underset{\mathrm{R}}{|}}{\mathrm{C}}\mathrm{{=}NH} \xrightarrow{\text{Hydrolysis}} \mathrm{R'{-}}\underset{\underset{\mathrm{R}}{|}}{\mathrm{C}}\mathrm{{=}O} \xrightarrow{\text{(H}} \mathrm{R'{-}}\underset{\underset{\mathrm{R}}{|}}{\mathrm{CH_2}}$$

By this method the exact position of the substituent was known and a more homogeneous product could be obtained. Reduction of the naphthalene ketones was exceedingly difficult, while benzene or Tetralin derivatives were reduced with ease.

It was found that most of the long-chain aromatics exist in several crystalline modifications, and a wide variety of melting points could be obtained, depending upon such factors as the rate of crystallization. (Table II gives figures for the highest melting modification.)

The preparation and purification of the hydrocarbons are summarized in Table I, and the physical properties are listed in Table II.

APPARATUS AND PROCEDURE. The automatic oxygen circulating system used (Figure 1) consists essentially of a closed circulating system, capable of automatically recording the rate at which oxygen is consumed as it circulates through the heated hydrocarbon. The inlet to the reaction cell, which is heated in a thermostated oil bath, consists of a sintered glass thimble on the end of a Pyrex tube and was found to produce excellent dispersion of the oxygen. The cold trap is held at 0° C. or slightly lower (use of carbon dioxide or liquid air cooling required considerable attention and frequently led to plugged lines). The water and carbon dioxide absorbers form a path of about 36 cm. through which the circulating gases flow and are necessary to obtain efficient removal of these constituents of the gas stream.

Table II. Physical Properties of Hydrocarbons

Hydrocarbon	Boiling[a] or Melting Point, ° C. (Mm. Hg.)	Density (° C.)[b]	Viscosity, Saybolt Universal Sec.		Viscosity Index	Aniline Point[c], ° C.	Refractive Index[b]			Specific Dispersion
			100° F.	210° F.			n_C	n_D	n_F	
Aliphatics										
n-Decane	112.5–114.5 (134)	....	....	....	....	....	.....	1.4125	.....	...
Cetane	17.4 m. p.	....	....	....	....	....	.....	.....	.....	...
Tetraisobutylene	65–75°(1)	....	....	....	....	....	.....	.....	.....	...
Polyisobutylene[d]	(Mol. wt. 765)	....	....	....	....	....	.....	.....	.....	...
Hydropolyisobutylene[e]	(Mol. wt. 690)	....	....	....	....	....	.....	.....	.....	...
Naphthenes										
Decalin	191–193	....	....	....	....	....	.....	.....	.....	...
Dicyclohexyl	214–216 (468); 3.5–4 m. p.	....	....	....	....	....	.....	.....	.....	...
n-Amylcyclopentane	179.2–181.2	....	....	....	....	....	.....	1.4330 (25.5)	.....	...
n-Hexadecylcyclohexane	35.6 m. p.	0.8122 (45) 0.8084 (50)	60.3	36.75	168	101.2	1.44933 (41.5)	1.45177 (41.5)	1.45732 (41.5)	98.5
n-Octadecylcyclohexane	43–43.5 m. p.	0.8143 (45) 0.8084 (55)	70.0	38.25	159	105.7	1.44793 (55)	1.45057 (55)	1.45583 (55)	99.0
n-Octadecyl Decalin	41 m. p.	0.8473 (45) 0.8441 (50)	135	44.55	141	....	1.46528 (41.5)	1.46771	1.47349 (41.5)	96.7
Perhydroanthracene[f]	146–147.5 (19)	0.9368	....	....	....	....	1.49837	1.50112	1.50749 (20)	97.4
9,10-Diisobutylperhydroanthracene[g]	133–139 (1)	0.9329	....	....	....	....	.....	1.50030	.....	99.3
Aromatic naphthenes										
Tetralin	205.4–205.8	....	....	....	....	....	.....	.....	.....	...
Octahydroanthracene	73–73.5 m. p.	1.0034[h]	....	....	....	....	1.5562[h]	1.5607[h]	1.5715[h]	162
9,10-Diisobutyl-9,10-dihydroanthracene	142 (0.5)	0.9899	3307	51.36	−1480	....	1.55830	1.56336	1.57600	179
9,9,10,10-Tetraisobutylanthracene	177.5 m. p.	....	....	....	....	....	.....	.....	.....	...
β-*n*-Octadecyl tetralin	32.5–33 m. p.	0.8722 (45) 0.8656 (55)	118	42.8	143	62.7	1.48280 (55)	1.48656 (55)	1.49371 (55)	126
α-Phenyl-Δ²-tetralylbutane	192.8–193.2 (1)	1.0045	97.3	37.82	27	....	1.56177	1.56664	1.57903	171
5-Isobutylacenaphthene	138–139 (0.5)	....	....	....	....	....	.....	.....	.....	...
Benzene aromatics										
n-Amylbenzene	204–204.5	0.8585	....	....	....	−11	1.48537	1.48791	1.49660	154
tert-Amylbenzene	185–187	....	....	....	....	....	.....	1.4916	.....	...
Hexaethylbenzene	127 m. p.	....	....	....	....	....	.....	.....	.....	...
n-Hexadecylbenzene	27 m. p.	0.8550 0.8388 (45) 0.8353 (50)	49.9	35.2	170	39.4	1.46648 (55)	1.46987 (55)	1.47694 (55)	126
n-Octadecylbenzene	36.5 m. p.	0.8439 (40) 0.8377 (50)	59.7	35.7	154	47.85	1.47022 (55)	1.47342 (55)	1.48136 (55)	133.5
Diphenylmethane	175.4–175.5 (72)	....	....	....	....	....	.....	.....	.....	...
Fluorene	113–114 m. p.	....	....	....	....	....	.....	.....	.....	...
Polynuclear aromatics										
Naphthalene	80 m. p.	....	....	....	....	....	.....	.....	.....	...
α-Methylnaphthalene	235–235.5	....	....	....	....	....	.....	.....	.....	...
β-Methylnaphthalene	34.5 m. p.	....	....	....	....	....	.....	.....	.....	...
α-Isoamylnaphthalene	287–289	....	....	....	....	....	.....	.....	.....	...
β-*sec*-Amylnaphthalene	130–131 (5)	....	....	....	....	....	.....	.....	.....	...
tert-Butylnaphthalene	114–118 (3)	....	....	....	....	....	.....	1.5714	.....	...
Diamylnaphthalene	.....	....	182.1	39.7	−167	....	.....	.....	.....	...
α-*n*-Octadecylnaphthalene	515–552	0.8849 (55) 0.8789 (65)	120	42.6	136	40.8	1.50568 (55)	1.51000 (55)	1.52097 (55)	173
Benzylnaphthalene	168.5–169 (1.5)	1.0777	62.8	34.4	15	....	.....	.....	.....	272 (Abbe)
5-α-Naphthyl-5-*n*-eicosene	230–238 (2.5)	0.9107	....	....	....	....	1.52536	1.53019	1.54290	192
Di-α-naphthylmethane	108–109 m. p.	1.1224 (52)	....	....	....	....	1.677 (52)	1.686 (52)	1.712 (52)	311
9,10-Diisobutylanthracene	137–138 m. p.	1.022[i] 1.003 (52)[i]	....	....	....	....	1.623 (52)[i]	1.661[i] 1.637 (52)[i]	1.669 (52)[i]	460
Phenanthrene	99.6–100 m. p.	....	....	....	....	....	.....	.....	.....	...

[a] Unless otherwise indicated, boiling points are at atmospheric pressure.
[b] Determined at 20° C. unless otherwise designated in parentheses.
[c] Aniline points are given for equal volumes of hydrocarbon and aniline.
[d] One double bond per mole.
[e] No unsaturation.
[f] Constants are for the liquid isomer.
[g] Possibly contaminated by unsaturates.
[h] Determined in Tetralin solutions.
[i] Determined in mesitylene solutions.

Operation of the automatic dispensing reservoir is briefly as follows: When the confining liquid reaches the upper contact due to absorption of oxygen and reduction of pressure, a system of relays connects the reservoir to a low-pressure oxygen supply until the liquid is forced to the lower contact, when the relay system again connects the dispensing reservoir with the oxidation system. Each time this cycle of operations occurs, a mark is made on a small waxed time tape. By proper adjustment of the size of the sample or of the size of the reservoir, any desired number of points can be obtained on the curve relating time to volume of oxygen absorbed.

In operating the apparatus, the hydrocarbon is weighed into the reaction cell and then connected into the system. The system is immediately evacuated until the sample is brought to temperature; then pure oxygen is run in. The process of evacuation and refilling is repeated three times. Circulation is started and the test begun. Some of the reaction cells are equipped with sampling tubes so that periodic samples can be withdrawn for analysis.

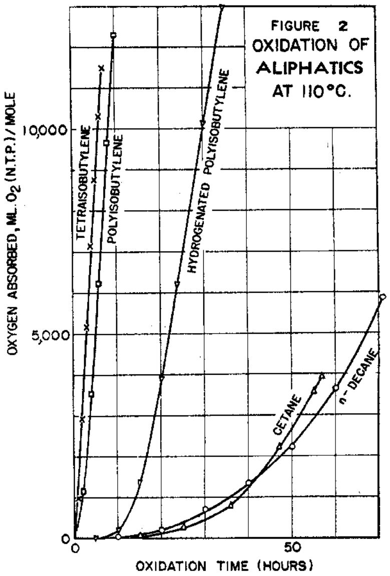
Experience showed that rate of circulation is not an important variable if only slightly more than the volume of oxygen being absorbed is circulated. However, to ensure an adequate supply, the rate of circulation is usually made at least ten times the rate of absorption.

In closed systems of this type there is an inevitable accumulation of gases which gradually dilute the oxygen; the chief constituents are light hydrocarbons, hydrogen, and carbon monoxide. Only in a few cases, however, particularly among the saturated hydrocarbons (cetane and *n*-amylcyclopentane were notable in this regard) did these gases affect the reaction rate, provided oxidation was not carried too far. In the cases cited above, the reactions were sharply interrupted by this accumulation but immediately resumed the usual rate when the system was evacuated and fresh oxygen added. The nature of the break indicated that the effect was not purely one of dilution.

Oxidation of Aliphatic Hydrocarbons

The aliphatic hydrocarbons studied had a chain length from 10 to about 50 carbon atoms. Some of the chains were normal, some branched, and some contained olefinic unsaturation. It is thus considered that satisfactory representatives of the aliphatics possibly to be encountered in petroleum practice have been chosen.

Representative of normal paraffins are *n*-decane and *n*-hexadecane; tetraisobutylene is an olefin of similar chain



length. The effect of a longer chain or homolog is ascertained by study of a higher polymer with about 13 isobutylene units. This polymer was completely hydrogenated to evaluate the effect of chain branching alone. Results are plotted in Figure 2 and show the rate at which one mole of hydrocarbon absorbs oxygen at 110° C.

The following conclusions were drawn:

1. Increase in chain length increases activity, although the effect is not marked and the increase in reactivity may be due to branching.
2. Saturated paraffins, either normal or branched-chain, exhibit a similar oxidation curve—i. e., one possessing a typical induction period followed by autocatalytic acceleration to constant rate.
3. The presence of a double bond in the molecule decreases stability considerably and appears to be the point of attack by oxygen. The latter point follows from the fact that reactivity of the isobutylene polymer appears to be quite independent of chain length.

The course of the oxidation is seen in Table III, which indicates the percentage of total oxygen consumed for each type of oxidation product.

In discussing type of oxidation products two factors tend to confuse the results: (*a*) The rates of formation of oxidation products vary with time; frequently maxima are reached in the rate of formation of one product while others may form at ever increasing rates. Thus no single analysis can give entirely characteristic data. While the rate of formation of oxidation products was studied in many cases, the large amount of material required sometimes made this impossible. (*b*) In many instances a molecule is a composite of two or three different-type hydrocarbon portions. Obviously such a substance may assume the characteristics of any of its portions. Frequently, however, it was found that some part of the particular molecule conferred upon the whole the general characteristics of that particular portion.

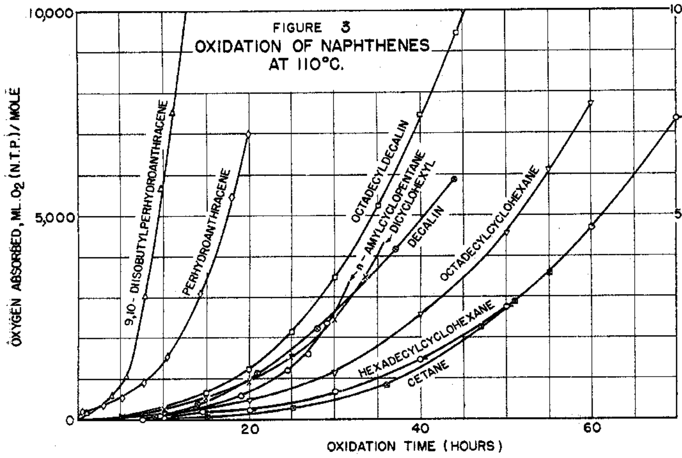
Oxidation of Naphthenes and Alkylnaphthenes

This study included mono-, di-, and tricyclic naphthenes. In some instances long paraffin side chains were attached to the cyclic nucleus. The oxidation curves are shown in Figure 3; included is that for cetane, a typical paraffinic hydrocarbon. Great similarity is apparent between the purely paraffinic and naphthenic and the combination naphthenic-paraffinic hydrocarbons. They all exhibit the same general type of oxidation curve—i. e., an induction period of slow oxidation accompanied by rapid acceleration to a steady state. The steady-state reaction is nearly the same in all cases, variations in over-all time being a result of variations in the duration of the induction period. Further, the dicyclic naphthenes are more reactive than the monocyclic derivatives. The tricyclics are the most reactive of all—for example, when perhydroanthracene is compared with Decalin. The reason is not clear but does not appear to be associated with ring fusion and production of tertiary carbon atoms, since Decalin and dicyclohexyl show great similarity. (Because of volatility cyclohexane cannot be included in this comparison.)

Addition of a paraffin side chain to the nucleus apparently increases reactivity to some degree, as seen when octadecyl Decalin is compared with Decalin or when diisobutylperhydroanthracene is compared with perhydroanthracene.

To afford a comparison with a five-carbon ring naphthene, *n*-amylcyclopentane was synthesized and studied. It behaved similarly to Decalin or cetane, and we may thus conclude that the cyclopentyl naphthenes relate to other saturated hydrocarbons in reactivity.

The similarity in type of curve of all saturated hydrocarbons leads us to conclude that, for practical purposes, we may consider the saturated compounds of a lubricating oil to possess similar properties and therefore to be a single class. The oxidation products of naphthenes are recorded in Table IV.



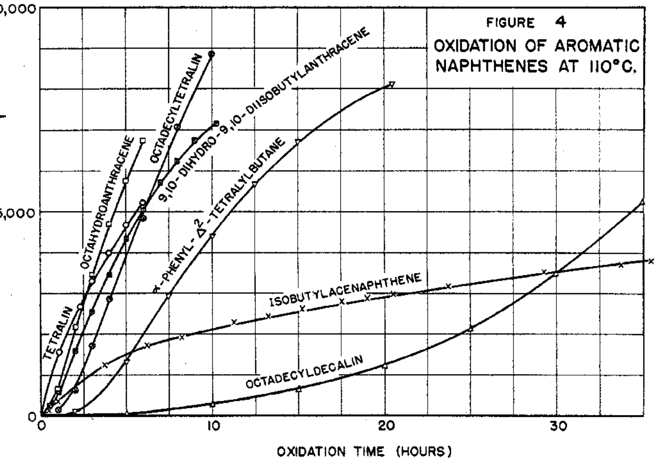


Table III. Products of Oxidation of Aliphatic Hydrocarbons at 110° C.

(All values expressed as percentage of total consumed oxygen)

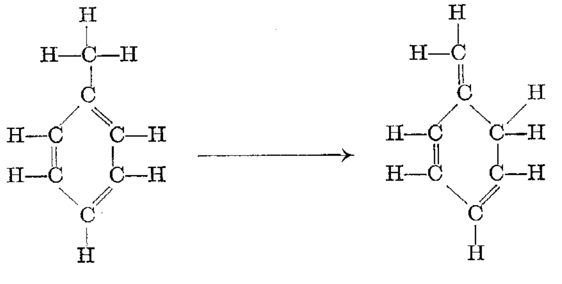
Hydrocarbon	Acid	Saponification Total	Saponification Combined	Peroxide	Alcohol	Carbonyl	Water	CO_2	Volatile Acids	Total
n-Decane (C_{10})	12.5	29.9	17.4	10.3	0	46	27	5.8	..	119
Cetane (C_{16})	27	49	22	1.6	3	..	56	3.5	..	113
Hydropolyisobutylene (C_{50})	3.3	13.0	9.7	0.3	2.7	..	48.7	4.7	6.0	75
Average paraffins	14.3	30.6	16.3	4.1	1.9	46	43.9	4.7	..	..
Tetraisobutylene (C_{16})	9.1	23.2	14.1	1.4	4.5	..	41	7.6	0.8	79
Polyisobutylene (C_{50})	4.1	22.8	18.7	0.7	7.9	..	35.4	1.3	6.3	74

Comparison with Table III indicates that production of acidic and saponifiable materials is approximately the same for naphthenic and paraffinic hydrocarbons. Peroxide concentration is definitely higher in the case of the cycloparaffins. This probably means that the ring forms the more stable intermediates. In the case of Decalin, a solid high-melting peroxide was actually isolated. Also, the production of carbonyl compounds in these derivatives is high. Less water is formed in the cycloparaffins than in the chain paraffins, which probably means that less complete oxidation has occurred; i. e., the ring system stabilizes the oxidation intermediates. The dicyclics appear to be more effective than the monocyclics in stabilizing these intermediates. Thus in Table II there is a definite decrease in peroxide concentration and increase in water production in going from Decalin to cyclohexane derivatives.

Oxidation of Aromatic-Naphthenic-Paraffinic Hydrocarbons

The hydrocarbons included in this group contain portions of three important types of hydrocarbons, and it might be argued that they could be classified under either of the three groups. The aromatic-naphthenic nucleus, however, is a group which apparently leads to a distinctly different type of chemical reactivity and thus to classification of this group as the aromatic naphthenes. Thus Tetralin, the simplest member of this group, is also the most reactive of the hydrocarbons studied. Further, it is characterized by an autoretardant type of oxidation rate which is to be contrasted with the autocatalytic type of the saturated hydrocarbons. This reactivity and general form of the rate curve is typical of molecules containing an aromatic-naphthenic nucleus, regardless of substituents (Figure 4). In this group are included both bi- and tricyclic molecules. The one notable exception is tetraisobutylanthracene, which will be discussed later.

The increased reactivity of the aromatic-naphthenic hydrocarbons probably is a result of the activation of the hydrogen atoms situated on the carbon atoms adjacent to the aromatic ring. It can be shown that there is a tendency for an aromatic ring to extend its conjugation into the side chain and thereby create a weak double bond, probably as a result of the increased mobility of the hydrogen atoms on the alpha carbon atom; it may be similar to the following mechanism:

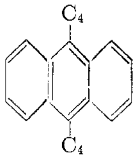


Thus, only a double bond in a position beta to the substituent group could enter into direct conjugation with that group. Since cleavage of aromatic rings is difficult, it is probable that oxidation of these substances occurs on the attached side chain, which has been rendered active by the aromatic ring in the manner shown. Further, the point of attack would probably be on the carbon atom alpha to the ring and not further along the chain. This view receives substantiation from the fact that benzaldehyde was frequently isolated or detected in the oxidation products of monoalkylbenzenes.

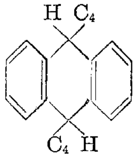
The one exception to the rule that aromatic-naphthenic hydrocarbons are reactive is 9,9,10,10-tetraisobutylanthracene. This hydrocarbon was scarcely attacked even at 180° C.:

Hours of Oxidation at 180° C.	Total Oxygen Absorbed (N. T. P.), Ml./Mole
21	455
69	714
111	746

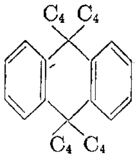
The reason for this is most readily seen by reference to the following structures:



I



II



III

As will be discussed later, the substituted anthracene, I, is quite stable, in keeping with other condensed ring aromatics. The aromatic naphthene II is very reactive (Figure 4), while aromatic naphthene III is exceedingly stable, even more so than I. These results all agree with the explanation given above since there is no hydrogen atom attached to the carbon atom alpha to either aromatic ring in form III; and it is the mobility of this hydrogen which can lead to conjugation into the side chain, with accompanying reactivity. In the case of anthracene derivative I, the isobutyl group contains the alpha carbon atom and a hydrogen atom. These concepts will be further substantiated in later examples.

The course of the oxidation of aromatic naphthenes is shown by Table V. Comparison with paraffins and naphthenes shows that acids, water, and carbon dioxide are produced in smaller amounts than in the other types of hydrocarbons. Saponification values are quite constant while peroxide values are about the same as for the paraffins. The low acid and water values suggest that, as in the case of the naphthenes, stable intermediate oxidation products are produced.

Oxidation of Aromatic Hydrocarbons

Oxidation of Benzene Derivatives. Since the benzene ring is capable of activating a substituent group, one would

TABLE IV. PRODUCTS OF THE OXIDATION OF NAPHTHENE HYDROCARBONS AT 110° C.

(All values expressed as percentage of total consumed oxygen)

Hydrocarbon	Acid	Saponification Total	Saponification Combined	Peroxide	Alcohol	Carbonyl	Water	CO_2	Volatile Acids	Total
Decalin	12.8	24.2	11.4	14.9	8.9	..	13.3	..	..	..
Dicyclohexyl	18.3	32.0	13.7	32.4	5.4	44	24.4	1.5	0.3	140
Octadecyldecalin	8.7	26.0	17.3	17.4	13.2	49	16.5	1.6	0.6	124
Octadecylcyclohexane	14.9	30.9	16.0	4.2	1.4	47.2	28.2	2.2	0.7	115
Hexadecylcyclohexane	17.1	30.8	13.7	8.2	3.8	44.5	21.1	3.2	0.7	112
Perhydroanthracene	4.5	18.0	13.5	19.8	22.6	62.0	10.2	0.7	..	133
Diisobutylperhydroanthracene	10.2	49.0	38.8	6.8	1.3	78.8	14.2	3.4	..	153
n-Amylcyclopentane	2.8	14.6	11.8	4.0	14.7	34.6	47.6	13.8	..	129
Average naphthenes	11.2	28.2	17.0	13.5	8.9	51.4	21.9	3.8	0.6	
Average paraffins	14.3	30.6	16.3	4.1	1.9	46.0	43.9	4.7	..	

TABLE V. PRODUCTS OF THE OXIDATION OF AROMATIC-NAPHTHENIC HYDROCARBONS AT 110° C.

(All values expressed as percentage of total consumed oxygen)

Hydrocarbon	Acid	Saponification Total	Saponification Combined	Peroxide	Alcohol	Carbonyl	Water	CO_2	Volatile Acids	Total
Tetralin	7.9	29.4	21.5	5.6	3.0	..	7.8	2.8	..	...
Octadecyl Tetralin	4.1	19.0	14.9	7.1	7.5	33.7	5.8	0.4	..	73.5
α-Phenyl-Δ^2-tetralylbutane	8.3	39.0	30.7	3.5	8.1	43.3	13.6	0.4	0.4	108.3
Octahydroanthracene	2.9	17.3	14.4	4.5	19.4	30.6	5.1	0.25	0.1	77.3
9,10-Dihydro-9,10-diisobutylanthracene	4.5	19.2	14.7	3.8	6.8	12.9	51.0	2.1	0.6	96.4
5-Isobutylacenaphthene	8.7	51.8	42.1	1.5	6.1	15.6	..	..	..	
Av. aromatic-naphthenic	6.1	29.3	23.1	4.3	8.5	27.2	16.7	1.2	0.4	
Av. naphthenic	11.2	28.2	17.0	13.5	8.9	51.4	21.9	3.8	0.6	
Av. paraffinic	14.3	30.6	16.3	4.1	1.9	46.0	43.9	4.7	..	

expect the substituted benzene hydrocarbons to be comparable to the aromatic naphthenes in reactivity, although they are frequently less reactive since there is often but one point of activation. A study of several representatives of this type confirms that a benzene ring attached to a long paraffin side chain leads to a considerable increase in reactivity as compared with the side chain alone. While benzene itself was not studied, it is known to be very resistant to oxidation; the frequent isolation of benzaldehyde from the oxidation products indicates that the ring is not attacked.

A striking characteristic of some benzene hydrocarbons compared with the types previously discussed is the ability of self-inhibition or autoretardation. This apparently occurs to some extent in the case of the aromatic-naphthenic hydrocarbons since the reaction rates are of the autoretardant types, but it is pronounced in the case of some benzene aromatics, particularly diphenylmethane. In all cases retardation occurs only after considerable oxidation has taken place and is undoubtedly associated with phenolic type inhibitors formed as a result of the oxidation. Obviously self-inhibition of this type cannot occur with a saturated hydrocarbon; hence the reactions are all of the autocatalytic type. The phenomenon creates a difficulty in interpreting oxidation characteristics of a given hydrocarbon since the rate of the reaction may depend more upon the efficiency and rate of formation of an inhibitor than upon the intrinsic stability of the hydrocarbon itself. To avoid confusion of this sort, the initial reaction rate is used whenever possible as an indication of stability.

Effect of Chain Length. Because of restrictions imposed by volatility of the hydrocarbons studied, the shortest side chain attached to a single benzene ring on which we have information is *n*-amylbenzene; diphenylmethane and fluorene afford a comparison with a short side chain to which two rings are attached. While fluorene might be considered an aromatic-naphthenic type, its oxidation characteristics are more like those of the benzene aromatics. Figure 5 indicates that all three hydrocarbons are closely comparable in initial reactivity. Diphenylmethane shows an exceedingly sharp break in its oxidation rate; then the reaction practically stops. Considerable benzaldehyde was formed, and a small amount of an unidentified inhibitor was isolated from the reaction products as a distillation residue.

When chain length is increased to 16 or 18 carbon atoms, reactivity is increased considerably. Since the postulated mechanism involves reactivity only at the alpha carbon atom, it should be independent of chain length. The explanation of increased activity must be that the long side chain can break into more reactive fragments than a short chain, each of which will be a new center of attack and will in effect create a greater concentration of reactive molecules.

Effect of Number of Side Chains. One would expect an increase in reactivity when the number of reactive centers is increased by increasing the number of substituent side chains. In Figure 5 this would seem to be the case, since hexaethylbenzene is somewhat more reactive than the monoamyl derivatives. Compared with a 16-carbon monoderivative it is less reactive, however; thus chain length may be more important than the number of chains. The effect of number of side chains is shown more clearly in connection with the naphthalene derivatives discussed in the following section.

Effect of Type of Side Chains. In discussing the activation of side chains by aromatic rings, it was pointed out that the alpha carbon atom must possess a mobile hydrogen atom if this activation is to occur. One would thus predict that a tertiary carbon in this position would be quite nonreactive.

The curve for *tert*-amylbenzene in Figure 5 shows this to be the case. Secondary side chains are apparently intermediate between the normal and tertiary chain. It would thus appear that the only important increase in stability would occur in the case of the tertiary substituent. This conclusion was also reached by Stephens and Rodata in their studies of autoxidation. They, however, indicated complete failure of *tert*-butylbenzene to react. The oxidation products of alkylated benzenes are described in Table VI.

Table VI shows that there is a wide variation among the different members of this series. This would be expected since an alkyl benzene such as octadecylbenzene is in reality about 75 per cent paraffinic, while one such as diphenylmethane is 92 per cent aromatic. Thus there is little in

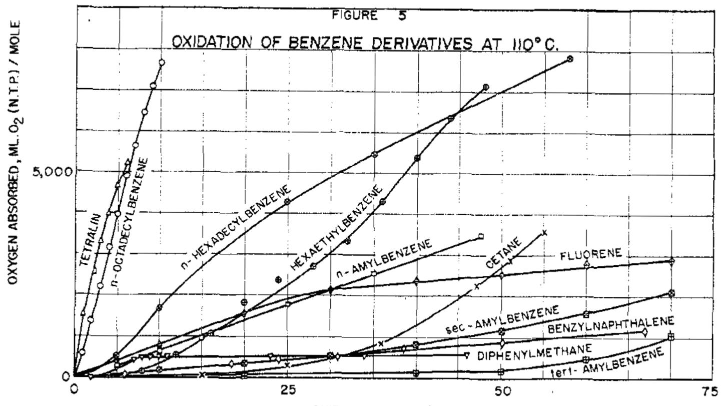


FIGURE 5
OXIDATION OF BENZENE DERIVATIVES AT 110° C.

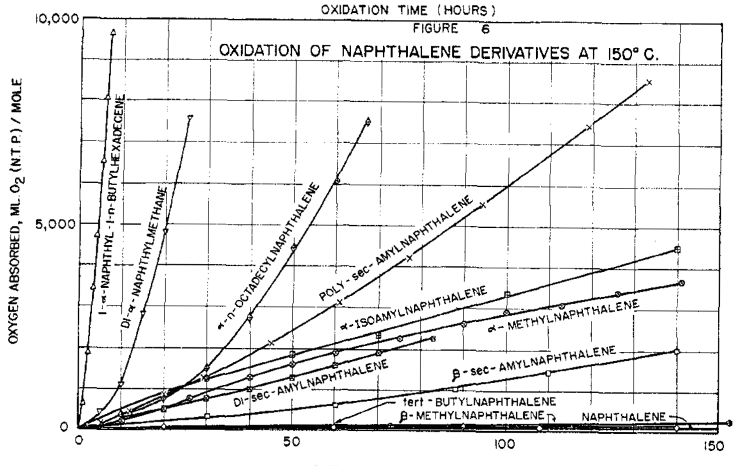


FIGURE 6
OXIDATION OF NAPHTHALENE DERIVATIVES AT 150° C.

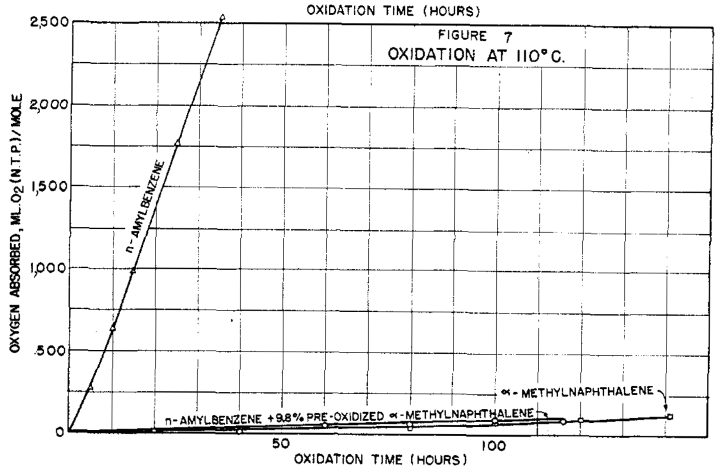


FIGURE 7
OXIDATION AT 110° C.

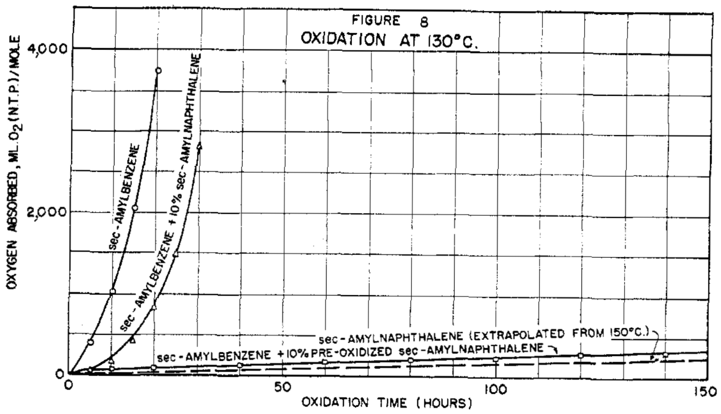


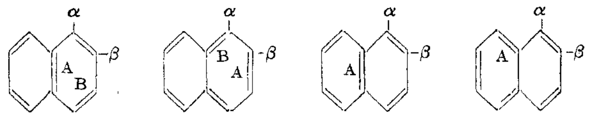
FIGURE 8
OXIDATION AT 130° C.

general to characterize an alkyl benzene. There does appear to be a trend toward lower carbonyl values as aromaticity is increased. Saponification values are quite close to those of other hydrocarbon types. Production of acids becomes similar to that of long paraffins as the chain length is increased; this suggests that the oxidation type is chiefly that of the paraffin side chain. With the exception of *tert*-amylbenzene, peroxides apparently depend upon chain length, being higher for increasing chain length. Benzaldehyde was isolated as the principal oxidation product of both diphenylmethane and octadecylbenzene. This suggests that the point of attack by oxygen is the carbon atom alpha to the ring. This conception receives substantiation from the work of Stephens and Rodata (*4*), who showed that the oxidation of substituted benzene derivatives produced aldehydes if the alpha side-chain carbon atom was primary, and ketones if it was secondary. If all the hydrogen atoms were substituted by alkyl groups, no oxidation occurred. Our results are not in complete agreement with theirs since from diphenylmethane they obtained benzophenone while we obtained benzaldehyde.

OXIDATION OF ALKYLATED NAPHTHALENES. Most of our work on alkylated aromatics was concerned with a study of naphthalene and its derivatives. The results are given in Figure 6. The naphthalene hydrocarbons show a markedly smaller reactivity than do hydrocarbons of other types. In consideration of the relative reaction rates and temperatures, as shown in Figure 6 in comparison with earlier figures, the naphthalenes are of the order of one thirtieth as reactive as paraffins, cycloparaffins, benzene derivatives, etc.

Effect of Position of Substituent on Nucleus. A comparison of α- and β-methylnaphthalene (Figure 6) indicates that substituents in the alpha position are more reactive than those in the beta position. This observed difference is in sharp disagreement with the work of Chernozhukov and Krein (*2*), who arrived at the opposite conclusion from a study of oxidation in a bomb under high temperature and pressure. The Russian authors argue that the alpha position is normally the vulnerable one and that substitution of a methyl group in this position does not increase the number of vulnerable points. On the other hand, substituting a methyl group in the beta position increases the possible points of attack and thus the reactivity. This view does not appear valid since in their own experiments they show that 1,6-dimethylnaphthalene is more reactive than either the α- or β-monomethylnaphthalene.

This difference in reactivity is readily explained by the concepts used in explaining the activating influence of the benzene ring. Thus when the possible resonating forms for substituted naphthalene hydrocarbons are written, it is seen that the alpha position is activated by both rings (by direct conjugation with the double bond marked A) while the beta position can only be activated by one ring (by conjugation with the bond marked B):



Thus the alpha position should be considerably more reactive than the beta position, as was found to be the case. This difference in reactivity can be demonstrated by other means. Thus α-naphthylamine is more easily oxidized than β-naphthylamine; α-naphthoic acid is more highly dissociated than β-naphthoic acid.

Effect of Size, Number, and Type of Side Chain. The general conclusions drawn regarding the effect of these various factors on benzene derivatives is confirmed with the naphthalene hydrocarbons, in some case even more clearly with the latter. Thus the methylnaphthalenes are more reactive than naphthalene itself, which confirms the fact that oxidation involves the side chain rather than ring cleavage.

The series of amylnaphthalenes shows a progressive and proportionate increase in reactivity with increased number of chains (the polyamylnaphthalene is predominantly a trisubstituted naphthalene). Eighteen carbon atoms in one long side chain appear to lead to greater activity than 15 in three short chains, confirming that chain length is more important than number of chains. As shown by the very reactive hexadecene derivative, a double bond in the side chain adjacent to the nucleus leads to an extremely accelerated reaction rate. The extreme stability of the *tert*-butylnaphthalene (*tert*-amyl and *tert*-octyl derivatives are similar) again confirms that the absence of a hydrogen atom from the alpha carbon atom greatly diminishes reactivity.

Reasons for Stability of Naphthalene Hydrocarbons. It is evident that naphthalene derivatives as a group are more stable than the analogous benzene derivatives. This result is contradictory to predictions based on the activating influence of the parent nuclei (on alpha substituents in the case of naphthalene), as well as on the reactivity of the nuclei themselves. Thus naphthalene is more reactive than benzene as evidenced by greater ease of substitution reactions (sulfonation, nitration) and oxidation (vapor phase).

The best of our evidence indicates that the naphthalene derivatives oxidize to efficient oxidation inhibitors while benzene derivatives do not. When one considers that oxidation apparently involves the alpha carbon atom of a saturated side chain, it becomes clear why all naphthalene derivatives might produce upon oxidation a naphthol inhibitor, while all benzene derivatives might produce a phenolic inhibitor. If, then, there is a pronounced difference in efficiency of the two types of inhibitors, a difference in reactivity of the two groups might be explained. Thus activation by aromatic rings of the type previously discussed may become only a secondary factor in determining the actual rate of oxidation.

Figure 7 gives data for the oxidation of *n*-amylbenzene plus oxidized α-methylnaphthalene. The observed reaction rate of the mixture falls exactly on that for the α-methylnaphthalene itself, in contrast with the rate for *n*-amylbenzene plus unoxidized α-methylnaphthalene. As shown in Figure 8, the reaction rate for *sec*-amylbenzene containing oxidized β-*sec*-amylnaphthalene is close to the extrapolated rate for *sec*-amylnaphthalene itself, again in contrast with the rate for the corresponding mixture with the unoxidized naphthalene derivative. The fact that the unoxidized naphthalene derivative has such a slight effect shows the importance of the preformation of the inhibitor. Otherwise direct oxidation of the benzene derivative predominates. It is thus apparent that reactions of mixtures of this type are competitive, the observed rate depending upon many factors.

TABLE VI. PRODUCTS OF THE OXIDATION OF ALKYL BENZENES AT 110° C.

(All values expressed as percentage of total consumed oxygen)

Hydrocarbons	Acid	Saponification Total	Saponification Esters, etc.	Peroxide	Alcohol	Carbonyl	Water	CO_2	Volatile Acids	Total
Octadecylbenzene	16.0	30.1	14.1	11.6	6.3	33.1	11.5	10.9	Trace	103.5
Hexadecylbenzene	18.8	27.4	8.6	10.7	6.3	37.6	10.9	14.3	Trace	107.2
Hexaethylbenzene	8.5	19.3	10.8	0.2	1.9	9.1	..	..	5.1	...
n-Amylbenzene	1.2	8.9	7.7	4.5	1.4	20.5	17.5	0	Trace	52.8
tert-Amylbenzene	3.2	27.7	24.5	12.1	..	90.1	..	..	Trace	...
Fluorene	9.4	20.0	10.6	0.8	0.9	27.5	32.9	0.7	None	82.8
Diphenylmethane	Oxidation products were distd. and produced benzaldehyde + residual inhibitor									
Av. benzene derivatives	9.5	22.2	12.7	6.7	3.3	36.3	18.2	6.5	Trace	
Av. paraffinic	14.3	30.6	16.3	4.1	1.9	46.0	43.9	4.7	..	
Av. naphthenic	11.2	28.2	17.0	13.5	8.9	51.4	21.9	3.8	0.6	
Av. aromatic-naphthenic	6.1	29.3	23.1	4.3	8.5	27.2	16.7	1.2	0.4	

TABLE VII. PRODUCTS OF THE OXIDATION OF NAPHTHALENE HYDROCARBONS AT 150° C.

(All values expressed as percentage of the total consumed oxygen)

Hydrocarbon	Free Acid	Saponification Total	Saponification Combined	Peroxide	Alcohol	Carbonyl	Water	CO_2	Volatile Acids	Total
Naphthalene	5.3	11.8	6.5	0	60.3	..	36.8	0	...	109
α-Methylnaphthalene	5.6	19.0	13.4	0.3	5.9	5.2	54.8	10.5	1.7	98
β-Methylnaphthalene	10.1	34.5	24.4	1.9	1.1	6.8	47.9	9.3	0	102
Isoamylnaphthalene	9.6	18.6	9.0	6.7	0	19.7	..	..	...	...
β-*sec*-Amylnaphthalene	4.9	23.6	18.7	0.4	2.9	7.9	79.2	1.9	0.6	116
Di-*sec*-amylnaphthalene	6.5	35.5	29.0	4.4	2.8	14.6	75.6	8.5	1.0	142
Poly-*sec*-amylnaphthalene	9.4	26.2	16.8	0.2	1.2	12.0	55.0	..	3.6	98
tert-Octylnaphthalene	3.1	15.0	11.9	0.6	19.8	0	58.0	16.9	0	110
α-*n*-Octadecylnaphthalene	9.3	28.6	19.3	0.5	5.1	13.8	53.0	19.8	1.2	122
1-Naphthyl-1-*n*-butylhexadecene	9.2	20.9	11.7	0.6	7.0	18.3	30.0	10.2	4.2	91
Di-α-naphthylmethane	8.9	24.1	15.1	0	4.9	7.1	22.7	1.3	0.2	60
α-Benzylnaphthalene	1.0	19.0	18.0	..	2.0	0	..	0	...	...
Av. naphthalenes	6.9	22.2	16.3	1.4	9.4	9.6	51.3	7.8	1.6	
Av. benzene derivatives	9.5	22.2	12.7	6.7	3.3	36.3	18.2	6.5	Trace	
Av. aromatic-naphthenic	6.1	29.3	23.1	4.3	8.5	27.2	16.7	1.2	0.4	
Av. naphthenic	11.2	28.2	17.0	13.5	8.9	51.4	21.9	3.8	0.6	
Av. paraffinic	14.3	30.6	16.3	4.1	1.9	46.0	43.9	4.7	...	

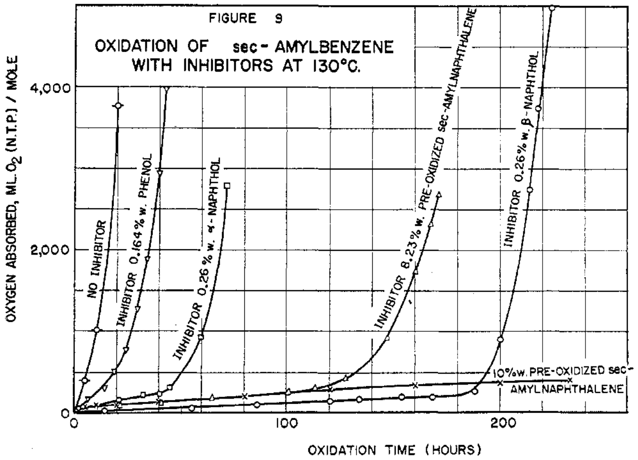


FIGURE 9
OXIDATION OF sec-AMYLBENZENE WITH INHIBITORS AT 130°C.

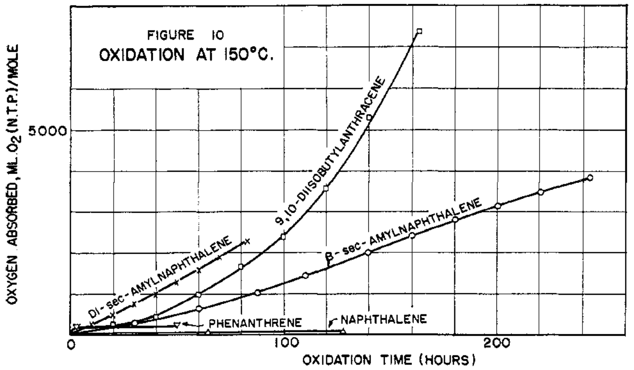


FIGURE 10
OXIDATION AT 150°C.

Additional confirmation for the proposed explanation was obtained by oxidizing *sec*-amylbenzene containing various naphthols and phenols, as shown in Figure 9. In these experiments the pure inhibitors were added in a concentration equivalent to at least three times that of the naphthols present in the mixture containing 10 per cent of oxidized β-*sec*-amylnaphthalene described above, which had absorbed 3500 ml. of oxygen (N. T. P.) per 100 grams; 3 per cent of the oxygen had been consumed in forming alcohols. As shown in Figure 9, this amount of β-naphthol is midway between 8 and 10 per cent of the oxidized amylnaphthalene in effectiveness. Equivalent molar concentrations of phenol and α-naphthol are much less effective. The spread between α- and β-naphthol is greater than would have been predicted on the basis of the relative stabilities of the hydrocarbons. However, the order of effectiveness with phenol and the two naphthols is the same as the order of stability of the corresponding alkyl aromatics. These experiments thus add considerable weight to the explanation of stability in terms of inhibitor formation.

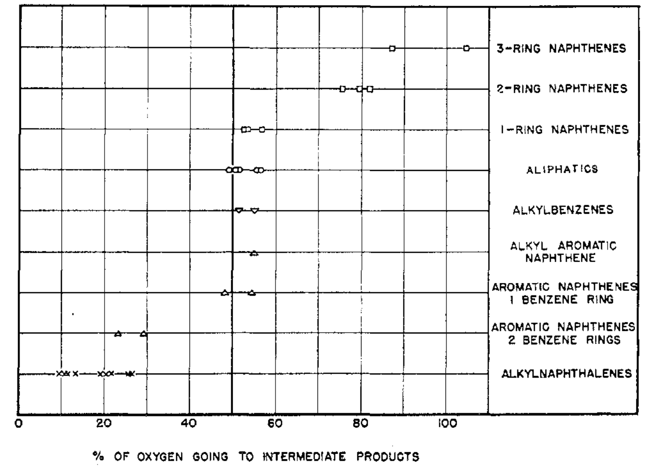


Figure 11. Relation between Structure and Amount of Oxygen Going to Intermediate Products

As the data in Table VII show, it is difficult to characterize the naphthalene aromatics as a group since a wide range is involved where the molecule changes from entirely aromatic to one third aromatic. Nevertheless, certain generalities are evident from comparisons with Tables III to VI. Acid values are lower than for any group except the aromatic naphthenes. Total saponification values again remain surprisingly constant. Peroxide values are definitely low. This may be accounted for by the higher oxidation temperatures which would destroy the thermally unstable peroxides. Alcohol production is high, especially in the case of naphthalene itself. These alcohols are probably naphthols. Production of aldehydes and ketones is decreased. On the other hand, production of water and carbon dioxide is high; this implies that the higher reaction temperature has led to more complete oxidation (i. e., oxygenated intermediates are less stable). Little significance can be given to the increase in

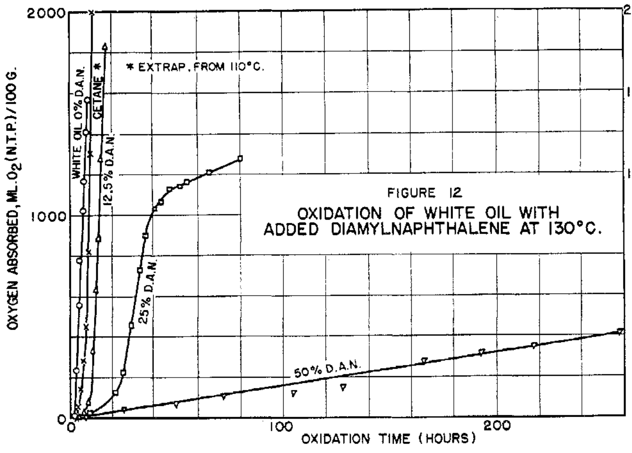


FIGURE 12
OXIDATION OF WHITE OIL WITH ADDED DIAMYLNAPHTHALENE AT 130°C.

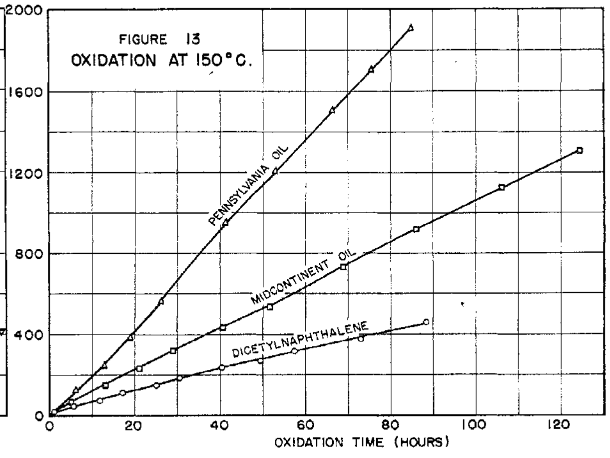


FIGURE 13
OXIDATION AT 150°C.

TABLE VIII. PRODUCTS OF THE OXIDATION OF POLYNUCLEAR AROMATICS AT 150° C.

(All values expressed as percentage of total consumed oxygen)

Hydrocarbon	Free Acid	Saponification Total	Saponification Combined	Peroxide	Alcohol	Carbonyl	Water	CO_2	Volatile Acids	Total
Diisobutylanthracene	4.1	25.7	21.6	0	2.5	10.3	48.3	4.3	0.7	96
β-*sec*-amylnaphthalene	4.9	23.6	18.7	0.4	2.9	7.9	79	1.9	0.6	121
Di-*sec*-amylnaphthalene	6.5	35.4	28.9	4.4	2.7	14.6	85	8.5	..	157
Phenanthrane	1.5	3.7	2.2	..	..	0	71	8.2	..	83
Naphthalene	5.3	11.8	6.5	0	60.3	..	36.7	0	..	103

production of volatile acids since the higher oxidation temperature would lead to a more rapid distillation of these materials.

Additional conclusions are possible from a study of Table VII. Thus, with naphthalenes, increasing the number of side-chain carbon atoms appears to increase acid production up to about 9 per cent of the oxygen consumed, which value is still considerably below that for the corresponding benzene derivatives. In spite of the great difference in reactivity, the one unsaturated naphthalene studied is similar to a corresponding saturated chain hydrocarbon in its course of oxidation.

Oxidation of Anthracene Derivatives and Phenanthrene

Our experience with alkylated derivatives of anthracene is rather limited, partly because the high melting points render it impossible to study them at reasonable temperatures. Figure 10 gives data comparing 9,10-diisobutylanthracene with di-*sec*-amylnaphthalene and mono-*sec*-amylnaphthalene, and the two dialkyl hydrocarbons are shown to be of comparable activity toward oxygen. From this it would appear that the naphthalene and anthracene nuclei have a similar effect on the oxidation of their alkylated derivatives.

The course of the oxidation of 9,10-diisobutylanthracene is shown in Table VIII. It is very nearly an average of di- and monoisoamylnaphthalene; the comparison is sufficiently good to warrant similar conclusions in both cases. Also shown in Figure 10 are the data for phenanthrene and naphthalene, which are closely similar. As Table VIII shows, the oxidation of phenanthrene differs somewhat from that of naphthalene, but the actual degree of oxidation involved is so low that the experimental error becomes appreciable.

The results on anthracene and phenanthrene derivatives, while meager, indicate that they resemble the naphthalene series in oxidation characteristics.

Effect of Structure on Type of Oxidation Products

As pointed out earlier, wide variation in amount of each type of oxidation product formed might be expected among the members of any one series of hydrocarbons, since they may range from 100 per cent aromatic to mostly paraffinic; however, an interesting relation has been found between structure and amount of oxygen absorbed going to the intermediate products—peroxides, alcohols, and carbonyls. This relation is shown in Figure 11. In the case of noncyclic or monocyclic hydrocarbons (with both saturated and unsaturated ring structures), approximately half the oxygen absorbed goes to these products. Hydrocarbons containing two or more saturated ring structures form more of these products, while hydrocarbons with two unsaturated ring structures (either two benzene rings or one naphthalene ring system) form less. In the case of the alkyl naphthalenes, the latter effect might be attributed to the higher oxidation temperature, but it is interesting to note that both fluorene and 9,10-dihydro-9,10-diisobutylanthracene, which were oxidized at 110° C., also fall in this group.

If the final oxidation products (i. e., acids, saponifiables, water, and carbon dioxide) had been used instead of the intermediate products, much the same distribution of oxygen would have been shown except in reverse order.

Oxidation Stability of Lubricating Oils

The results of this study have led us to the conclusions that the rate of oxidation of an oil free of aromatics, such as a medicinal oil, should be very high and, at the same time, be of the autocatalytic type. Indeed, this is found to be the case as shown by the data of Figure 12, where a medicinal oil is compared with cetane. The stability of well-refined lubricating oils must then be a result either of content of aromatics or of content of natural inhibitors. To examine this, diamylnaphthalene was added to white oil; it developed that rather large quantities were required to produce stability, which indicated that a small percentage of stable aromatic constituents could not stabilize the reactive saturated constituents.

To consider the alternative possibility that lubricating oils may consist largely of polyalkyl-substituted aromatics, an oil having physical properties almost identical with a Pennsylvania or extracted mid-continent mineral oil was synthesized by condensing cetene with naphthalene. The comparison of properties follows:

Property	Dicetylnaphthalene	Penna. Oil	Extd. Mid-continent Oil
Viscosity, Saybolt Universal sec.			
100° F.	650.5	650.5	667.6
210° F.	74.7	72.76	71.12
Viscosity index	106	101	93
Molecular weight	576	550	550
Specific dispersion	150	117	106

Figure 13 shows that the alkylated naphthalene is equal to either oil in oxidation stability. From the value of the specific dispersion it is evident, however, that the alkylated naphthalene is much more aromatic than either oil. It would thus appear that oxidation stability of the natural oil cannot be explained simply on the basis of aromaticity, and therefore that naturally contained inhibitors and not the basic hydrocarbon constituents determine stability of a lubricating oil.

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