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Chemistry of Fuel Deposits and Sediments and Their Precursors

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1. SUMMARY

The objective of the work reported here was to determine how and why deposits are formed on hot engine parts from jet turbine fuels. Deposit formation is associated with oxidation of the fuel. Previous work on oxidations of pure hydrocarbons and fuels at 130°C was continued with emphasis on jet Fuel B (of intermediate stability), tetralin, 2-ethylnaphthalene, and Fuel D (a synthetic fuel containing 10 mole% tetralin in dodecane). Oxidations of hydrocarbons and fuels in the presence of $t\text{-Bu}_2\text{O}_2$ were begun at 100°C. Fuel B reacted very slowly initially, but the oxidation was strongly autocatalytic. Repeated treatments with acid alumina had little effect on this behavior.

Data on rates of oxidation and gum formation (mostly soluble) are correlated. Most of the pure hydrocarbons oxidize faster than most of the fuels. To a first approximation, the materials that oxidize fastest also produce gum fastest, but the pure hydrocarbons require the most oxygen to produce a milligram of gum and the fuels give the most gum for the oxygen absorbed. 2-Ethylnaphthalene, purified at NASA-LeRC by fractional distillation in vacuum, oxidized faster and produced gum faster than any other materials tested at SRI except indene and N-methylpyrrole, which copolymerize with oxygen to give alternating polyperoxides. High-resolution field ionization mass spectrometry shows that the most stable Fuel A contains the least alkylnaphthalenes and other condensed aromatic hydrocarbons and that unstable Fuel C contains the most of these compounds.

Results with ~ 0.04 M $t\text{-Bu}_2\text{O}_2$ at 100°C are qualitatively similar to those without initiator at 130°C, but some relative rates of oxidation vary significantly. These differences are attributed to different abilities of hydrocarbons to initiate and continue their own oxidations. However, the ratios of the rates of oxidation and gum formation for a single fuel are little affected by rate of oxidation or

temperature, indicating that gum formation is intimately associated with the oxidation process.

Oxidations of dodecane, tetralin, and Fuels B and C are autocatalytic. Oxidations of ethylnaphthalene and Fuel A are self-retarding, but the ratios of rates of oxidation and gum formation appear to be nearly constant with time for each substrate. Efforts to determine the dependence of rates of oxidation and gum formation on the concentration of $t\text{-Bu}_2\text{O}_2$ suggest that the autocatalytic oxidations are half-order in peroxide, and that the oxidations of ethylnaphthalene and Fuel A are first order on peroxide, as expected for a self-retarding oxidation. Most of the available rates of gum formation are first order in peroxide, indicating that they are closely related to the rate of chain termination in oxidation.

Hydroperoxide yields were measured and expressed as the percentage of the oxygen absorbed that could be found as hydroperoxide. Yields range from >90% in 1- to 3-h oxidations of the reactive 2-ethylnaphthalene to ~ 0 in a 140-h oxidation of stable Fuel A.

2. INTRODUCTION

This report is the third^{1,2} in a continuing study of the mechanism of formation of deposits on hot engine parts from jet turbine fuels. We assume that these hard deposits come mostly from soluble deposit precursors (gum) formed on previous storage. The objective of the work reported here was to determine how and why these precursors are formed and thus how deposit formation can be minimized, but the important conversion of soluble gum to hard deposits is not considered here. Some data from a similar concurrent study of diesel fuels, supported by the U.S. Army Research Office,³ are included. Our approach was to oxidize various pure hydrocarbons, their mixtures, and fuels in air, either at 130°C without added initiator or at 100°C with added tert-butyl peroxide ($t\text{-Bu}_2\text{O}_2$); we then measured oxygen consumption by gas chromatography of the remaining air and the amounts of gum formed.

Although most other work on fuel stability has emphasized suspended and adherent solids formed on storage or heating, this project emphasizes total gum, the material remaining when a sample of ~ 4 mL of fuel is evaporated to dryness, brought to constant weight in a slow stream of nitrogen at 200°C, and weighed to micrograms. We have noted separation of deposits when it occurred, but the amounts of deposit are small compared with the total gum, in which they are included. Further, appearance of deposits depends on the solubility of the oxidation and condensation products in the fuels, which range from n-alkanes to aromatic hydrocarbons. The soluble and insoluble gums have similar elemental compositions and molecular weights, and the deposits that separate from hydrocarbon fuels are readily soluble in acetone and pyridine. Even the gums brought to constant weight at 200°C can be easily removed from the aluminum dish by pyridine at room temperature.

The principal advances in this report are comparison of rates of oxidation (R_o , in μmol of oxygen absorbed per g fuel/h), gum formation

(R_g , in mg gum/100 g fuel/h), and their ratios (R_o/R_g as 100 $\mu\text{mol O}_2/\text{mg}$ gum), at each temperature. These ratios show the close association of gum formation with oxidation and what kinds of hydrocarbons produce the least and the most gum for the oxygen absorbed.

3. FUELS

3.1. Origin

All fuels and hydrocarbons were distilled at reduced pressure before use; the forerun and tails were rejected. Fuels A, B, and C were supplied by NASA-LeRC. Fuel A was a stable jet turbine fuel, b.p.₅ 48-90°C. Fuel B was a jet turbine fuel of intermediate stability, b.p.₄ 45-90°C. Fuel C was a No. 2 home heating oil, taken as representative of an unstable fuel. It was dark brown, with sediment, as received. After distillation, b.p.₁₇ 54-203°C, it was pale yellow.

Dodecane (DOD) was 99% pure grade from Phillips Chemical Co. Tetralin (TET) was 99% pure grade from Aldrich Chemical Co. 2-Ethyl-naphthalene (EtN), 99+%, and 2-methylnaphthalene (MeN), 98%, were obtained from Aldrich Chemical Co. MeN froze at 31-29°C, recorded m.p. 34.6°C. EtN was found in the ARO Program³ to give exceptionally high yields of gum for the oxygen absorbed.

In March 1984, ~ 100 g of a different lot of Aldrich 2-ethyl-naphthalene was supplied by Dr. David Bittker of NASA-LeRC, who had fractionally distilled it in vacuum through a good column. This "new" material oxidized much faster than the "old" 2-ethylnaphthalene, and some of the "old" results are not reported here.

Some oxidations of Aldrich 2-methylnaphthalene were performed, but because it oxidized so slowly and because of the varied results with 2-ethylnaphthalene, many data are not reported here.

Fuel D was a mixture of 10 mol% TET and 90 mol% DOD, intended as a synthetic fuel, but both the components and the mixture gave poor yields of gum. Several hydrocarbons and fuels were passed through a column of Baker's Analyzed Aluminum Oxide, Acid, and eluted with hexane, which was then removed by warming at reduced pressure. Portions so treated are designated as "chromatographed."

3.2. High-Resolution Field Ionization Mass Spectrometer System (S.E. Buttrill, Jr., and G. A. St. John)

With the support of the Naval Research Laboratory, SRI has assembled a high-resolution field ionization mass spectrometer (FIMS) system as part of a project to develop a rapid, quantitative method for analyzing distillate fuels for the amounts of each component by both carbon number and hydrocarbon z-series. The system consists of a completely rebuilt MS-9 high-resolution mass spectrometer together with a Kratos DS-5C Data System. The MS-9 has been fitted with an SRI volcano-type field ionization source in place of the electron impact ionization source normally used in this instrument. Maximum mass resolution of the mass spectrometer operating in field ionization (FI) mode is about 25,000, much more than required to completely resolve all of the hydrocarbon doublets encountered in the analysis of distillate fuels.

The general formula for a hydrocarbon can be written as C_nH_{2n+z} , with z having different values for different types of hydrocarbons. For example, one of the most important pairs of compound classes having the same approximate molecular weights are the alkanes (C_nH_{2n+2}) and the naphthalenes (C_nH_{2n-12}), starting with nonane and naphthalene, both with molecular weights slightly >128 . The usefulness of a high-resolution FIMS for separating and identifying the molecular ions of these two compound classes can be seen in the following example. The saturated hydrocarbon decane, $C_{10}H_{22}$, has a principal molecular ion with an exact molecular weight of 142.1722, whereas methylnaphthalene, $C_{11}H_{10}$, has a molecular ion with an exact molecular weight of 142.0783, a difference of 0.0939 mass units. The molecular ions of these two compounds, both of which have a nominal molecular weight of 142, can be separated by a mass spectrometer with a resolving power of $142/0.0939 = 1500$. Compounds of higher molecular weight require a higher resolution to separate ion pairs of this type. Therefore, we normally operate the high-resolution FIMS at a resolving power of about 4000.

The mass spectrometer together with the data system allows us to measure accurately the molecular weights of all the hydrocarbon compounds present in a distillate fuel sample, and the data system calculates the molecular formulas. It is then possible to determine the relative amounts of the different hydrocarbon types present in a particular fuel sample.

The analysis procedure for a fuel sample is as follows. A 2- μ L aliquot of the fuel is placed in a sample holder together with 1- μ L of a mixture of marker compounds. The sample holder is attached to the glass batch inlet system of the mass spectrometer. The sample is frozen with liquid nitrogen and the air pumped away by the batch inlet vacuum system. The valve to the vacuum pump is closed, and the sample is heated to about 200°C. At this temperature, the sample is completely vaporized and expands to fill the 0.5-L glass batch inlet system. A small fraction of the vaporized sample is continuously leaked into the field ionization source. The composition of the vapor mixture in the ion source is therefore representative of the composition of the original fuel sample and does not change significantly during the analysis. The mass spectrometer scanned repeatedly over the mass range from above 400 down to 60 mass units. After about 10 spectra are collected, the data collection is stopped, and the sample is pumped away from the batch inlet. Normal procedure is to average 4 to 8 spectra to improve the accuracy of the relative peak intensities as well as the accuracy of the mass measurement. Plots of the averaged FIMS are produced by the data system together with printed listings of the relative intensities and elemental compositions of the various hydrocarbon molecular ions. These reports provide information about the relative amounts of different hydrocarbon types in the fuel sample. In the future, a computer program will be used to automatically correct peak intensities for measured field ionization efficiencies and to sort the individual peaks into a table of amounts of compounds by both carbon number and z number.

3.3. High Resolution FIMS of Fuels A, B, and C

Our NASA jet turbine Fuels A, B, and C were analyzed after vacuum distillation but without oxidation by high-resolution FIMS with the results indicated in Table 1. The components of each fuel are listed in order of decreasing peak intensities, accompanied by the molecular weights and the class of hydrocarbons to which they belong. P indicates a saturated aliphatic hydrocarbon; the U designation indicates the numbers of double bonds and rings in other hydrocarbons. Thus, U1 includes alkenes, cyclopentanes and cyclohexanes; U2 includes unsaturated cycloalkanes and bicyclic aliphatics; U4, alkylbenzenes; U5, indanes and tetralins; and U7 alkylnaphthalenes. U designations in parenthesis indicate minor fuel components. The data are summarized as follows.

In stable Fuel A, U1 is most plentiful (ranks 1, 2, 3, 5, 15) followed by U2 (4, 6, 12, 13, 14), U4 (7, 8, 9), and P (10, 11, 16). There were no alkylnaphthalenes (U7) among the 16 compounds ranked. In intermediate Fuel B, alkylbenzenes (U4) are most plentiful (ranks 1, 2, 3, 11, 14), followed by U1 (4, 7, 15, 16), U7 (5, 6), U2 (8, 13), P (9, 10, 18), and U5 (12, 17). Where the U7 and P have the same molecular weight (142 and 156), the U7 predominates. In unstable Fuel C, U7 compounds are most plentiful (ranks 1, 2, 3, 8, 16), then U4 (4, 5, 9, 11), U5 (6, 7, 10, 12), U8 (acenaphthenes, 14, 15), and a P (13). No U1 or U2 was seen.

Thus, the most stable fuel contains mostly alicyclics and almost no naphthalenes, and the least stable fuel contains large amounts of naphthalenes and very little alicyclics. Fuel B is in between. Section 4 shows that 2-ethylnaphthalene is a fast oxidizer and fast gum-former.

Table 1

COMPONENTS OF FUELS IN ORDER OF ABUNDANCE

Fuel A			Fuel B			Fuel C		
Class	Mol. Wt.	Intensi- sity	Class	Mol. Wt.	Intensi- sity	Class	Mol. Wt.	Intensi- sity
U1	168	1935	U4	134	3210	(P)U7 ^a	156	9246
U1	154	1904	U4	120	3009	(P)U7	170	5199
U1	84	1533	U4	148	2197	(P)U7	142	4763
U2	166	1477	U1	154	1963	U4	134	1860
U1	182	1456	U7	142	1944	U4	120	1750
U2	152	1385	U7	156	1790	U5	146	1669
U4	134	1345	U1	140	1735	U5	160	1289
U4	106	1264	U2	152	1630	(P)U7	184	1227
U4	120	1233	P	170	1625	U4	176	993
P	156	1189	P	156	1610	U5	132	906
P	170	1175	U4	106	1414	U4	106	841
U2	96	1128	U5	146	1328	U5	174	839
U2	180	1067	U2	166	1289	(U8)P	198	809
U2	82	1044	U4	162	1225	(U1)U8	154	802
U1	140	1034	(U8)U1 ^a	182	1167	(U8)U1	168	735
P	184	1008	U1	84	1060	(P)U7	128	731
			U5	160	999	U2	166	679
			P	142	963			

^aClasses in parentheses are minor components of mixtures.

4. NEW DATA ON OXIDATION AND GUM FORMATION AT 130°C

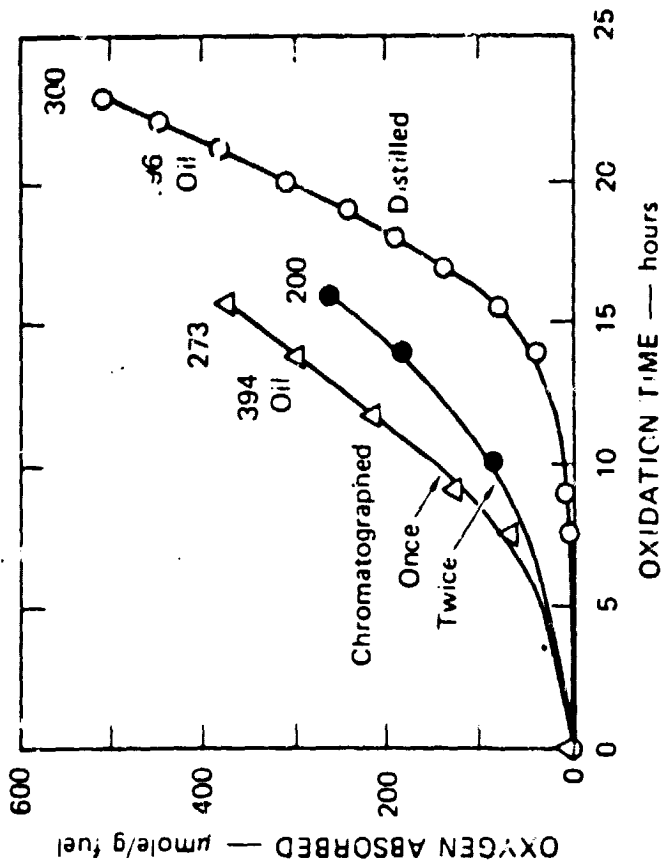
4.1. Single Hydrocarbons and Fuels

Most oxidations were performed with 10 mL of fuel in flasks of 100-120 mL capacity, filled with air at atmospheric pressure at ambient temperatures. Pressures were higher at 130°C, but the concentrations of oxygen were the same. The progress of the reaction was followed by withdrawing 70- μ L gas samples through a septum and analyzing them for O₂/N₂ ratio by gas chromatography at 50°C with a 30 mL/min helium flow rate on a 183 by 0.32 cm stainless steel column packed with 13X molecular sieve. Oxygen absorption is reported as μ mol oxygen absorbed/g fuel, and the rate, R_O is that quantity per hour. The amount of gum formed was determined by evaporating weighed samples of ~ 4 mL in 6 mL narrow-necked flasks almost to dryness in a stream of nitrogen in a small electrically heated furnace at 200°C, transferring the residue with ~ 3 portions of 0.4 mL of acetone to aluminum dishes ~ 15 mm in diameter and weighing about 50 mg, evaporating the acetone with gentle warming, and then bringing the dish and gum to constant weight in a gentle stream of nitrogen at 200°C. Typical weights of gum formed were 1 to 10 mg, weighed on a microbalance. Numbers at the ends of plots of the oxidation curves are the yield of gum (or oily precipitate in a few cases) found at those points in units of mg/100g fuel. The gum formation rate, R_g is the gum yield per hour.

In some oxidations, dark precipitates formed at points marked "ppt" in the figures.

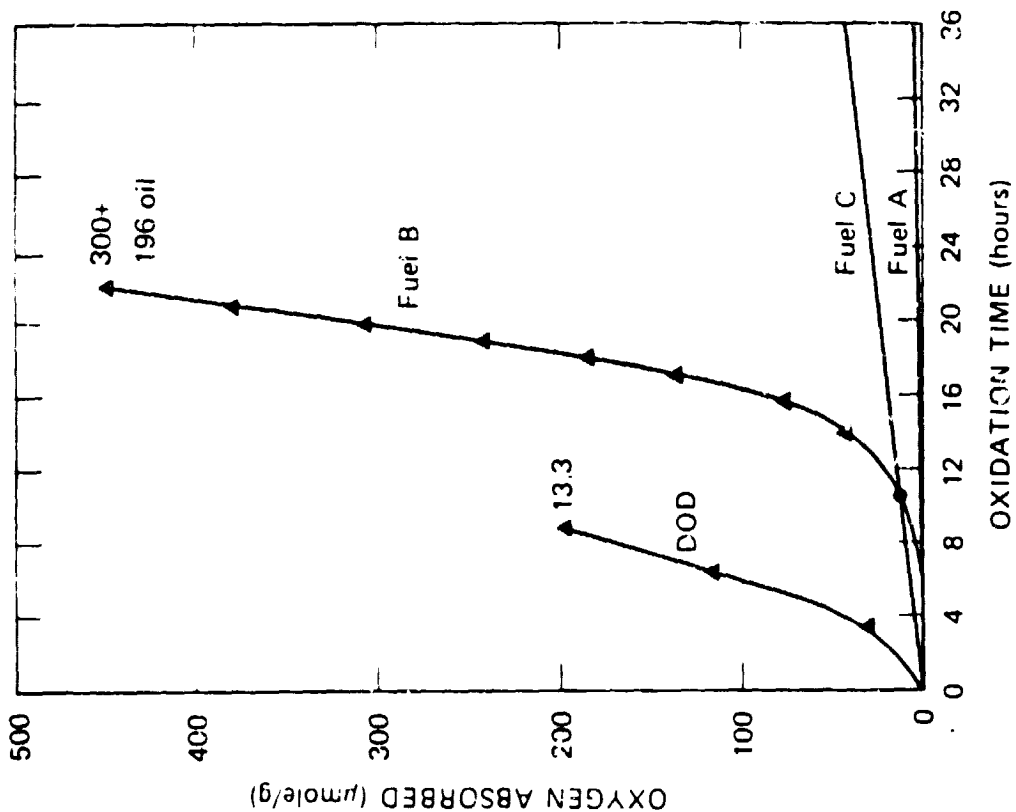
4.1.1. Fuel B

Figure 1 shows the oxidation of distilled Fuel B in air at 130°C with similar curves for Fuels A and C and DOD for comparison. There is an induction period with a sharp increase in rate after 16 hours of oxidation. This induction period makes Fuel B appear to be moderately stable. The final rate is close to that of neat n-dodecane, which has



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FIGURE 2 OXIDATION OF DISTILLED AND CHROMATOGRAPHED
FUEL B AT 130°C



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FIGURE 1 OXIDATION OF DISTILLED FUEL B IN AIR AT 130°C

about an average rate for our pure hydrocarbons. An oily precipitate formed (196 mg) and 299.6 mg gum/100 g fuel was also found after 23 hours. Only 2.77% of the absorbed oxygen was found as peroxide.

To determine if the induction period in oxidation of Fuel B might be due to an impurity, we chromatographed the fuel twice with the results shown in Figure 2. Either Fuel B has an inherent induction period or contaminant is hard to remove.

4.1.2. Tetralin

The oxidation of distilled and chromatographed TET at 130°C was performed as part of an investigation of Fuel D (10% TET/90% DOD) and other DOD/TET mixtures, and the details are described in Section 4.2. TET was one of the fastest oxidizing pure hydrocarbons that we have investigated but only average in rate of gum formation among those compounds. The oxidation products were analyzed by FIMS (not high resolution). The four major peaks corresponded to tetralin hydroperoxide and tetralol. The next products corresponded to two connected tetralin residues plus one oxygen atom (an alcohol) and the corresponding ketone. Thus, from both the FIMS data and the literature, the principal oxidation product is 1-tetralyl hydroperoxide, formed in a long and relatively fast chain reaction.

4.1.3. 2-Ethyl-naphthalene.

In March 1984 about 100 g of new 2-ethylnaphthalene, fractionally distilled in vacuo, was received from Dr. David Bittker of NASA-LeRC. To see how it behaved in oxidation, samples were oxidized without peroxide at 130°C. The material oxidized much faster than anticipated, and reaction times were decreased successively to obtain rates of oxygen absorption (R_o) and gum formation (R_g) that were not limited by oxygen exhaustion.

Results are summarized in Table 2. Even in one hour at 130°C, oxygen was so depleted that the oxidation nearly stopped. The lower R_o and R_g values at longer reaction times also show that reaction was

nearly complete after one hour. With these rate revisions, the new 2-ethylnaphthalene oxidizes and produces gum nearly 20 times as fast as the old material, faster than any of the materials tested except indene and N-methylpyrrole. (see Section 4). However, the R_o/R_g ratio does not change much from the 0.7 previously reported for 130°C, indicating that this apparently very pure sample still has much the same association of oxidation with gum formation as the previous material.

Table 2

UNINITIATED OXIDATIONS OF 10-ML (~ 9.9-g) SAMPLES OF
2-ETHYLNAPHTHALENE IN AIR AT 130°C

Reaction time (h)	R_o^a $\frac{\mu\text{mol O}_2}{\text{g fuel}\cdot\text{h}}$	$R_g^{a,b}$ $\frac{\text{mg gum}}{100 \text{ g fuel}\cdot\text{h}}$	R_o/R_g $\frac{100 \mu\text{mol O}_2}{\text{mg gum}}$	Final O ₂ Pressure ^a torr
0.94	89	68	1.31	14.9
3.0	28 ^c	16 ^c	1.75 ^c	11.3 ^c
7.0	12	7.2	1.71	11.3

^aBased on concentrations at 23-15°C and 1 atmosphere.

^bAverage of two blanks on unoxidized 2-ethylnaphthalene, 2.34 mg gum/100 g fuel.

^cLeast reliable value.

4.1.4. 2-Methylnaphthalene

The R_o and R_g data for methylnaphthalene are of such dubious value that details are omitted, but they can be found in Monthly Report 16, dated November 15, 1983.

4.1.5. Reproducibility of Oxidations

Reproducibility of our oxidation experiments has ranged from

remarkably good (e.g., oxidations of diesel Fuel 10 in triplicate)⁴ to poor. Thus, different lots of 2-EtN have varied in R_o by a factor of 20; different lots of TET have varied in R_o by a factor of 2, and different lots of DOD have varied in R_o by a factor of 1.3, but only in the case of DOD has the R_o/R_g ratio changed much. These differences appear to be due to impurities.

Although reproducibility of experiments appears better with $t\text{-Bu}_2\text{O}_2$ than in thermal oxidations, Table 9 will show significant differences between lots of DOD and TET, with different storage times under nitrogen at -8°C . Usually, however, R_o and R_g change together, with little effect on R_o/R_g , indicating that some unknown variable is affecting R_o and not the mechanism of deposit formation.

Another possible variable is the surface of the reaction flasks. For most of the experiments described in this report, flasks were cleaned by rinsing with acetone, heating with concentrated nitric acid, and rinsing with distilled water. In the more recent experiments described in the previous paragraph, the used reactors were rinsed with acetone and then heated in a glass annealing oven. However, no clear difference in results has been observed. We need to repurify and oxidize the fuels that have given the most trouble with reproducibility.

4.2. Tetralin-Dodecane Mixtures

Figure 3 shows oxygen absorption and gum formation for TET, DOD, and Fuel D. When TET is diluted with excess DOD, both oil and crystals separate during oxidation. The amount of gum formed in the remaining solution was determined at room temperature. Figure 3 shows that dilution with DOD retards the oxidation of TET at the beginning of the oxidation, but that the retardation later disappears, possibly because of increasing autocatalysis. The Fuel D mixture produces much less soluble gum than either pure hydrocarbon, probably because the soluble gum is more soluble in the oily precipitate than in DOD. However, this low yield of gum is more than offset by the precipitation of 630 mg of oily precipitate and 1543 mg of white crystals per 100 g Fuel D. The

analyzed crystals showed 73.19% C, 7.27% H, and no nitrogen, very close to tetralin hydroperoxide ($C_{10}H_{12}O_2$). They melted at 43-45°C (literature 56°C) and contained by titration only 28% of the calculated peroxide if the sample were 100% hydroperoxide. The analyzed oil showed 65.52% C, 6.33% H, and no nitrogen, very close to what would be expected for a dihydroperoxide of TET. The oil contained by titration 24.5% of the hydroperoxide in this formula. The TET hydroperoxides are apparently soluble in TET but not in DOD.

Other TET/DOD mixtures were then oxidized similarly, and the results are summarized in Table 3 and plotted later in Figure 8. The results vary so erratically that we are unable to interpret them although it appears that the pure hydrocarbons require the least oxygen to produce a milligram of gum. We do not know if the results are reproducible although those in Figure 3 look reasonable and consistent. When dealing with mixtures, we are concerned with the stability and autocatalysis by at least two kinds of hydroperoxides and a mixture of chain termination reactions that may produce the gum. Precipitates were noted only with Fuel D.

Similar experiments were performed with $t\text{-Bu}_2O_2$ at 100°C in the hope of obtaining more consistent results; these are described in Section 7.4.1.

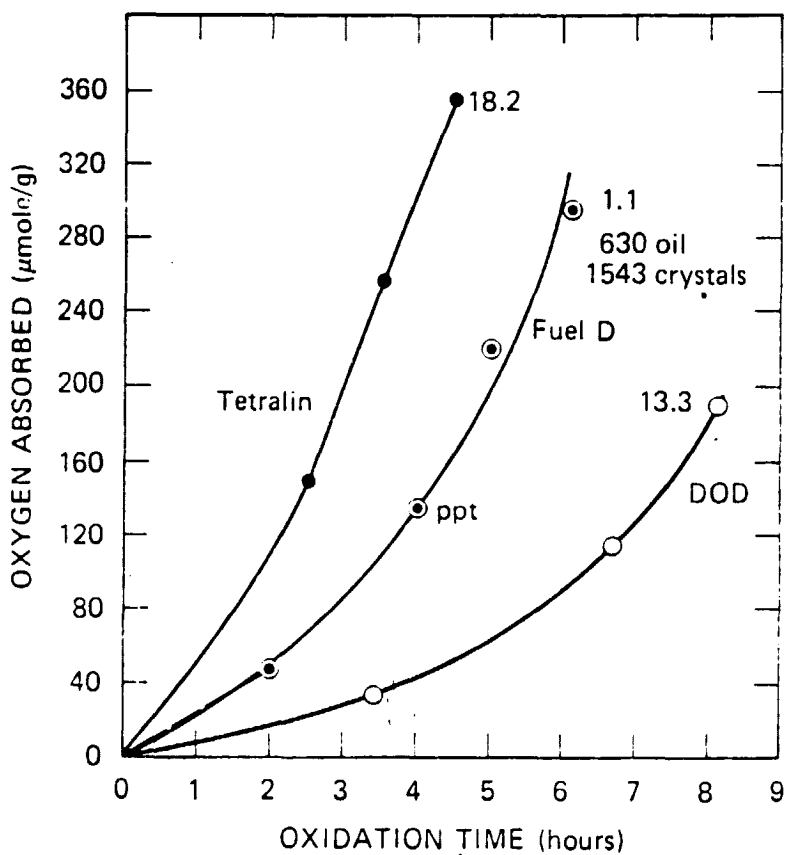
Table 3

OXIDATIONS OF DODECANE, TETRALIN, AND THEIR MIXTURES AT 130°C

DOD/TET	R_o ($\mu\text{mol O}_2/\text{g fuel}\cdot\text{h}$)		R_g ($\text{mg gum}/100\text{g fuel}\cdot\text{h}$)	R_o/R_g
	Initial	Average		
0/100 ^a	141	160	11.3	14
10/90 ^a	44	48	0.60	81
50/50 ^a	27	131	3.6	36
90/10 (Fuel D)	20	45.6	0.185 ^b	246
100/0	9	24	1.62	15

^aThese oxidations were probably run (by error) at $\sim 124^\circ\text{C}$ instead of 130°C .
^bSoluble gum, not including oily precipitate and white crystals.

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FIGURE 3 OXIDATIONS OF TETRALIN AND FUEL D
IN AIR AT 130°C

5. CORRELATION OF RATES OF OXIDATION AND GUM FORMATION AT 130°C

Data on rates of oxidation (R_o) and gum formation (R_g) at 130°C from both the NASA and ARO Contracts are summarized in Table 4. Fuels and pure substrates, with abbreviations, are arranged at the left in order of decreasing R_o . In the middle, the same fuels are listed in order of decreasing R_g , and at the right, in order of decreasing R_o/R_g ratios.

Table 4

RATES OF OXIDATION (R_o) AND GUM FORMATION (R_g) AND R_o/R_g RATIOS AT 130°C

Fuel	R_o	R_g		R_o/R_g	
N-Methylpyrrole (NMP)	97	IND	1300	IND	~ 0.07
Indene (IND)	91	NMP	700	NMP	~ 0.13
2-Ethyl-naphthalene (EtN)	89	EtN	68	D	259
Tetralin (TET)	79	B	13	1PH	40
Fuel D (90/10 DOD/TET)	48	C	5.1	TET	20
1-Phenylhexane (1PH)	28	TET	4.0	DOD	15
n-Dodecane (DOD)	24	BCH	3.9	BCH	4.7
Fuel B (jet)	22	DOD	1.6	B	1.7
Bicyclohexyl (BCH)	19	1PH	0.71	EtN	1.3
Fuel C (jet)	3.8	14	0.58	14	1.3
Fuel 14	0.78	13	0.48	A	1.0
Fuel 13	0.20	15	0.28	C	0.75
Fuel 15	0.17	1	0.19	10	0.65
Fuel 10	0.09	D	0.19	15	0.59
Fuel 1	0.06	10	0.14	13	0.42
Fuel A (jet)	0.05	A	0.05	1	0.34

^aNumbered fuels are diesel fuels supplied by the U.S. Army Fuels and Lubricants Research Laboratory.

The pure hydrocarbons, the known mixture (Fuel D), and pure NMP oxidize faster than any of the fuels, and (with the exception of Fuels B and C) they also form gum faster than any of the fuels. There are several parallels in the orders for R_o and R_g and also some notable discrepancies, which make possible some advance in our understanding of gum and deposit formation.

The R_o/R_g column shows the amount of oxygen required to produce a milligram of gum from each substrate. In general, the pure hydrocarbons require the most oxygen to produce gum. Conversely, the fuels at the bottom of the column give the most gum for the oxygen absorbed. As far as we can tell, R_o/R_g is remarkably constant for each substrate, notwithstanding considerable variations in R_o with different lots of hydrocarbon or purifications. It thus appears that gum formation is intimately associated with the oxidation process but that different substrates can vary several hundred fold in their abilities to produce gum for the oxygen absorbed.

These relations are new, unique, and important in understanding fuel stability, at least in terms of formation of soluble gum. 2-Ethyl-naphthalene is the most interesting of the pure hydrocarbons. It is the fastest oxidizer and the fastest gum former we have tested except indene and NMP (see below). Related polynuclear aromatic hydrocarbons are major components of the least stable fuels (Section 3.3). These relations are discussed further in Section 7.3.

Indene and N-methylpyrrole are in a class by themselves and should not be present in jet fuels. They absorb oxygen faster than anything else that we have tested, and nonvolatile polymeric peroxides are almost the sole products. The polyperoxides cannot survive our gum analyses, but enough decomposition products survive to give them the highest R_g and the lowest R_o/R_g values that we have observed.

6. OXIDATIONS AT LOW OXYGEN PRESSURES AT 130°C

Our Second Annual Report² described oxidations of Fuel C at high and low oxygen pressures and was the point of departure for the work described here. Those oxidations used measurements of total pressure and an oxygen analyzer. In the experiment starting with an initial 465 torr of oxygen, the decrease in total pressure corresponded closely to the consumption of oxygen and so this experiment is included in Table 5. However, in the experiment starting with 48 torr of oxygen, the total decrease in pressure was five times the apparent consumption of oxygen. This experiment has therefore been disregarded.

Table 5 summarizes valid experiments with Fuels C, A, and D at initial partial pressures of oxygen of 16 to 465 torr (measured at 23-25°C) in oxidations at 130°C without added initiator. The data have been recalculated on a consistent basis from the initial atmospheric pressures and the O/N ratios from GC, but most changes are negligible. Each set of data usually represents one oxidation and shows how the oxygen concentration changed with time.

6.1. Fuel C

Fuel C absorbs oxygen faster than any other fuel that we have tested, but not faster than most pure hydrocarbons; it also produces gum faster than any other fuel except Fuel B after its induction period.

The results of the first two experiments agree fairly well. They show that R_0 decreases with decreasing oxygen pressure and approaches zero at 9 to 14 torr of oxygen. The longest experiments have the lowest R_0 values, at least partly because these long times include periods of little reaction. The next two experiments establish a higher R_0 in air and maintenance or increase of R_0 when oxygen pressure is maintained. The last experiment with Fuel C and 60% oxygen in nitrogen shows no further significant difference except marked autocatalysis. The

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Table 5
EFFECTS OF OXYGEN PRESSURES ON RATES OF OXIDATION
AND GUM FORMATION AT 130°C

Time (h)	O ₂ Pressure, (torr) ^a	R _o	R _g	R _o /R _g	Notes ^b
FUEL C					
0	18.0				
19	12.4	0.20			Nearly stopped at 43 h and 9.2 torr O ₂
160	7.53	0.044	0.18	0.24	
0	30.3				
43	16.2	0.22	1.22	0.18	Nearly stopped at 69 h, 14.2 torr
134	11.0	0.11	0.31	0.36	
0	152.3				
3	150.0	0.51			
17	72.2	3.1			
17	152.1				Original gas mixture restored
23.8	101.7	3.7			Original gas mixture restored
23.8	152.6				
28.8	124.7	3.8	5.0	0.74	
0	153.9				Chromatographed
3	127.0	6.4			
11.5	40.8	7.0			
11.5	152.6				Original gas mixture restored
16.5	130.2	5.9	11.3	0.52	
0	464.8				Used oxygen analyzer
4.5	433.2	3.2			
14.0	301.2	7.7	21	0.37	
FUEL A					
0	20				
44	18.5	0.016			
162			0.017	0.92	[O ₂] increased
0	18.7				
43	17.5	0.0203			
286			0.0122	1.66	[O ₂] increased
0	16.5	--	--	--	
21	11.4	0.18	0.073	2.5	[O ₂] increased
50	12.6	0.055	0.044	1.25	
0	158.0				
24	143.7	19.7			
262	114.9	0.0451			
262	154.7				Original gas mixture restored
399	119.3	0.037	0.0497	0.744	Also 0.334 g wall ppt/g fuel·h
FUEL D					
0	20.1				9.15 mol% TET in DOD
1.5	6.53	6.4			
2.5	5.36	4.1		20	Nearly stopped at 2.5 h, 5.4 torr
5.0	5.00	2.2	0.21	10	
0	152.0				11.8 mol% TET
2	95.6	20.3			
2	153.5				Gas changes
4	46.7	24.0 (interval)			
6.1	65.1	42.4	0.125	229	After 2 more gas changes, also 230 mg crystals and 94 mg oil/100 g fuel·h.

^aFrom initial total pressure and O/N ratio by GC.

^bOn distilled fuel after storage under N₂ at 0°C except where marked "Chromatographed."

important conclusion is that R_o/R_g changes by a factor of less than two between oxygen pressures of 18 and 465 torr. Thus, oxygen concentration affects gum formation mostly through its effect on R_o ; there is no evidence of a direct effect of oxygen concentration on gum formation. However, at about 10 torr of oxygen, both reactions become very slow.

6.2. Fuel A

Fuel A is one of our slowest oxidizers and gum formers, and in any experiments R_o and presumably R_g decrease steadily from the beginning of the oxidation, as shown in the last two Fuel A experiments in Table 5. This Table summarizes three experiments at initial oxygen pressures of 16 to 20 torr. All showed similar initial R_o values, but then a slow increase in oxygen pressure. Because a similar increase occurred in a reactor with no fuel, the increase must be due to leakage of air into the reaction vessel, probably on cooling of the flask that had been previously heated at more than atmospheric pressure. In all three experiments, the early R_o values are divided by the total average R_g values and all the ratios are higher than in the 158 torr experiment. Apparently the R_g values are small because both R_o and R_g decreased with time; thus, ratios based on early R_o values are too high. However, in experiments A-1 and A-2 the ratios are only about twice those found at high pressure. Therefore, there is no evidence for a significant effect of oxygen pressure on the mechanism or efficiency of gum formation in the range 19-158 torr.

Our difficulties with low oxygen pressure runs with Fuel A arise because the oxidation is normally so slow and because it becomes slower with time and lower oxygen pressures. Leakage then becomes important. We therefore carried out the third oxidation of Fuel A by determining O/N ratios at 0, 21 and 50 h in separate but very similar runs, all using previously unpunctured septa for removing gas samples. In all three runs, air-filled reaction vessels were evacuated to 80 torr, then nitrogen was admitted to 760 torr, all at 24°C.

The R_o results are inconsistent; only 72% as much oxygen was absorbed per gram of fuel in 50 h as in 21 h, which we attribute to poor reproducibility in 130°C oxidations. However, the R_o/R_g values agree fairly well with each other and with other data for Fuel A. If more low pressure oxidations are performed, an initiator should be added to improve reproducibility.

6.3. Fuel D

Two experiments with Fuel D are listed in Table 5. In air, the reactions are fast and autocatalytic. With an initial 20 torr of oxygen, the reaction starts about one-third as fast, but this rate decreases steadily until it approaches zero at 5 torr of oxygen.

6.4. Correlation of Results

The following is a simple and reasonable, but unproved, correlation of the results presented in this section. R_o , R_g , and R_o/R_g for each fuel are insensitive to oxygen partial pressures above ~ 20 torr. Further, Fuel A is self-retarding even with plenty of oxygen available. Above ~ 20 torr of oxygen, the termination mechanism for all fuels involves the usual combination of two alkylperoxy radicals; in this range, the data in Table 5 do not tell us whether gum formation is associated mostly with the propagation or the termination reaction. At lower oxygen pressures, the termination shifts to the much faster reaction of alkyl radicals with alkylperoxy radicals, and reaction stops for practical purposes. These results imply that complete oxygen removal is unnecessary to stop oxidation and gum formation at 130°C; decrease of oxygen partial pressure from 150 to ~ 10 torr will essentially stop both reactions. Similar experiments should be performed at storage temperatures of 20-50°C.

The sharp decrease in R_o with change in termination mechanism is neither new⁵ nor surprising. The results also imply that further efforts to measure the effects of still lower oxygen partial pressures on R_o and R_g will be unrewarding; the oxidations will be extremely slow, and they will therefore have little or no practical significance. This conclusion should be checked.

7. NEW DATA ON OXIDATION AND GUM FORMATION AT 100°C

7.1. Oxidations of Single Hydrocarbons and Fuels

Table 6 summarizes the results of oxidations of hydrocarbons and fuels at 100°C. The initial concentrations of t-Bu₂O₂ listed in recent monthly reports have been multiplied by 0.967 to reflect a recent determination of its purity by the Hercules III method.⁶ Attention is directed first to experiments containing an initial concentration of t-Bu₂O₂ of about 0.04 M. (Many of these concentrations were stated as 0.1 M in the monthly reports until a consistent error was discovered.) Fuels B and Fuel C showed autocatalysis and oxidized at an increasing rate. EtN and TET oxidized fastest, and Fuel A oxidized slowest and with a slightly decreasing rate, as shown in Figure 4. EtN was by far the fastest gum former. However, Fuel A produced about as much gum for the oxygen absorbed. Although Fuel D formed very little gum according to our test, it did form oxidation products insoluble in dodecane after 7.5 hours of oxidation. DOD and TET, and their combination, Fuel D, are among the fastest oxidizing hydrocarbons at 100°C as well as 130°C.

7.2. Effect of t-Bu₂O₂ Concentration

In most free-radical chain oxidations with sufficient oxygen, the rate controlling reaction is $\text{RO}_2\cdot + \text{RH} \xrightarrow{k_p} \text{ROOH} + \text{R}\cdot$. The oxidation rate can be expressed as

$$R_o = (R_i/2k_t)^{1/2} k_p [\text{RH}]$$

where the rate of initiation, R_i , is proportional to the concentration of initiator; k_p is the propagation constant for reaction of $\text{RO}_2\cdot$ with hydrocarbon, RH; and k_t is the bimolecular termination constant for interaction of $2\text{RO}_2\cdot$. From the steady-state condition, $R_i =$ rate of chain termination $= 2k_t(\text{RO}_2\cdot)^2$. Measuring the dependence of R_o and R_g on the concentration of t-Bu₂O₂ should therefore tell us whether R_o is behaving normally and whether R_g is associated with chain propagation

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Table 6

Fuel	[t-Bu ₂ O ₂] ₀ (M)	Time (h)	OXIDATIONS AT 100°C			
			Time to Pptn (h)	R _o ^a	R _g ^b	R _o /R _g
	0	255	>250	0.0059 steady	0.0054	1.09
	0.0044	277	140	0.054 dec.	0.051	1.05
	0.035	140	75	0.288 dec.	0.27	1.07
	0.33	19	> 19	5.18 steady	3.0	1.71
	0.041	40.5	> 40	3.61 inc.	0.54	6.65
	0.036	52	35	3.20 inc.	2.18	1.47
	0.042	13.3	9	6.74 dec.	0.056	120
	0.34	6		17.3 dec.	0.63	31
DD	0	309		0.33	0.02	16.5
	0.0097	103		1.5	0.03	50
	0.036	40	> 30	3.2 steady	0.29	10.9
	0.038	15	> 15	1.78 steady	0.025	71
	0.097	54.5		2.80 steady	0.063	45
ET	0.031	20	> 20	12.3 steady	2.8	4.4
	0.038	5	> 5	29.2	1.02	29
tN						
Old ^c	{ 0.064	9	> 9	9.7 dec.	3.6	2.7
	{ 0.59	7	> 7	29 dec.	15.5	1.9
New	{ 0.033	1.03	> 6	36 ^d	19	1.9
	{ 0.034	3.0	> 6	29 ^{d,e}	31 ^e	0.92 ^e
	{ 0.035	6.0	> 6	13 ^d	10.1	1.3

Average rate of oxygen absorption in $\mu\text{moles O}_2/\text{g fuel}\cdot\text{h}$ over stated reaction time.

Notes indicate whether rate was increasing, decreasing, or steady during this interval.

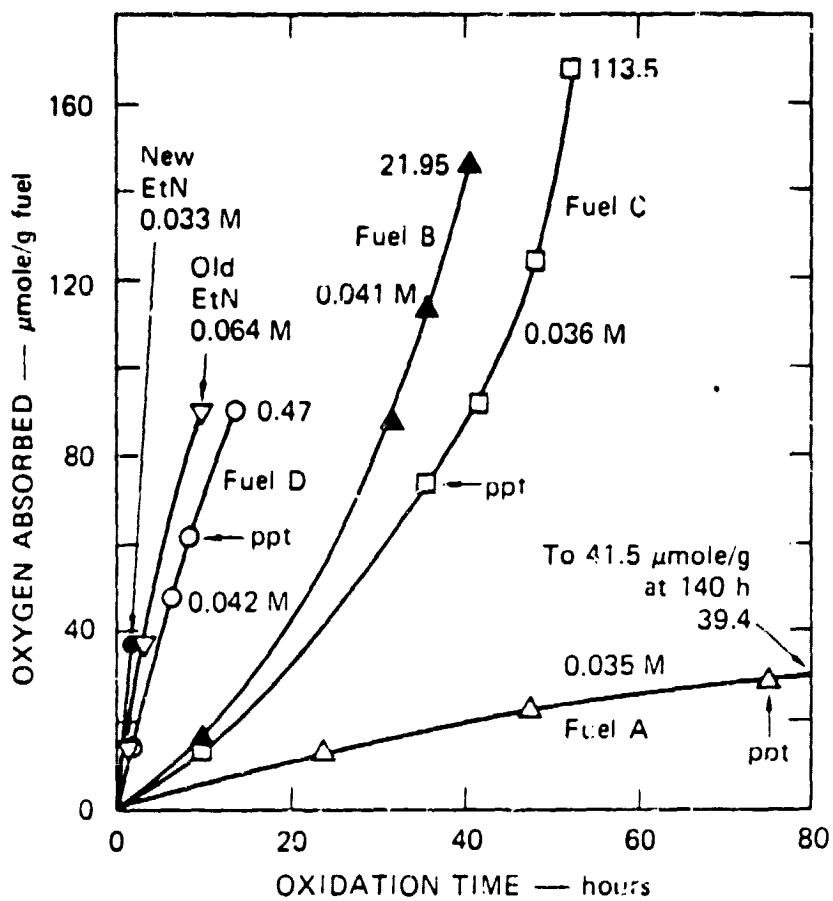
Rate of gum formation in $\text{mg gum}/100 \text{ g fuel}\cdot\text{h}$.

Distilled and chromatographed.

Final oxygen pressures 97, 131, and 29 torr.

Least reliable value

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FIGURE 4 OXIDATIONS OF FUELS WITH $\sim 0.04\text{M}$ $t\text{-Bu}_2\text{O}_2$ IN AIR AT 100°C
Initial concentrations of peroxide are indicated on the curves. The numbers at the ends of the curves are the amounts of gum formed in mg/100 g fuel.

(half order on R_1) or chain termination (first order on R_1).

Available data are summarized in Table 7. Details for fuel A are in Figure 5 and for DOD⁷ in Figure 6. R_O is clearly first order with jet turbine Fuel A and diesel Fuel 10; thus, chain termination is abnormal. This termination could involve polynuclear aromatic hydrocarbons or their phenolic oxidation products and provide a separate route to gum formation. R_g is also first order in R_1 , and therefore we cannot tell whether it is associated with chain propagation or chain termination.

With Fuels D and 13, R_O is nearly half order (with some first-order contribution in 13) and R_g is nearly first order. Their oxidations are nearly normal, and the R_g results indicate that gum formation is associated with chain termination, as if at least part of the coupling in chain termination involves large as well as monomeric radicals. The low orders for R_O and R_g in the oxidations of DOD will be discussed near the end of this section.

Figure 5 shows a slow steady R_O for Fuel A in the absence of peroxide and higher but decreasing rates in the presence of peroxide and at 130°C, consistent with the accumulation of retarders during oxidation.

Figure 6 shows substantial oxidation of DOD in the absence of peroxide and substantial autocatalysis at 0 and 0.01 M peroxide. The rates of oxidation and gum formation listed in Table 7 are the average rates between zero time and the end of the measured reaction. The autocatalysis therefore confuses the estimates of reaction order. When the initial rates of oxidation in Figure 6 are used for the calculations, n for DOD is 0.43. Further correction for the purely thermal oxidation would bring n closer to 0.5. For a better determination of n for gum formation, gum determinations at shorter reaction times are needed. However, as Table 7 stands, the rate of gum formation is first order in $[t\text{-Bu}_2\text{O}_2]$, with the possible exception of DOD, whether the rate of oxidation is half order or first order in peroxide concentration. Thus, gum formation appears to accompany the initiation or termination reaction.

Table 7

KINETIC ORDERS OF R_o AND R_g

Fuel	[t-Bu ₂ O ₂] (M)	Conc. Ratio ^a	R_o		R_g	
			Ratio ^b	Order, n ^c	Ratio ^b	Order, n ^c
A	0.004 - 0.33	75	96	1.055	59	0.94
D	0.042 - 0.34	8.1	2.86	0.51	11.2	1.16
DOD ^d	0.01 - 0.10	10	1.87 2.67 ^e	0.27 0.43	2.1	0.32
10 ^d	0.01 - 0.10	10	10.2	1.01	9.6	0.98
13 ^d	0.01 - 0.10	10	4.5	0.65	10.9	1.04
EtN (old)	0.064 - 0.59	9.3	2.97	0.49	4.3	0.65

^aHighest [t-Bu₂O₂]/lowest [t-Bu₂O₂].

^bRate of O₂ absorption at highest t-Bu₂O₂/rate at lowest [t-Bu₂O₂], or ratio of R_g values.

^cFrom R_o ratio (or R_g ratio) = (conc. ratio)ⁿ.

^dFrom Reference 7.

^eBased on initial rates of oxidation.

7.3. Comparison of Oxidations at 100° and 130°C

Comparison of results without t-Bu₂O₂ at 130°C (Table 4) with those obtained with 0.03 to 0.04 M peroxide at 100°C (Table 8) leads to the following conclusions:

(1) The spread in reactivities with t-Bu₂O₂ (highest R_o /lowest R_o) is much less (~100) than without t-Bu₂O₂ (~400). Thus, the peroxide decreases R_o differences among hydrocarbons.

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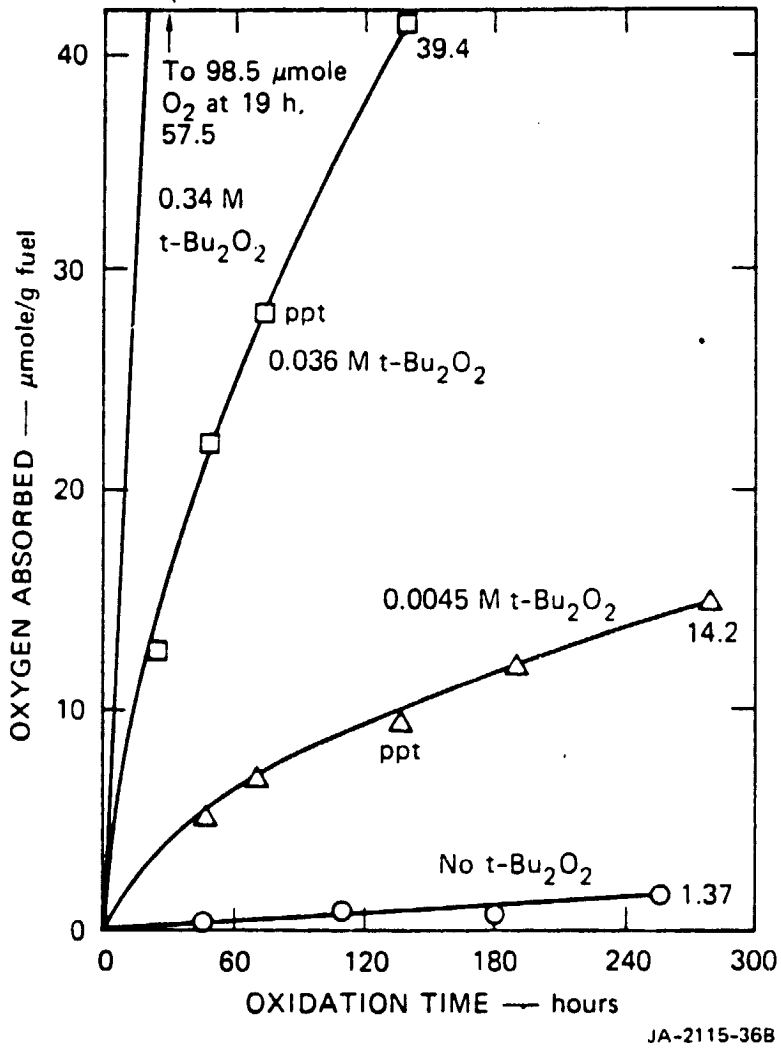
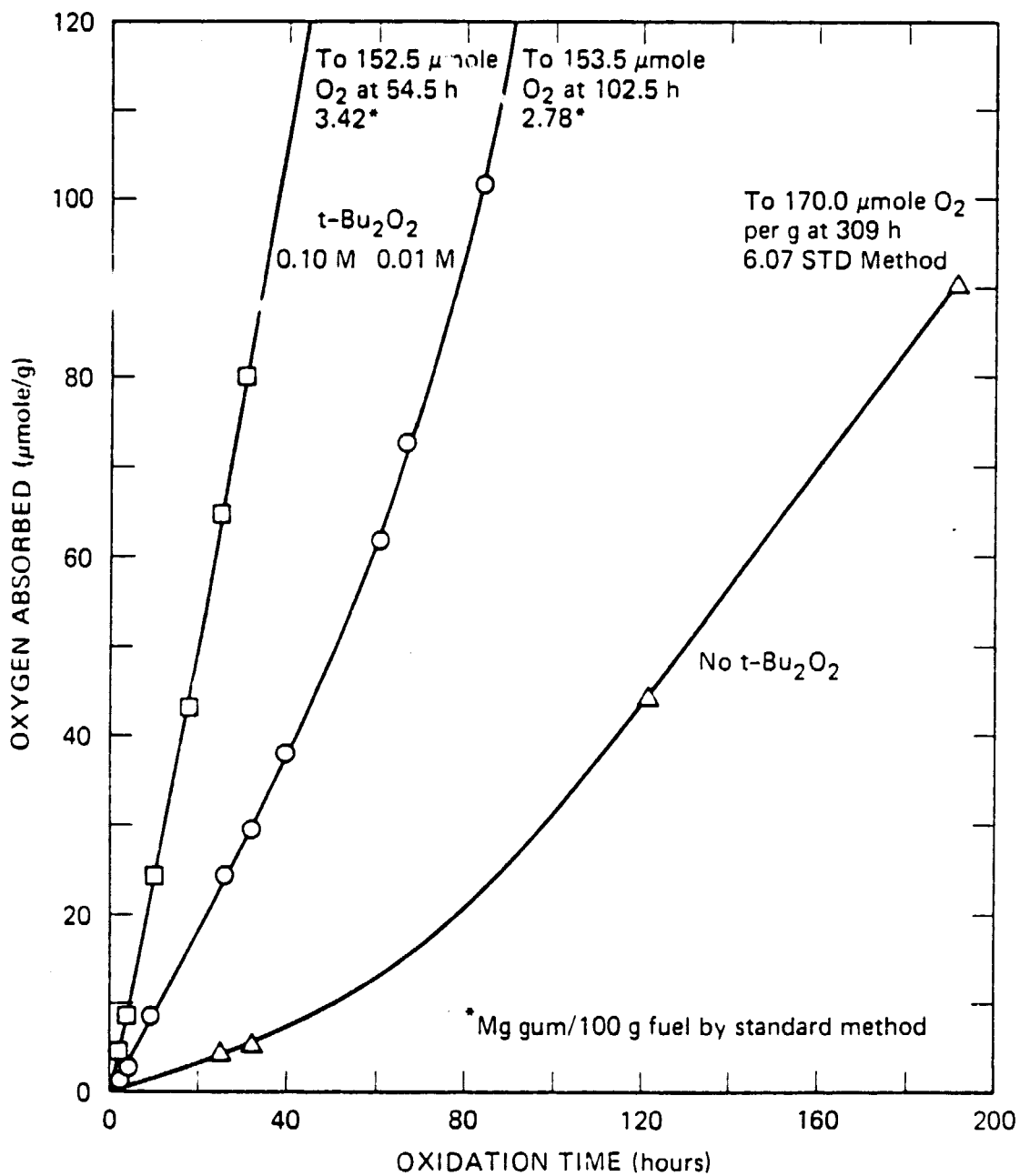


FIGURE 5 OXIDATIONS OF FUEL A IN AIR AT 100°C WITH $t\text{-Bu}_2\text{O}_2$

In this and other figures, the numbers at the ends of the lines are mg gum found/100 g fuel.

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FIGURE 6 OXIDATIONS OF $n\text{-DODECANE}$ AT 100°C ⁷

Table 8
OXIDATIONS WITH ~ 0.04 M t-Bu₂O₂ AT 100°C

Fuel	R _o ^a	R _g ^b		R _o /R _g	
EtN (new)	36	EtN	19	D	279
TET	29	C	2.2	DOD	71
PCH	7.6	13	1.04	TET	29
D	6.7	PCH	1.3	B	6.7
B	3.6	TET	1.0	PCH	6.0
C	3.2	10	0.57	EtN	1.9
DOD	1.8	B	0.54	C	1.5
10	0.34	A	0.28	A	1.1
A	0.30	DOD	0.025	10	0.6
13	0.32	D	0.024	13	0.31

^aRate of oxygen absorption in μmoles O₂/g fuel·h.

^bRate of gum formation in mg gum/100 g² fuel·h.

(2) To a good approximation, the most reactive substrates are the same at the two temperatures. Most of these substrates react faster at 130°C than at 100°C, indicating that initiation is not a problem with these hydrocarbons and fuels.

(3) The slowest oxidizing substrates, Fuels A, 10, and 13, are the same at both temperatures and in a class distinct from the fast substrates. They oxidize faster at 100°C than at 130°C. They have a wide spread in R_o at 130°C, but no really significant spread at 100°C.

These are the hydrocarbons and fuels that lack adequate self-initiation or are self-retarding, or both.

(4) 2-Ethyl-naphthalene falls between the fast and slow oxidizers. It oxidizes and forms gum somewhat faster at 130°C than at 100°C, but the R_o and R_g ratios are closer together.

(5) n-Dodecane behaves differently from the other fast oxidizers. It shows the largest decrease in R_o (13 times) in the temperature change from 130° to 100°C, but gum formation also decreases (27 times) so that R_o/R_g at 100°C is twice that at 130°. These data suggest that chain initiation is so easy in DOD at both temperatures that the slower propagation at lower temperature becomes the dominant factor. Results with Fuel D (10 mol% of TET in DOD) tend to confirm the results with dodecane. Fuel D shows the next largest decrease in rate between 130° and 100°C (7.2 times) and also a large decrease in R_g (7.9 times) with little change in R_o/R_g .

(6) Although the R_o and R_g patterns vary at 100° and 130°C, most of the R_o/R_g ratios are similar at these two temperatures, confirming the close relation between R_o and R_g for each substrate. The largest discrepancies, about fourfold, are with DOD and Fuel B, where R_g seems unduly small at 100°C.

(7) The effect of temperature on R_o/R_g becomes important in developing an accelerated test for fuel stability at 40°C. If gum formation is indeed closely associated with chain initiation or termination in oxidation, then the R_o/R_g ratio should become sensitive to rate of chain initiation and kinetic chain length. If an accelerated test is to be developed, then use of an initiator is desirable, perhaps essential. Before a reliable test for fuel stability at 40°C can be developed, experiments at that temperature will be required.

7.4. Oxidations of Mixtures

7.4.1. Dodecane/Tetralin.

Section 4.2 showed that oxidations of DOD/TET mixtures in air without initiator at 130°C gave unexpected results for R_o and R_g . Similar mixtures were then oxidized with ~ 0.038 M t-Bu₂O₂ at 100°C in an effort to check our results at constant rate of initiation. Table 9 contains the basic rate and gum data for mixtures at 100°C. Some oxygen absorptions are plotted against time in Figure 7. The numbers at the ends of the lines are the mg gum found per 100 g fuel; the accompanying numbers in parentheses are the yields of hydroperoxides on the oxygen absorbed. Most of the peroxide yields are in the 7-11% range, but neat dodecane gave 25% yield of hydroperoxide. Thus, tetralyl hydroperoxide is less stable than dodecyl hydroperoxide; only one-fourth as much survived in one-third of the reaction time.

Figure 8 summarizes our results at both temperatures with R_o points on solid lines, R_g points on broken lines, and R_o/R_g ratios inserted near each oxygen absorption point. First, oxidations are consistently faster at 130°C without initiator than at 100°C with 0.038 M t-Bu₂O₂. Second, the rate anomalies at 130°C are partially corroborated at 100°C: TET oxidizes significantly faster than DOD and the rates are high for the 50/50 mixtures. The R_o data at 100°C are fairly consistent at both extremes in concentration, but R_o decreases substantially between 50% and 70% DOD. A similar pattern occurs with the R_g data at 100°C, but the R_g decreases relatively more between 50% and 70% DOD. Thus, the R_o/R_g ratio increases by a factor of 7 in this range; that is, the high DOD mixtures require more oxygen to produce a milligram of gum.

The precipitation of TET oxidation products from Fuel D (see Section 4.2) as well as comparisons of relative reactivities toward peroxy radicals,⁸ indicates that relatively little DOD reacts even in 90% DOD mixtures with TET. The decrease in R_o between 50% and 70% DOD must be partly due to dilution of TET, but there must also be significant effects of changes in termination, initiation, and/or

Table 9

COOXIDATIONS OF PURE HYDROCARBONS AND FUELS

<u>Substrate^a</u>	<u>t-Bu₂O₂ (M)</u>	<u>Time (h)</u>	<u>R_o^b</u>	<u>R_g^c</u>	<u>R_o/R_g</u>
Neat DOD	0.038	15	1.78 steady	0.025	72
9% TET in DOD	0.043	13.2	5.8	0.056	122
30% TET in DOD	0.039	5.8	2.37	0.14	17
51% TET in DOD	0.038	5.5	39	1.58	25
90% TET in DOD	0.033	5.5	30	1.08	28
Neat TET	0.038	5.0	29	1.02	29
Neat old EtN	0.064	9	9.7 dec.	3.5	2.8
9.1% old EtN in DOD	0.043	50	1.80 steady	0.146	12.3
Neat Fuel A	0.035	140	0.30 dec.	0.28	1.06
10.1% old EtN in Fuel A	0.041	60.7	0.53 dec. ^d	0.56	0.94
Neat DOD ^e	0.036	40	3.15	0.29	11
<5.2% anthracene in DOD ^e	0.050	40	1.02	0.30	3.4
Neat TET ^e	0.031	20	12.3	2.8	4.4
10.4% anthracene in TET ^e	0.030	20	10.8	1.20	9.0
9.8% MeN in TET ^e	0.042	20	9.5	1.9	5.2
Neat MeN	0.053	75	0.67	3.4	0.20

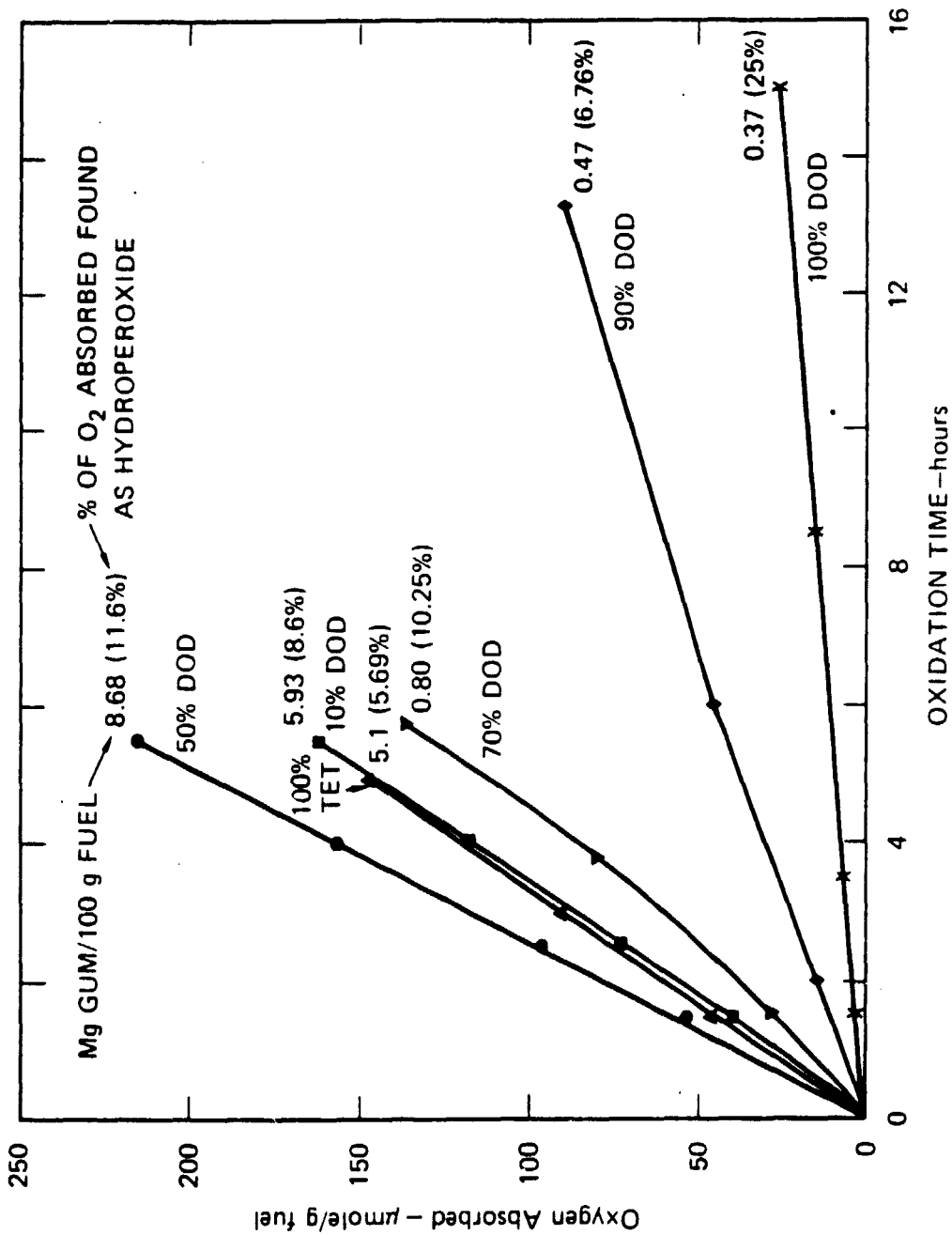
^aMinor components are stated in mole fractions.

^bRate of oxygen absorption in $\mu\text{mole O}_2/\text{g fuel}\cdot\text{h}$ over the stated period. Notes indicate whether the rate was decreasing or steady over this period.

^cRate of gum formation in $\text{mg gum}/100 \text{ g fuel}\cdot\text{h}$ over stated period.

^dMaximum rate was 1.18 between 3.5 and 21.7 h.

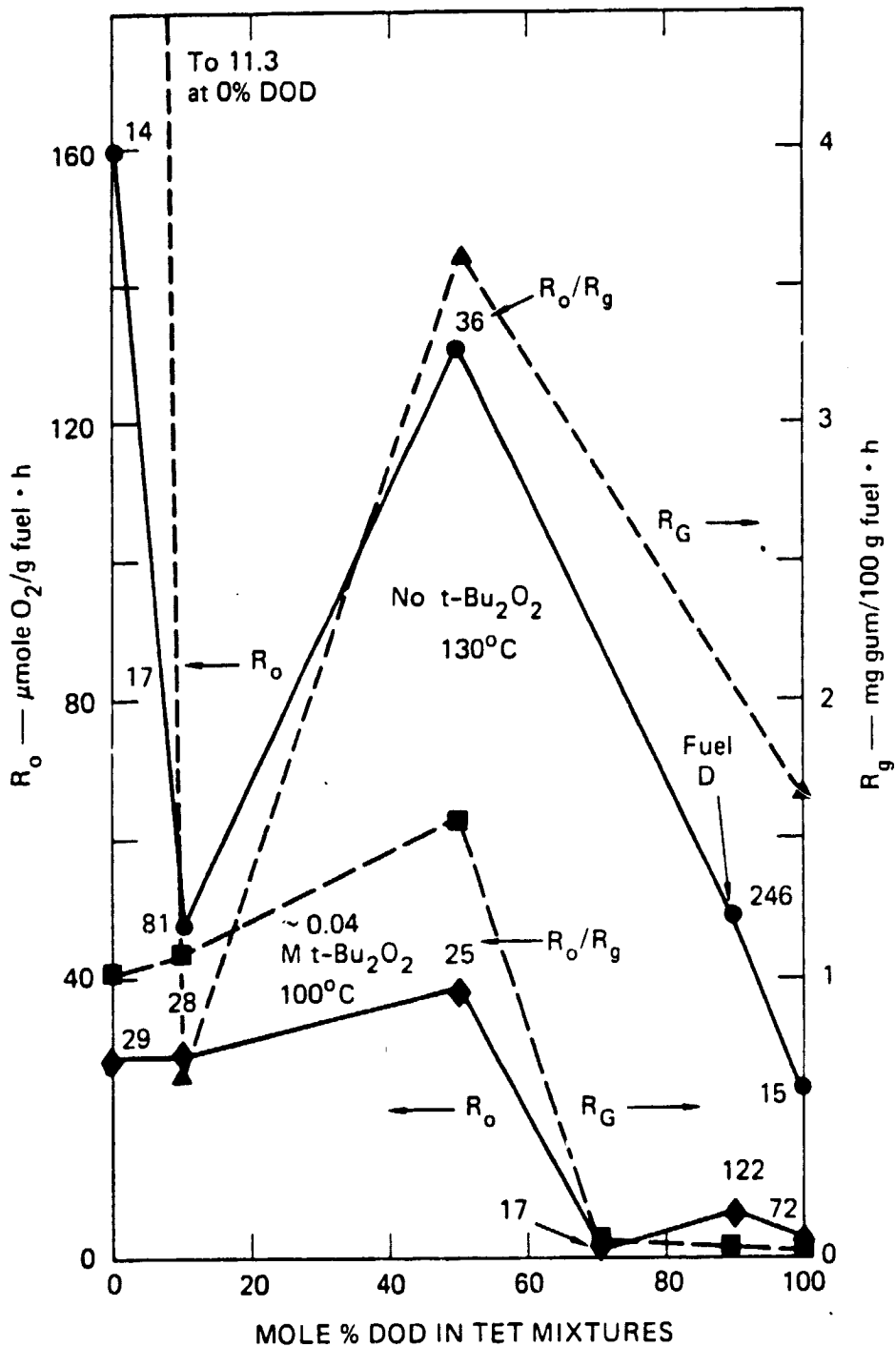
^eNew lot of freshly distilled DOD.



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FIGURE 7 OXIDATION OF DOD/TET MIXTURES WITH ~0.04M t-Bu₂O₂ IN AIR AT 100°C

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FIGURE 8 RATES OF OXIDATION AND GUM FORMATION FOR DOD/TET MIXTURES

reaction medium. We are not yet able to assess the importance of these findings to the fuel deposit problem or how much effort will be required to elucidate them.

7.4.2. Other Mixtures

We oxidized several other mixtures at 100°C, mostly with ~ 0.04 M peroxide, to determine if small proportions of selected hydrocarbons would have large effects on R_o and R_g of major components. Only one large effect was found, that of anthracene on DOD.

Figure 9 shows that 10% of TET in Fuel C eliminates the initial slower oxidation of Fuel C and increases the rate of gum formation without much effect on the time of precipitate appearance.

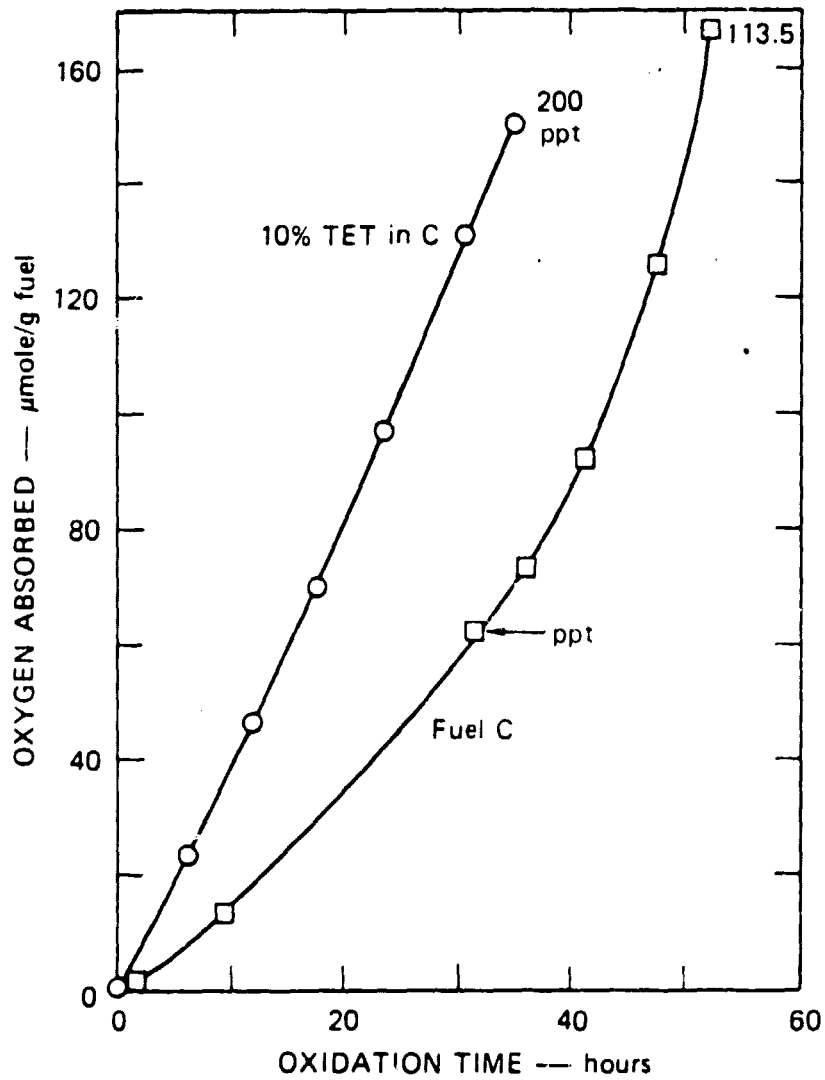
Oxidations of 9% of old 2-ethylnaphthalene in DOD and of 10% in Fuel A are also summarized in Table 9. With DOD, the old EtN increases R_g without much effect on R_o . EtN moderately increases both R_o and R_g of stable Fuel A.

2-Methylnaphthalene oxidized very slowly, but because of the effects of purification on EtN, the results for MeN are suspect. Figure 10 shows that 10% of 2-MeN behaves like an inert diluent in TET and thus that it may be inherently unreactive.

The 1969 papers of Bourdoncle and Parc were recently examined. The first^{9a} describes the oxidations of 21 pure hydrocarbons for 7 h at 140°C and 1 atm of oxygen. Total oxygen absorption, maximum rate, and times to maximum rate are reported. For oxygen absorption, the fastest oxidizing hydrocarbons are squalane, n-dodecyclohexane, its branched analogs, then the n-alkanes and hydroaromatics. All these hydrocarbons exhibit induction periods, maximum rates, and then decreases in rate. The slowest oxidizing hydrocarbons are phenanthrene, biphenyl, and 1-methylnaphthalene, which have no induction period and with which the rate of oxidation decreases from the beginning.

The second paper^{9b} describes, among other experiments, the oxygen absorption by paraffin oil for 4 h at 150°C in the presence of 0.01 M

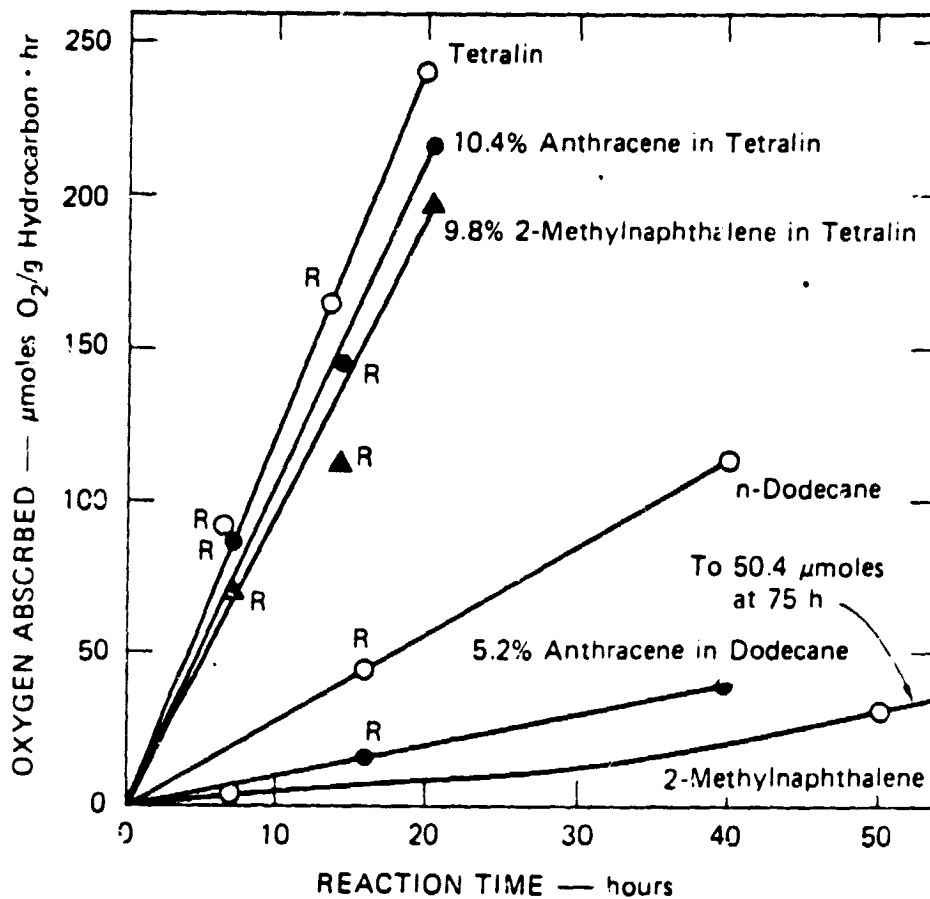
CRITICAL EVALUATION
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FIGURE 9 OXIDATION OF FUEL C AND FUEL C + 10% TETRALIN
WITH 0.04M $t\text{-Bu}_2\text{O}_2$ IN AIR AT 100°C

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OF POOR QUALITY



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FIGURE 10 OXIDATIONS OF TETRALIN, DODECANE, 2-METHYLNAPHTHALENE,
AND SOME MIXTURES AT 100°C

Open symbols are used for pure hydrocarbons. R indicates replacement of air.

tetralin hydroperoxide and 10 wt% hydrocarbon additives. None of these hydrocarbons accelerates the oxidation but several are strong retarders. Ratios of the retarded to the pure paraffin rates are given for each hydrocarbon: anthracene, 0.0063; phenanthrene, 0.045; octahydroanthracene, 0.103; octahydrophenanthrene, 0.110; acenaphthene, 0.178; fluorene, 0.195.

On the basis of these results, we tested the effects of anthracene on oxidations of TET and DOD with $t\text{-Bu}_2\text{O}_2$ at 100°C in air. Most of the 0.104 mole fraction of anthracene dissolved eventually in TET at 100°C , but precipitated when the mixture was cooled. Less than half of the 0.052 mole fraction of anthracene dissolved in the DOD at 100°C . The effect of the anthracene on the oxidation of TET is small, apparently because the two compounds have similar activities in oxidation⁸ and the proportion of anthracene was small. Table 9 and Figure 10 show that even the small proportion of anthracene dissolving in DOD reduced the rate of oxidation to 28% (corrected to the same $t\text{-Bu}_2\text{O}_2$ concentration) of the rate with DOD alone. However, because the rate of gum formation was not reduced by anthracene, the efficiency of gum formation was increased.

Our conclusion is that anthracene is probably a good inhibitor of the hydrocarbons that are unreactive and that its effectiveness decreases as the other hydrocarbon becomes more reactive. However, this principle must be used with caution. Minimizing the oxidation rates of mixtures of two hydrocarbons requires that the hydrocarbon that is more reactive in chain propagation must also be more reactive in chain termination. The slowest oxidizing aromatic hydrocarbons of Bourdoncle and Parc apparently fulfill this requirement.

7.5. Hydroperoxide Contents of Oxidation Products

Hydroperoxides have been found in many of our oxidation products. Hydroperoxide yields are summarized in Table 10 where the data are generally arranged in order of decreasing yields of hydroperoxides as percent of oxygen consumed. Among the experiments

Table 10

HYDROPEROXIDE YIELDS AS PERCENT OF O₂ ABSORBED

<u>Reaction Temp. (°C)</u>	<u>Fuel</u>	<u>[t-Bu₂O₂]₀ (M)</u>	<u>RO₂H, (%)</u>	<u>Reaction Time (h)</u>
100	EtN, old	0.064	32	9
		0.038	20	15
		0.59	11	7
	EtN, new	0.033	96	1
		0.034	35	3
	D	0.34	15	6
		0.038	8.6	5.5
		0.042	6.8	13.3
	B	0.041	13	40.5
	50% TET in DOD	0.038	12	5.5
	30% TET in DOD	0.038	10	5.75
	TET	0.038	5.6	5
	10% TET in C	0.038	5.4	35
	C	0.036	2.4	52
	A	0.035	~0	140
130	EtN, new	0	90	3
		0	5.3	23
	B	0	2.1	40
	TET	0	3.3	4.5
	D	0	2.0	6.1

with initial 0.04 M t-Bu₂O₂ at 100°C, by far the best yields of hydroperoxides were obtained from EtN, mostly because of its short reaction time, but even at long reaction times EtN hydroperoxide survives better than the others. Other peroxide yields depend on their rates of formation and decomposition; the best yields are obtained at the shortest reaction times and with the most reactive hydrocarbons. Decomposition of accumulating hydroperoxides is expected to accelerate the rate of oxidation. As indicated in Section 7.4.2, the concentration of hydroperoxides goes through a maximum as an oxidation proceeds.

8. GUM DETERMINATIONS ON STRESSED EtN FOR LEWIS RESEARCH CENTER

Eight samples of thermally stressed 2-EtN were sent by Dr. David Bittker from NASA-LeRC to SRI for gum determinations, in accordance with our contract. Gum contents are reported in our Monthly Reports 22 and 23. Details of stressing and discussion of the results will appear in Dr. Bittker's own report.

For these determinations, blanks were run on freshly redistilled (new) 2-EtN from NASA-LeRC. The best results indicate 1.2 mg gum/100 g fuel, which must correspond to gum formed during the determination or during distillation at 13 torr at SRI. This high gum content in the blank is not surprising, considering the remarkable reactivity of EtN in oxidation and gum formation (Table 4). What is remarkable is that this gum content of this blank is higher than in many of the stressed samples supplied by NASA LeRC. These results may mean that the stressing at NASA-LeRC produced a retarder (e.g., 2-naphthol) that retarded gum formation during gum determination. An alternative explanation is that distillation at 13 torr of the new EtN from NASA-LeRC somehow gave a different material than what was used in their stress experiments.

9. CONCLUSIONS

Combining measurements of rates of oxidation and gum formation is a new and greatly improved approach to studying fuel stability. There is a close proportionality between these two rates in oxidations of a single fuel, but the ratio of these rates among fuels shows a wide range of efficiencies of gum formation for the oxygen absorbed. To a first approximation, pure hydrocarbons oxidize faster than the fuels, but the fuels give more gum for the oxygen absorbed. EtN is the fastest oxidizer and gum former of all the substrates that we have studied except indene and N-methylpyrrole, which copolymerize with oxygen and are therefore in a separate class of materials. EtN is comparable to the fuels in gum formed for the oxygen absorbed.

The compositions of jet Fuels A, B, and C were determined by high-resolution field ionization mass spectrometry (FIMS). Fuel stability decreases with increasing concentration of alkylnaphthalenes, with stable Fuel A having the least and unstable Fuel C the most. Thus, fuel instability appears to be associated mostly with unsaturated compounds, alkylnaphthalenes, and acenaphthenes, not with paraffins, alicyclics, or alkylbenzenes.

Oxidations at 130°C without added initiator and at 100°C with added $t\text{-Bu}_2\text{O}_2$ indicate that different fuels have different abilities to use the hydroperoxides formed to continue oxidation chains. Thus, several reactive hydrocarbons oxidize faster at 130°C than at 100°C, indicating that self-initiation is facile enough at 130°C that no additional initiator is required. Fuels A, 10, and 13 oxidize faster at 100°C, indicating that self-initiation is more difficult or that there is self-retardation by the fuel or its oxidation products.

Although oxidations of most substrates tend to be autocatalytic, oxidations of EtN, Fuel A, and some condensed aromatic hydrocarbons⁹ are autoretarding. We have observed more than 90% conversion of oxygen to

hydroperoxides in 1- to 3-h oxidations of EtN, but FIMS analysis shows considerable proportions of 2-naphthol, as if the hydroperoxide were decomposing during FIMS. Thus, phenols formed from condensed aromatic hydrocarbons might account for self-retardation.

Oxidations of Fuels A, C, and D at low oxygen pressures at 130°C show that both oxidation and gum formation stop when the oxygen pressure is decreased to about 10 torr. Thus, complete removal of oxygen should not be necessary to prevent gum formation on storage.

The dependence of gum formation on the concentration of $t\text{-Bu}_2\text{O}_2$ suggests that the condensation of fuel units to gum and deposit precursors involves interaction of radical pairs and may be a small part of the termination step in free-radical chain oxidations:

10. REMAINING PROBLEMS

This section lists problems arising from this research and some recommendations for future work.

1. This work assumes that deposits on hot parts of engines arise mostly from soluble gum formed during previous storage. This assumption is now being tested at NASA-LeRC. How the fuel and/or soluble gum are converted to hard deposits is a very important but unsolved problem not considered in this report.

2. This and other work has found that insoluble (precipitated) gum is only a small proportion of the total gum. This work assumes that the insoluble gum makes only a small contribution to the hard deposits. This assumption needs to be tested. Soluble and insoluble gum should be measured and analyzed as a function of oxidation time with at least one fuel.

3. Reproducibility of oxidations with some fuels has been good, with others, poor. One possible variable is the Pyrex flasks used. They are now being baked before use in a glass annealing oven. Alkali washes to remove phenols from fuels should be tested when the need arises.

4. The very rapid oxidation and gum formation from the new, purified 2-EtN need to be investigated further. Is this oxidation self-retarding? What is the effect of added 2-naphthol, a possible oxidation product? What is the order of these reactions on t-Bu₂O₂? Why is this hydrocarbon such a fast gum-former?

5. 2-Methylnaphthalene should be purified and oxidized to see how it compares with pure EtN.

6. The oxidation of jet Fuel B acts as if a stabilizer had been added. This fuel should be washed with alcoholic KOH and retested.

7. The oxidation of tetralin/dodecane mixtures gave very peculiar results (see Figure 3). Because results at 100° and 130°C are qualitatively similar, some of the results may be real and significant for understanding fuel stability. The results with the most practical potential are those obtained with 90% and 100% dodecane, but because these experiments were performed several months apart, they should be checked before the investigation of these mixtures is extended.

8. Previous tests for coupling of fuel by hydroperoxides were done with fuels of low hydroperoxide content. Now that we know that a 3-h oxidation of EtN at 130°C gives 90% yield of hydroperoxide on the oxygen absorbed, such a mixture should be heated in vacuum to see how much additional gum is formed.

9. After our gum determinations, the residues have survived many hours at 200°C and so they do not contain peroxide links. If the fuel units are joined by C-C links or C-O-C links, how are they formed?

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