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We examined two aspects of the stability of diesel fuels in storage: the formation of sediments in suspension, which subsequently clog filters, and the formation of soluble gum, which passes the filters but then forms hard deposits on hot engine parts. Research on fuel stability at SRI during the last 6 years has shown that soluble gum appears first on storage, and then part of it grows into sediment. If the oxidation mixture is agitated gently, the precipitating gum grows on the surface gum, and no loose sediment is formed. We distinguished three mechanisms of gum formation: (1) a process intimately associated with chain propagation and termination during oxidation, (2) a coupling of fuel molecules by decomposing peroxides in the absence of oxygen, and (3) a condensation of naphthols and			
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aldehydes from the oxidation of alkylnaphthalenes. The polymeric oxidation products from a JP-8 fuel are shown to be largely responsible for deposits in the Jet Fuel Thermal Oxidation Tester (JFTOT). JES) ←

Oxidations of several pure hydrocarbons at 100° and 43°C gave a wider range of reactivities but no gum formation. Oxidations of fuels give gums at 100° and 130°C in about the same ratios as oxygen uptake; oxygen rate dependence on added initiator showed a range from zero to first order, indicating several different mechanisms for oxidation.

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GUM AND DEPOSIT FORMATION IN DIESEL FUELS

FINAL REPORT

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May 25, 1988

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INTRODUCTION

The principal investigator, Dr. Frank R. Mayo, died in October 1987. This Final Report summarizes work conducted by him under Army Research Office Contract DAAG29-84-K-0161 on the stability of hydrocarbon fuels. Two reprints and a manuscript (Appendices A through C) provide many of the data for this report.

Many fuels oxidize slowly during storage, and the sediment that forms may precipitate and clog filters. When the filtered fuel, containing soluble gum, comes in contact with hot metal, it may leave hard deposits that clog screens and narrow passages, making diesel and jet turbine engines inoperable. The clogging process is difficult to study because the yields of problem-causing deposits are small compared with the large volumes of fuel passing through filters and small openings.

It is generally accepted that formation of both sediment and hard deposits results from oxidation of fuel, mostly during storage. Deaerated fuels require higher temperatures to produce deposits.

The objectives of this work were to devise specifications for stable diesel fuels, a test for the stability of fuel on hand, and a mechanism for the formation of hard deposits from soluble gum on hot metal. The specifications for stable diesel fuels and the test for the stability of fuels are not addressed in this report.

EXPERIMENTAL METHODS AND RESULTS

Oxidations at 130°C

Research at SRI International on diesel fuel stability has been supported by the Army Research Office for 6 years (Contract DAAG29-84-K-0161); in addition, NASA supported research on jet turbine fuels for the first 3 years of that period (Contract NAS3-22510). Generally, in these experiments, the fuels were distilled in vacuum to remove preexistent gum. We then measured the oxygen absorbed from air at constant temperature and the amounts of soluble gum and sediment formed. Most previous investigators measured sediment only, which is a minor proportion of the total oxidation product. Our work began with experiments at 130°C, where most oxidations proceed at a convenient rate without added initiator.¹ We used field ionization mass spectrometry (FIMS) to identify the components of the fuels and the oxidation products, with very little fragmentation of either.

Experiments with an unstable fuel showed that dimeric and trimeric oxidation products accumulated in solution and then a precipitate formed, with partial clearing of the discolored oxidized solution. This observation is our best evidence that sediment comes from growth and accumulation of soluble gum. Experiments were also performed with pure hydrocarbons, n-dodecane, Tetralin, 1-phenylhexane, and phenylcyclohexane, which never gave any sediment, so that the oxidation products could be identified by molecular weight alone. The monomeric oxidation products were the hydroperoxides and the related alcohols and ketones. Dimeric and trimeric products were also found; they contained two or three complete hydrocarbon residues, less a few hydrogen atoms, and up to five oxygen atoms per molecule, but how the oxygen is distributed among peroxide, alcohol, ketone, and ether groups is unknown.

A preliminary survey of nine diesel and two jet turbine fuels showed a wide range in rates of oxygen absorption and times at which sediment appeared, but there was no correlation between the oxygen

absorbed and appearance of sediment. All the fuels absorbed oxygen slower than n-dodecane, although two were nearly as fast. Addition of 0.1 M t-Bu₂O₂ increased rates of oxygen absorption tenfold.

Simultaneous measurement of oxygen consumption and gum formation showed that the pure hydrocarbons oxidize much faster than most fuels. There is a different but somewhat similar order for rates of gum formation, with some overlap among pure hydrocarbons and fuels. However, the ratio of rate of gum formation to rate of oxygen absorption measures the milligrams of gum produced per μ mole of O₂ absorbed. By this relation, the fuels give much more gum for the oxygen absorbed than most pure hydrocarbons. A notable exception is 2-ethylnaphthalene, which has the highest rate of gum formation that we have measured and gives more gum for the oxygen absorbed than some fuels.

N-Methylpyrrole and indene are in a class by themselves and are not included in the discussion above. They have higher rates of oxygen absorption and gum formation and give more gum for the oxygen absorbed than any other substances we have tested. They are unacceptable in fuels that are stored.

Cooxidations, especially of small proportions of indene or N-methylpyrrole in dodecane led to the following conclusions. To affect the rate of oxidation, minor components of oxidation mixtures have to be very reactive, and then they are rapidly consumed. These reactive components may either accelerate or retard oxidation of the major component, depending on their proportions. We have found no example of a catalytic effect (without consumption) of a reactive additive.

Metal Surface Effects in Fuel Oxidation

One of our objectives was to determine the effect of metal surfaces on fuel stability. However, a book appeared that treated this subject competently.² The book has been translated but not published by NASA,³ and both versions have a very limited availability in the United States. Chapter 6 deals with relative rates of oxidation and gum formation in the presence of many metal and alloy surfaces. In this

section, review this chapter and draw some conclusions.

The authors used 0.5 g of metal powder in 50 g of T-6 jet fuel for their experiments. This fuel was produced by hydrodearomatization. It contains no significant quantities of N, and S and has a low tendency toward deposit formation in fuel systems. Some of its properties follow: <10% boiling below 220°C, <98% below 315°C; density at 20°C, 840 g/L; <22% aromatic hydrocarbons, <1.5% bicyclic aromatic hydrocarbons. Oxygen absorption was measured over an unstated period at 150°C and presented as the quotients of the rates of oxygen absorptions with and without metal. At the ends of the experiments, solid products and soluble gum were determined. These are presented as milligrams of material per 100 g of fuel and also as the quotients of these weights in the presence and absence of metal surfaces. These gum data are treated as if they were rates over the same periods as the corresponding oxygen absorptions.

Table 1 summarizes the results in Table 6.3 on pages 208-209 of the book. We have added code letters and arranged the relative rates of oxidation in order of decreasing rates. These relative rates range from eight times to one-seventh the rate in the absence of metal (q). The second column of figures gives the relative rates of gum formation in order of decreasing rates; the code letters are repeated because the orders in the two columns, though similar, are not identical. The spread in rates of gum formation is small, from one-half to twice the rate in the absence of metal. The third column of figures shows the quotients of the same code numbers in the first two columns, arranged in order of decreasing magnitude. The larger numbers at the top of this column show that more oxygen is required to produce a milligram of gum with these metals; the small numbers at the bottom show that these metals give the most gum for the oxygen absorbed.

Denisov and Kovalev conclude that the principal effect of the metal surfaces is to affect the rate of homogeneous oxidation by decomposing hydroperoxides on the metal surface. If this decomposition produces

Table 1
OXYGEN ABSORPTION AND GUM FORMATION BY T-6 JET

Code Letter	Metal Surface ^a	Relative R_o^b	Relative R_g^c	Relative R_o/R_g
a	100 Cr	8.12	a no datum	a no datum
b	Cu +20 Pb ^e	5.16	d 2.16 ^d	c 2.54
c	Cu +11 Pb +10 Sn	5.16	b 2.04 ^d	b 2.53
d	100 Pb	5.08	c 2.03	d 2.35
e	Cu +11 Al ^f	3.12	f 1.76	e 1.91
f	65 Cu +33 Zn + 2 Pb	3.10	e 1.63	g 1.90
g	Cu +10 Al ^g	3.02	g 1.59	p 1.84
h	Cu + 6.2 Sb	2.57	h 1.51 ^d	o 1.77
i	100 Cu	2.51	i 1.49	f 1.76
j	Stainless steel	1.96	w 1.44	m 1.75
k	60 Cu + 40 Zn	1.86	j 1.31	h 1.70
l	Fe + 12 Cr	1.86	k 1.18	i 1.68
m	100 Fe	1.56	l 1.13	l 1.65
n	100 Al	1.55	q 1.000	k 1.58
o	100 Sn	1.47	n 0.99	n 1.57
p	Low-Ni stainless	1.42	m 0.89 ^d	s 1.56
q	<u>No metal</u>	<u>1.000</u>	x 0.88 ^d	j 1.50
r	100 Zn	0.88	u 0.86	r 1.09
s	100 Mo	0.78	o 0.83	q 1.000
t	100 Nb	0.78	v 0.81	t 0.99
u	100 Mg	0.70	t 0.79	w 0.81
v	100 Ni	0.24	p 0.77	v 0.39
w	100 V	0.14	v 0.62	x 0.16
x	100 W	0.14	s 0.50 ^d	w 0.097

^a Metal powder, composition in weight %, with a surface area of about 300 cm²/L. However, a, m, n, r, t, and v apparently have surface areas up to 19000 cm²/L.

^b (Rate of oxygen absorption with metal)/(Rate of oxygen absorption without metal). Latter rate was 1.97×10^{-5} M^{1/2}/sec.

^c (Gum + deposit with metal)/(gum + deposit without metal). Latter number is 57.0 mg /100g fuel.

^d Deposit noted. ^e +3 each Zn, Sb. ^f +5.5 each Fe, Ni. ^g +3 Fe + 1.5Mn.

free radicals, the oxidation is accelerated; if it does not, the oxidation is retarded because the hydroperoxide is wasted.

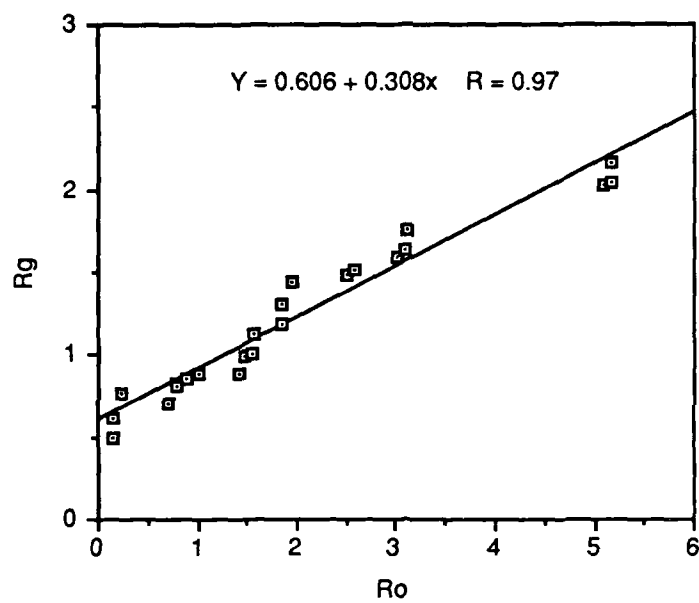
Figure 1 is a revision of Denisov and Kovalev's Figure 6.2 on page 210. The straight line corresponds to our correlation of the data. Although this line predicts considerable gum formation without any oxidation, it shows that, generally, rates of oxidation correlate well with rates of gum formation. Chromium (a), which causes the fastest oxidation, does not appear in Figure 1 because no gum data are available.

We conclude that the effects of metal surfaces on rates of oxygen absorption and gum formation are not now a promising field for investigation. Even with 300 cm² of surface per liter of fuel, the effects of the metals and alloys tested are small to moderate, and the effects in larger containers would be less. Our data suggest that differences among fuels are greater than differences among effects of metals (see below). Use of the proper stabilizers (e.g., BHT, Ionol) will probably essentially eliminate the effects of metals on the homogeneous reactions.

Oxidations at 100°C

Our work at 130°C was followed by experiments at 100°C, mostly with added t-Bu₂O₂ to accelerate reactions.⁴ Both papers^{1,4} contain references to the relevant literature that are not repeated here. Copies of the papers are appended to this report. The t-Bu₂O₂ experiments were needed to accelerate reactions at lower temperatures nearer to service temperatures and to determine the effects of initiator concentrations on rates of oxidation and gum formation.

At 100°C, oxidations of dodecane, Tetralin, and two fuels are autocatalytic; oxidations of the alkylnaphthalenes and all the other fuels are self-retarding. With other pure hydrocarbons, trends are not clear. No precipitate was obtained from any pure hydrocarbon, but most of the fuels gave adherent (not particulate) precipitates (as well as soluble gum) as uniform films on the parts of the reactors that were in



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Figure 1. Relative rates of oxidation vs gum formation.

contact with liquid. We attribute the predominance of film formation to the gentle agitation that was used and a tendency of precipitating gum to precipitate on other gum. These results suggest that constant gentle stirring of a fuel during storage might cause the sediment to adhere to the tank walls, thereby reducing or even eliminating filtration problems.

2-Methylnaphthalene and three fuels oxidize faster at 100°C with 0.03 M $t\text{-Bu}_2\text{O}_2$ than at 130°C without initiator. Thus, these substrates have less ability to initiate and maintain their own oxidations than the other and faster oxidizing fuels; they are self-retarding in oxidations.

The ratios of the rates of gum formation and oxygen absorption indicate the relative amounts of gum formed for the oxygen absorbed. If the mixture of mechanisms for gum formation is the same at 100°C and 130°C, then the ratios at the two temperatures should be the same; the majority of them are similar, even with large differences in individual rates of gum formation and oxygen absorption. Details of these measurements are found in the paper on 100°C oxidations.⁴

Experiments with different concentrations of $t\text{-Bu}_2\text{O}_2$ show three patterns for rates of oxidation.⁴ In the classic pattern, the rate of oxidation is half-order in initiator, corresponding to an initiation that is first order in initiator and a termination that is second order in peroxy radicals. However, in a second pattern, the rate of oxidation is nearly independent of initiator concentration. We propose that this fast oxidation gives a moderately unstable peroxide, the initiating effect of which swamps that of $t\text{-Bu}_2\text{O}_2$. The third pattern, shown best by two fuels,⁴ gives a rate of oxidation that is first order in initiator, characteristic of inhibited oxidations. Many hydrocarbons and fuels tested fall between these simple patterns.

A later set of measurements on the rates of gum formation and oxidation (R_g/R_o) is shown in Table 2 for several fuels. These data show that this ratio is in the range of 0.2-4.4 for all but two fuels.

Table 2

COMPARISON OF RATES OF OXIDATION AND GUM FORMATION AT 100° AND 130°C^a

Fuel	R _o 130°	R _o 100°	$\frac{R_o}{R_o} \frac{130}{100}$	Fuel	R _g 130°	R _g 100°	$\frac{R_g}{R_g} \frac{130}{100}$	Fuel	R _g /R _o 130°	R _g /R _o 100°	$\frac{R_g/R_o}{R_g/R_o} \frac{130}{100}$
TET	69	31 ^b	2.2	EtN	42	19	2.2	DOD	0.018	0.092	0.20
EtN	64	36	1.8	B	13	0.54	24	1-PH	0.027	0.39	0.07
1-PH	28	5.0	5.6	TET	6.9	13 ^b	0.53	TET	0.10	0.39 ^b	0.26
PCH	27	7.6	3.6	PCH	5.7	0.90	6.3	PCH	0.21	0.12	1.8
B	22	3.6	6.1	C	5.0	0.42	12	14	0.38	2.8	0.014
DOD	15	3.2	4.8	13	0.85	0.42	2.0	B	0.59	0.15	3.9
C	3.8	3.2	1.2	1-PH	0.75	1.9	0.39	EtN	0.66	0.53	1.3
14	0.77	0.22	3.5	14	0.30	0.62	0.31	C	1.33	0.13	10
13	0.20	0.44	0.45	DOD	0.27	0.29	0.93	A	1.45	0.95	1.5
MeN	0.098	0.22	0.45	MeN	0.16	0.87	5.4	10	1.47	1.5 ^b	0.98
10	0.096	0.29 ^b	0.33	10	0.14	0.44 ^b	0.32	MeN	1.65	1.4	2.4
A	0.038	0.30	0.13	A	0.055	0.28	0.20	13	4.2	0.95	4.4
Spread ^c	1816	164	47		764	83	68		233	30	63

^aRates at 130° were measured without added initiator; rates at 100° were measured with 0.03-0.04 M t-Bu₂O₂. 100° data are from experiments marked with * in Table I.

^bGeometric mean of 0.01 and 0.10M t-Bu₂O₂ rates.

^cRatios of highest to lowest value in each column.

Mechanisms of Gum Formation

We now discuss our three mechanisms of gum formation.^{1,4} The first mechanism is associated with chain propagation and termination during oxidation. When enough oxygen is present to convert nearly all alkyl radicals to alkylperoxy radicals, then one termination mechanism is $2RO_2 \longrightarrow R_2O_2 + O_2$, and this reaction is apparently a start in building up larger molecules. However, this reaction alone gives only dimeric products. To obtain trimeric and heavier products, the R_2O_2 must participate in chain propagation and then in more coupling to $R-O_2-R-O_2-R$, and so on. Experimentally, we find that the orders of rates of oxidation and gum formation in $t\text{-Bu}_2O_2$ are nearly the same even though they vary from 0.3 to 1.0 for different substrates. Thus, it appears that both chain propagation and chain termination contribute to gum and deposit formation.

A second mechanism of gum formation occurs in the absence of oxygen when a peroxide or hydroperoxide decomposes to a pair of alkoxy and/or hydroxy radicals. These radicals abstract hydrogen atoms from adjacent fuel molecules to give alkyl radicals, which combine quickly in a cage or near-cage reaction. Yields of 60% on the peroxide of coupling products have been obtained with ethylnaphthalenes. However, oxygen can intercept the alkyl radicals and convert the coupling to an oxidation reaction. This mechanism may be important in determinations of gum in the absence of oxygen. The postulated peroxides in the original gum may give more thermally stable materials when the concentrates are heated.

A third mechanism is proposed for alkylnaphthalenes because, among the pure hydrocarbons, they have high ratios of gum formation to oxidation. Their hydroperoxides can decompose to naphthols and aldehydes, which may condense to resins. The retarding properties of the naphthols formed may account for the generally low rates of oxidations of fuels and for the self-retarding oxidations of the alkylnaphthalenes and many fuels.

The picture that emerges from our work is that most pure hydrocarbons oxidize by long kinetic chains to give relatively high

yields of hydroperoxides and little gum for the oxygen absorbed. Ethylnaphthalene is outstanding in giving a high rate of gum formation, and methylnaphthalene is notable for giving a very low rate of oxidation, very short kinetic chains, low yields of hydroperoxide, and a high ratio of gum formation to oxidation, more like a fuel. The slow oxidations and high ratios of gum formation to oxidation in fuels may be associated with their contents of alkylnaphthalenes.

Two new approaches to the mechanism of gum and deposit formation were introduced during 1986. They are discussed below.

Deposits from the Jet Fuel Thermal Oxidation Tester (JFTOT). In one approach, a jet fuel of narrow boiling range was oxidized at about 100°C and then separated by fractional distillation in vacuum into (mostly) recovered fuel, monomeric oxidation products (hydroperoxides, alcohols, ketones), and polymeric oxidation products. Results on mixtures of these fractions show that the polymeric oxidation products are the principal contributor to JFTOT deposits (see Appendix C).

Oxidations at 43°C. The second new approach involves oxidations at 43°C, the favored temperature for stability tests. This approach uses the commercial peroxide, Lupersol 221, $(\text{PrO}-\overset{\text{O}}{\text{C}}-\text{O})_2$, which has a half-life of 7 h at 43°C. Thus, more than 90% of this peroxide is decomposed in 24 h and more than 99 percent in 48 h. Tests with a few hydrocarbons and fuels show that some oxidations continue fairly rapidly after 24 h, whereas others show a steadily decreasing rate and still others show intermediate effects. We expect that the persistent oxidations indicate unstable fuels and that the slowest oxidations will correspond to stable fuels; even after the oxidations of the stable fuels have been started, they are not self-sustaining.

RECOMMENDATION FOR FUTURE WORK

The results with metal ions, shown in Table 1, were obtained with a stable jet fuel. A few results might be checked with a stable U.S. fuel (diesel or jet) to see if they are comparable, and an unstable fuel might also be tested. with an unstable fuel. A few oxidation and gum experiments might be done with dissolved metals. The effects of the soluble metals might be larger, but the pattern should be the same, assuming that both dissolved metals and surfaces mostly affect peroxide decomposition and free radical production. The missing effect of a chromium surface on gum formation should be checked to see if it is interesting.

Metals seem to be necessary to convert soluble gums to hard deposits. The effects of dissolved metals and surfaces on this reaction should be checked. This field could be the most important remaining problem in fuel stability.

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Appendix A

GUM AND DEPOSIT FORMATION FROM JET TURBINE
AND DIESEL FUELS AT 130°C

[Published in Ind. Eng. Chem. Prod. Res. Dev., 25, 333 (1986)]

GUM AND DEPOSIT FORMATION FROM JET TURBINE AND DIESEL FUELS AT 130°C

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ABSTRACT

The ultimate objective of this work is to devise an accelerated test to compare rates of soluble gum and deposit formation from jet turbine and diesel fuels in storage and of hard deposits on hot engine parts. This paper describes rates of oxygen absorption and gum formation in air at 130°C. For a single fuel or hydrocarbon, the rate of gum formation is closely proportional to the oxygen absorbed, even when this rate varies with purification and additives. In general, pure hydrocarbons absorb oxygen much faster than the fuels, but the fuels and 2-ethylnaphthalene give more gum for the oxygen absorbed than the other pure hydrocarbons. Gum has two main sources. One appears to be associated with the chain termination mechanism in oxidation, the other with coupling of fuel molecules by peroxides in the absence of oxygen. Other possibilities are discussed.

1. INTRODUCTION

This research is concerned with soluble gum and deposit formation from jet turbine and diesel fuels during storage at ambient temperatures and on oxidations with air at temperatures up to 130°C, and ultimately with the hard, insoluble deposits that form on hot engine parts. These two groups of fuels have similar boiling ranges and are presumed to have the same mechanism of oxidation, but the jet fuels have lower sulfur contents and higher specified thermal stabilities. Extensive previous work has been mostly empirical, measuring deposit, and sometimes soluble gum, formation from numerous fuels at temperatures up to about 150°C. The field has been repeatedly reviewed (see, e.g., Nixon 1962, CRC 1979, Goetzinger et al., 1983).

The consensus is that most gum and deposit formation is associated with oxidation by oxygen but that the rate of oxidation is not a measure of rate of gum formation, that some sulfur, nitrogen, and oxygen compounds increase gum formation and some do not, that the first deposits are often rich in these elements, and that olefins, especially conjugated ones, increase gum and deposit formation.

The object of the fuel research described here is to determine how and why gum and deposits form in very small yields in oxidations of fuels and pure hydrocarbons at 130°C, a convenient reaction temperature. A subsequent paper will describe similar reactions at 100°C with added di-t-butyl peroxide.

We assume that the soluble condensation products (gum) are the principal source of deposits that separate from solution and of the very insoluble carbonaceous deposits that cause engine problems. Whether and how the soluble gum is converted to hard deposits is a major unsolved problem.

Our first publication (Mayo et al., 1976) on fuel stability showed that oxidation of a jet turbine fuel of average molecular weight 198 gave tiny fractions of molecular weight up to 400 or 1500 by gel chromatography and precipitation from pentane. These products contained hydroperoxides, alcohols, ketones, esters, and probably aldehydes. Heating 5% of a fuel hydroperoxide concentrate with fuel in a sealed, evacuated vessel at 200° produced a small brown deposit, part of which had a molecular weight of 1500. Hazlett et al. (1977) investigated the oxidation of n-decane over a stainless steel surface and concluded that deposit formation is closely associated with pyrolysis of hydroperoxides. Ceransky et al. (1985) investigated reactions of n-dodecane in a JFTOT with an aluminum heater at 200 - 400°C. They obtained no deposits but examined the effluent by gc and lc. Decomposition products of dodecyl hydroperoxides and C₂₄ products appeared at the highest temperatures. The present paper will give some support to these suggestions and present alternatives.

This paper differs from most previous papers in four respects. All fuels were distilled in vacuo and stored under nitrogen below 0°C. Thus, we studied the inherent properties of the fuels instead of properties after an unknown history. Second, we measured oxygen absorption and gum formation together and found large differences in the

amount of gum produced for the oxygen absorbed. Third, we dealt mostly with soluble gum formation rather than with deposits (which were measured when found) because none of our pure hydrocarbons and some of our fuels gave no deposits under our experimental conditions. Fourth, gum formation is discussed in terms of two distinct mechanisms, coupling of free radicals during oxidation and coupling of fuel molecules by peroxides in the absence of oxygen. We admit that gum and deposits formation can be augmented temporarily by very reactive nitrogen, oxygen and sulfur compounds in fuels (CRC Report, 1979), but these compounds are soon consumed. We have had no reason to give them special consideration in our fuels.

2. EXPERIMENTAL PROCEDURES

2.1. Fuels

Fuels A and B were stable and moderately stable jet turbine fuels and Fuel C was a No. 2 home heating oil, representing a very unstable jet fuel. All were supplied by Dr. Ed Wong of NASA-Lewis Research Center. The numbered fuels are diesel fuels supplied by Mr. S. R. Westbrook of the U.S. Army Fuels and Lubricants Research Laboratory at San Antonio. The boiling ranges of the most-used fuels are in Table I.

All of our hydrocarbons and fuels were distilled through a Vigreux column at 5-20 torr before use. This step eliminated the highest boiling 2-5% of the fuels but was essential to eliminate whatever gum

had accumulated before the fuel was distilled. The fuels were then stored under nitrogen at -8°C until used. Some of the purchased "pure" hydrocarbons exhibited marked induction periods on oxidation, but in some instances, chromatography through acidic alumina resulted in faster oxidations at fairly steady rates.

Several fuels were chromatographed over acidic alumina and eluted with hexane. The polar constituents were then eluted with ether. Table II summarizes available elemental analyses of fuels, a distillation residue, their polar fractions (see Section 3.4), and their condensed oxidation products. The atomic H/C ratios of the fuels range from 1.62 (Fuel C) to 1.89 (Fuel I), but the residue from the vacuum distillation of "unoxidized" Fuel C contains less hydrogen and nearly 5% oxygen. The gums and deposits from oxidations have still lower H/C ratios and still higher oxygen contents.

Figure 1 shows the gc traces for the polar fractions of Fuels 10 and 13. In Fuel 10, the major components are fluorene ($\text{C}_{13}\text{H}_{10}$), anthracene and phenanthrene ($\text{C}_{14}\text{H}_{10}$), their methyl derivatives ($\text{C}_{15}\text{H}_{12}$), dihydroanthracenes and phenanthrenes ($\text{C}_{14}\text{H}_{12}$), methyl derivatives of the dihydro compounds ($\text{C}_{15}\text{H}_{14}$ and $\text{C}_{16}\text{H}_{12}$), and $\text{C}_{15}\text{H}_{12}$. The polar eluent of Fuel 13 gave a wider mix of products. The identified major peaks are carbazole ($\text{C}_{12}\text{H}_9\text{N}$) and its homologs. The data suggest that the polynuclear aromatic hydrocarbons retard oxidation and gum formation in Fuel 10 and that the carbazoles accelerate oxidation and gum formation in Fuel 13.

Field ionization mass spectrometry (FIMS, also used for spectrum) was used to analyze both unoxidized and oxidized fuels. To obtain the complete molecular weight profiles of unoxidized fuel samples, a

5- μ L sample of the unoxidized fuel was injected through a septum into the evacuated 0.5-L glass expansion bulb of the batch inlet system. The resulting FIMS is therefore a molecular weight profile of the fuel sample. Details are given by Malhotra et al. (1985).

A second field ionization mass spectrometer system was used to analyze deposit precursors. It was equipped with SRI's activated foil field ionization source. Fuel samples were analyzed for deposit precursors using vacuum evaporation preconcentration (St. John et al., 1978). The resulting FIMS represents the composition of the least volatile components of the oxidized fuels, but the cutoff point was not reproducible.

Table III summarizes FIMS of several fuels and illustrates the evolution of our analyses. Analyses marked a come from high resolution FIMS that distinguishes among hydrocarbons with nearly the same molecular weight, but do not include minor components of the fuels. Other analyses are complete. These fuels were analyzed after vacuum distillation but without oxidation. Fuel components are listed according to their z numbers: z is defined by expressing the molecular formula of a hydrocarbon as C_nH_{2n+z} . Thus $z = +2$ includes open-chain alkanes; $z = 0$ includes alkenes and monocyclic alkanes; -2 includes unsaturated cycloalkanes and bicyclic aliphatics; -6 , alkylbenzenes; -8 , indanes and tetralins; -12 , alkylnaphthalenes; and -18 , anthracenes and phenanthrenes.

Figure 7 (presented with Figures 8 to 11 to facilitate comparisons there) represents the molecular weight profile by FIMS for unoxidized Fuel C. The first three numbered peaks differ by 14 units and

correspond to alkylbenzenes, starting with xylenes. The next set of prominent homologs, starting at 142, is mostly alkylnaphthalenes plus some paraffins. Another set, starting at 168, corresponds to acenaphthenes or $z = 0$ compounds. The higher boiling fraction of Fuel 14 is usually rich in hydrocarbon with high z number and may contain some sulfur compounds.

2.2. Oxidations

Our oxidations were performed with ~ 10-mL weighed samples of hydrocarbon or fuel in reactors of measured volume like that shown in Figure 2, usually filled with air at ambient temperature and pressure and then shaken in a silicone oil bath at 130°C. At intervals, the reactors were cooled to room temperature and 70- μ L samples of gas were withdrawn through a septum and analyzed for oxygen/nitrogen ratio by gas chromatography on a 183 x 0.32 cm O.D. stainless steel column packed with 13X molecular sieve and attached to a thermal conductivity detector. The average O_2/N_2 ratio found by gc for fresh air was 0.2553. The O_2/N_2 at the end of a reaction period was compared with that of fresh air at the same time to determine the fraction of oxygen consumed, which was then used with the accepted O_2/N_2 ratio in air, 0.2682. ~ 11 torr pressure of water at 50% relative humidity was neglected.

2.3. Determinations of Gum and Deposits

Soluble gum was determined by evaporating a weighed 4-mL sample of fuel in a stream of nitrogen from a capillary, without spattering, at $>200^{\circ}\text{C}$. The exact temperature depends on the evaporating fuel. Evaporation took place from a 6-mL bottle like that shown in Figure 3, preferably with the capillary resting lightly on the neck of the bottle to avoid return of condensate. Evaporation required 10-20 minutes, was carried nearly to completion, and was followed by prompt cooling under a nitrogen stream. The residue (~ 0.1 mL) was then transferred with 1-2 mL of reagent acetone to a tared aluminum dish, 25 mm in diameter, weighing about 50 mg. This sample was then heated and brought to nearly constant weight (~ 20 h) in a gentle stream of nitrogen in a furnace at 200°C . Weighings were made on a Perkin Elmer AD-2Z Electro Micro Balance. This method usually gave results reproducible within 30% at low levels of gum, about 5% at higher levels. In general, the gum data are averages of two determinations.

Insoluble gum usually appeared as a fairly homogeneous dark film on the glass in contact with the fuel. After removal of the fuel, the film was rinsed with hexane and then dissolved in small portions of reagent acetone or equal parts of acetone, ethanol, and benzene. The solutions were transferred to our aluminum evaporating dishes and the residues dried in vacuum. We propose that agitation of our oxidation flasks caused deposition of films instead of sediments, consistent with our idea that solids come from soluble gum.

3. OXIDATION PRODUCTS

3.1. Fuel C

Table IV summarizes the results of an oxidation of distilled Fuel C; they show steady increases in rate of oxygen absorption (autocatalysis) and in concentration of higher molecular weight material.

Figure 4 shows the molecular weight profile of distilled but unoxidized Fuel C. The abscissa corresponds to the mass number of the ions in the mass spectrometer. The full ordinate is 10% of the sum of all the ion intensities. Thus the 156 mass unit bar means that 8.8% of the whole fuel consists of material of molecular weight 156. All the principal components have even mass numbers, as will all compounds of C, H, and O (but not N). However, 1.1% of natural C is ^{13}C , and so for any 12-carbon compound, about 13% of the molecules will contain one ^{13}C and have a molecular weight that is higher by one unit. Therefore, all the major peaks will have an obvious satellite with mass number one unit greater. Thus the 156 peak in Figure 4 is accompanied by a 157 peak that is 13% as high. Other odd mass number are fragments of molecules. Homologous series were discussed in Section 2.1.

Figures 5 to 8 summarize FIMS data after the four periods indicated in Table IV. Each sample was spiked with 20 ppm of decacyclene ($\text{C}_{36}\text{H}_{18}$, molecular weight 450). The ordinate and the numbers in the upper left corners of the figures are the percentages of the summed ion intensities. Figure 5 shows the highest molecular weight fraction of distilled but unoxidized Fuel C. Traces of the higher molecular weight

products can be seen in Figure 4. Figure 5 brings out the minute traces of a great number of compounds swept over in the distillation or formed between distillation and taking the spectrum.

Figures 6 to 8 show the FIMS after the three oxidation periods in Table IV. Most of the material of molecular weight ~ 250 corresponds to incorporation of one to four atoms of oxygen into fuel molecules (precursor monomers), retained because they are less volatile than the fuel. Most of the material with molecular weights between 300 and 450 represents dimers of monomeric products plus oxygen. Material of intermediate molecular weight presumably represents condensation of monomer precursors and their fragments formed by cleavage of alkoxy radicals. Figures 6 and 7 show that the development of monomeric precursors and dimeric precursors, like the rate of oxygen absorption, is autocatalytic. Development of trimers can also be seen.

During the oxidation period that ended with the product in Figure 8, the solution became lighter and a dark brown precipitate formed on the reactor walls. During this period, the concentration of precursor monomers increased sharply (these may be the ones that don't condense easily); and the concentrations of dimers and trimers appear to decrease perceptibly (compared with the decacyclene standard), probably because they have separated from the fuel mixture. This experiment is our best evidence that soluble gum evolves into fuel-insoluble deposits.

The precipitate that formed, after washing with hexane and drying, weighed about 3 mg/g of initial fuel. Acetone extraction of this residue gave 0.137 mg of extract/g initial fuel; its $\bar{M}_n$ in N-dimethyl formamide was ~ 600 . It therefore appears that the deposits precipitate

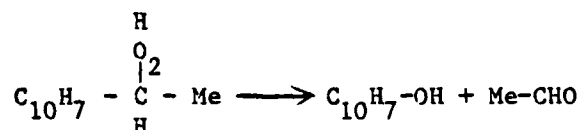
because of their heteroatom contents as well as their higher molecular weights.

Although the research described above provides excellent evidence for the deposit formation by stepwise condensation of deposit precursors, the data give us little indication of the chemical structures or mechanisms involved. However, there is an indication with Fuel C of a problem that becomes much more obvious with n-dodecane. Comparing Figures 5 through 8 with Figure 4 shows that the oxidized products have higher proportions of materials with odd mass numbers (in the spaces between the peaks with even mass numbers). Odd mass numbers in C, H, and O compounds, except those due to ^{13}C or N compounds, mean that fragmentation of parent molecules has occurred in the FIMS.

3.2. Pure Hydrocarbons

The multiple oxidation products from the many components of Fuel C made further examination of oxidation products of Fuel C unpromising and so our investigation of oxidation products turned to pure hydrocarbons. This work encountered two problems, decomposition of some products during FIMS, and low yields of gum. We take up first the monomeric products (e.g., C_{12} products from n-dodecane) and then polymeric products (e.g., with multiples of 12 carbon atoms). Because the extents of evaporation of the oxidation products in FIMS varied, so do the proportions of monomeric and dimeric products reported. The principal products measured by FIMS are therefore not listed in absolute terms but in order of their observed abundance.

The major primary oxidation products are the hydroperoxides, as shown by titration (notes c-e to Table VIII. However, the hydroperoxides are decomposed during FIMS. Thus, the DOD oxidation products (Table V) show no ions from the hydroperoxide and only a few from the alcohol. Unoxidized 3-dodecanol shows little parent ion; 2-docanone is also cleaved during FIMS. Instead, the hydroperoxide and alcohol decomposition products predominate: dodecene, dodecyl, dodecyloxy. However heating the oxidation product to 180°C in the absence of air showed that it still contained labile products such as hydroperoxides. The hydroperoxides from the phenylhexanes and tetralin are more stable (Table VI) but the FIMS show more of the ion corresponding to loss of -O₂H from the hydroperoxide. 2-Ethyl-naphthalene shows no significant amounts of hydroperoxide but many products corresponding to a reaction in the FIMS:



This reaction resembles to the liquid-phase, acid-catalyzed rearrangement of cumyl hydroperoxide to phenol and acetone.

We now consider the polymeric oxidation products. The products from dodecane (Table VII) still show many products corresponding to loss of H or OH (odd mass numbers) but no firm indication of cleavage of the dodecane skeleton. Some unsubstituted dimer and trimer were detected, but most of the dimers contain oxygen, up to five atoms per dimer, apparently from the associated oxidation and coupling process. The prominent dimers from the other hydrocarbons also contain oxygen (Table

VI) but the unsubstituted dimer is prominent in the product from phenylcyclohexane. Thus, coupling of hydrocarbons with benzyl hydrogen atoms may be easier than with dodecane.

We know considerable about the structures of the polymeric products; they contain an integral number of hydrocarbon units (minus two hydrogen atoms per coupling) and several oxygen atoms. What we don't know is the distribution of oxygen atoms among peroxide, ether, alcohol, and carbonyl groups.

4. RATES OF OXIDATION

4.1. Preliminary Study

In our first oxidations, we measured rates of oxygen absorption by several fuels at 130° and observed the points where formation of a precipitate, on the vessel walls or in suspension, was first seen, as noted by solid points. The results are shown in Figure 9.

Figure 9 shows a wide range of rates of oxidation. Deposits appeared in most fuels at about 100 to 150 hours, but over a considerable range of oxygen absorptions. Fuel 8 and dodecane, which oxidized the fastest, gave no deposits. The slow oxidizing jet turbine Fuel A also gave no deposits. Addition of 0.01 M $t\text{-Bu}_2\text{O}_2$ to fuels 12 and 15 greatly accelerated rates of oxygen absorption but had no large effect on the amount of oxygen consumed at the point where deposits appeared. Fuel C, the least stable fuel, oxidized fairly rapidly and had absorbed the least oxygen when deposits appeared. Thus, there is no obvious correlation between rate or amount of oxygen absorption and sediment formation.

Curves with fuel numbers in circles were oxidized at 56°C with 2500 rad/hr of γ -radiation. The radiation made the oxygen absorption at 56° about half as fast as at 130°, but no deposits appeared in any of the radiated runs, even though Fuels 3 and 14 had absorbed more than enough oxygen to give a precipitate at 130°C. Apparently, at 56°C the gum molecules did not become large enough to precipitate.

CRC Report No. 509 (p. 75, 1979) concluded that deposits separate mostly because of the incorporation of heteroatoms into the oxidation products rather than from increases in molecular weight. We propose that precipitate formation also depends on the aromaticity and solvent properties of fuel, and that gum formation, which usually far outruns precipitate formation (see, e.g., Stavinocha, Brinkman, 1980), and precipitate formation together would be a better guide to the formation of hard deposits on hot engine parts.

4.2. Rates of Oxidation and Gum Formation in Air at 130°C

Table VIII contains most of the data on which this paper is based, usually the better experiments, and abbreviations for the fuels used. The experiments are numbered in nearly the order in which they were done. "Dup." on some runs indicates that substantially the same results were obtained in another experiment. Although additional data points were measured for most runs, usually only the first and last are given in Table VIII to provide a measure of autocatalysis or self-retardation. In most runs, gum was determined only on the final oxidation product; the rates of oxygen absorption (R_o) and gum formation (R_g) are average values since zero times.

Yields of hydroperoxides on the oxygen absorbed are given in footnotes c to f. The yields appears to be highest with the fastest oxidizing fuels but solvent effects apparently affect the stabilities of the peroxides.

About half the oxidations were autocatalytic, but those of EtN and Fuels A, 14A, and 15 were autoretarding. IND, NMP, 1-PH, and Fuels C, 1, 10, and 14B showed no clear trend. Fuel B oxidized rapidly after a long induction period and apparently contained a retarder. The first oxidation of DOD (B59) was the slowest. The last two runs shown, G69 and K80 (where the DOD was washed with concentrated H_2SO_4) agree well. The oxygen supply for the EtN run, J44, was nearly depleted in one hour; the K86 runs, where fresh air was supplied after 30 minutes, are faster. Without further addition of oxygen, the indicated R_0 during the second hour is 20. The decrease is probably real, because 35% of the oxygen in the last charge remained.

Chromatography over acidic alumina caused faster oxidation of BCH, the old and slower oxidizing EtN, and Fuels C, 1, 10, and 15, but slowed the oxidation of Fuel 14. Usually, the reconstituted fuels, where the original proportions of the ether extracts of the alumina were put back into the hexane extracts, oxidized at the original rate. In oxidations of Fuel 1, the original distilled fuel oxidized slowest the reconstituted, fastest. These data suggest that alumina may remove either a retarder or an accelerator, or both, and that the latter is eluted by ether while the former is not recovered. However, these effects are not well beyond experimental error.

Figure 10 shows a clear pattern with Fuel 10 where experiments with distilled, (lower set of solid points), chromatographed, (upper set of solid points), and reconstituted (middle set of unfilled points) fuel were run in triplicate. The intermediate runs in each set are listed in Table VIII as F51, F54, and F58. The chromatographed fuel oxidized fastest, at least initially, but the distilled and reconstituted fuels are almost indistinguishable. Figure 10 shows the consistency of our data on R_o and R_g and their close relation; gum formation in all runs increases regularly with the oxygen absorbed. Precipitate formation is delayed in oxidation of the chromatographed material, which gives only an average amount of total gum. 0.25% of the original Fuel 10 was eluted from the alumina by ether. Figure 11 shows the effects of returning one-tenth (F64) and ten times (F65) this much of polar fraction to the fuel eluted by hexane. F64 shows no significant effect on R_o but precipitate formation is delayed. F65 shows a marked increase in R_o and earlier formation of precipitate. Comparison of results in Figures 10 and 11 suggests that the polar fraction from Fuel 10 contains both a retarder and an accelerator, but an effect of the latter appears only with a large proportion of polar fraction.

In general, Table VIII shows that none of the pure hydrocarbons give insoluble precipitates during oxidation but all the fuels do. The single exception is Experiment H34, with 11.8 mole % TET in DOD. During this experiment, 630 mg of oily precipitate and 1543 mg of white crystals per 100 g hydrocarbon separated during the oxidation. Analyses are in Table II. They suggest that the crystals correspond to impure tetralin hydroperoxide, melting at 43-45°C (literature, 56°). Analysis of the oil corresponded closely to a dihydroperoxide of tetralin. The

yields of gum in the homogeneous solution were unexpectedly low, probably because much of the soluble gum dissolved in the precipitates. It appears that even the monomeric oxidation products of TET are insoluble in DOD.

Figure 10 shows that our measurements of R_o and R_g are reliable and consistent but that some unknown variable causes small differences in R_o and parallel differences in R_g among supposedly identical runs. The differences might be associated with the Pyrex reactor walls. At first, the reaction flasks were rinsed with reagent acetone; later they were treated with boiling nitric acid and rinsed; recently they have been rinsed with reagent acetone and then heated in a glass annealing oven, after which they glisten like new.

5. CORRELATION OF RATES OF OXIDATION AND GUM FORMATION

Table IX summarizes and ranks rates of oxidation and gum formation from Table VIII, using the data marked (*) in that table, which are usually from the longer runs. These average values neglect autocatalysis and autoretardation. However, the range of results in each column of data is so great that changing rates are not critical to the rankings. The data in the R_o and R_g columns are listed in order of decreasing magnitude but the ratios of R_o/R_g are listed in order of increasing magnitude, to correspond better to the order for R_o . The orders for substrates are somewhat different in each column and so the

fuel abbreviations are listed with each column of figures. NMP and IND absorb oxygen fastest. At least IND, (Russell, 1956) and probably NMP, absorb oxygen below 100°C to give nearly 100% yield of a nonvolatile, alternating polyperoxide. Although this peroxide as such does not survive our gum test, the residual gum and the yields of gum for the oxygen absorbed are higher than for any other substrate that we have tested (last column). These conjugated unsaturated compounds are not acceptable in fuels and they are neglected in the following discussion.

Among the other hydrocarbons and fuels, the rates of oxidation vary over a range of 1800. The pure hydrocarbons oxidize faster than the fuels, with a range in rates of 4.6. There is a larger spread of 580 between Fuels B and A. The upper part of the R_o column lists all the hydrocarbons and only one fuel, B. Table 8 shows that B would have a much lower R_o at a shorter reaction time.

Rates of gum formation for EtN and Fuel A vary by a factor of nearly 800. To a first approximation, the order in the R_g column resembles that in the R_o column, but there is more overlap among the hydrocarbons and fuels. The discrepancies between R_o and R_g are partly resolved in the last R_g/R_o column where the largest numbers correspond to the formation of the most gum for the oxygen absorbed. Because of parallels between R_o and R_g , the spread in the R_g/R_o ratios is smaller, about 230 between DOD and Fuel 13. Except for EtN, all the hydrocarbons produce less gum for the oxygen absorbed than all the fuels.

The instabilities of Fuels A to C increase with their alkyl naphthalene contents. All the diesel fuels are unstable as measured by their R_g/R_o ratios (Section 3.4) and contain substantial

proportions of naphthalenes and more condensed aromatic hydrocarbons. Thus, the alkylated condensed aromatic hydrocarbons (not alkylbenzenes) present in all the fuels appear to be the an important cause of gum formation.

6. COOXIDATIONS OF FUELS AND ADDITIVES

6.1. Previous Work

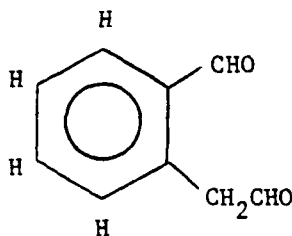
In discussing our work on oxidations of mixtures, we shall present first a summary of previous work, starting with the classic cooxidation of cumene and tetralin by Russell (1955). These oxidations were done in the presence of 0.02 M t-butyl perbenzoate to give a constant rate of initiation at 90°C. The pure TET oxidized three times as fast as pure cumene, but there is a minimum rate at 2.8% TET. The important point is that addition of a fast-oxidizing hydrocarbon to a slow-oxidizing hydrocarbon may either retard or accelerate the oxidation of the slow hydrocarbon, depending on how much of the fast hydrocarbon is present. The explanation by Russell (1955) still holds. A sharp minimum in rate of cooxidation requires that one component have a high propagation constant and the other have a low termination constant, which is characteristic of t-alkylperoxy radicals. Plots of rates of cooxidations of most hydrocarbon mixtures are linear or slightly curving functions between the rates of oxidation of the pure hydrocarbons, often concave upward (Alagy et al., 1961; Mayo et al., 1968). We know of no mixture that oxidizes faster than either component.

6.2. Dodecane and Indene

We shall use these relations first to account qualitatively for our results on the oxidations of DOD with small proportions of IND.

As shown in Figure 12 IND alone oxidizes faster than DOD, and has larger propagation and termination constants than DOD (Howard, 1972). In cooxidations with 0.009 M IND, IND retards the oxidation of DOD, but then the rate increases with increasing concentrations of IND and acts increasingly like oxidations of IND in an inert solvent.

The oxidation of IND alone gives a polyperoxide in high yield (Russell, 1956). The high molecular weight portion is only sparingly soluble in hydrocarbons. By analogy with poly(styrene peroxide) (Mayo, Miller, 1956), poly(indene peroxide) probably decomposes thermally to give a dialdehyde,



much of which would be lost in our usual gum test. In our cooxidations of DOD and IND, some light-colored oily reaction products separated during the oxidation and were later collected by centrifuging, but no solid precipitates were observed. To include a maximum of poly(indene peroxide) in the gum, we vacuum-distilled the reaction mixture almost to dryness below 100°C. Gum was then determined as usual except that the drying temperature was held to 100°C for 17 hours. All IND experiments

gave more gum than oxidized DOD, even though more oxygen was absorbed in the DOD experiments. Gum formation increases rapidly with the concentration of IND up to 0.1 M indene, where gum formation was >50 times that in with DOD.

Some gum determinations were made at 200°C instead of at 100°C; these results are also shown in Figure 12. The data suggest that the 200°C procedure finds only about half as much gum as the 100°C procedure for low amounts of gum, but that the difference decreases as the gum increases.

6.3. Other Dodecane/Hydrocarbon Mixtures

Cooxidations at 130°C of pure DOD and of ~10% of three pure hydrocarbons with DOD are described in Table VIII and Figure 13. The G19 and G23 1-PH experiments show that the 10% solution in DOD gave a lower rate of gum formation and required more oxygen to give a mg of gum than either pure hydrocarbon. This 1-PH had not been chromatographed and the result was so unexpected that the 1-PH was chromatographed and the oxidation (G52) and cooxidation (G66) were repeated, with very good checks. These experiments indicate that ~10% of 1-PH in DOD reduces somewhat the rates of gum formation and oxygen absorption by DOD alone.

The oxidation of our first lot of EtN (G35) was so slow and gave so much gum that it was checked and confirmed. Cooxidation showed that 10% of this hydrocarbon reduces the rate of oxidation of DOD but reduces more the rate of gum formation so that R_g/R_o decreases many fold (Figure 14). This unexpected result requires confirmation with the faster

oxidizing EtN. In the FIMS for this product, all the identified oxidation peaks were associated with EtN.

A mixture of DOD containing 12% mole TET (H34 in Table IV) oxidized at a rate about half way between the rates for DOD (K80) and TET (K81). Neither hydrocarbon alone gave any precipitate during oxidation but both oil and crystals separated from the mixture. The mixture produced 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 contained 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.

6.4. Mixtures of Dodecane with Nitrogen Compounds or Formic Acid

Figure 14 shows that there is no significant effect of 0.2 M pyridine, t-butylamine, or formic acid on the rate of oxidation of DOD. These compounds are apparently inert in oxidation. However, 0.0176 M NMP strongly retards the oxidation of DOD, but only initially. With 0.17 M NMP, the retardation is prolonged. NMP alone

oxidizes rapidly and so it must be incorporated in the products. FIMS of the oxidation products of DOD, with the nitrogen-containing additives, show that dodecenones and dodecenones + H are the principal C_{12} products. The principal C_{24} products are the dimer + 2 O and dimer + 2 O + H, except with NMP where a different, unidentified group of products is obtained.

6.5. Phenylcyclohexane and N Compounds

Distilled PCH was chromatographed through acidic alumina and oxidized at 130°C. In Expt. F15, with three intermediate points not shown in Table VIII, the rate of oxygen absorption by PCH was remarkably constant over the whole 11 hours of reaction. 0.12 M t-BuNH₂ in C73 retarded slightly the initial oxidation, but at 4 hours as much oxygen has been absorbed as without t-BuNH₂. The R_g/R_o ratio is about twice that without t-BuNH₂ but steady while the rate is increasing.

Table VIII shows that 0.14 M NMP retards oxygen absorption by PCH, especially at the beginning, but increases gum formation to produce cloudiness. The initial NMP corresponds to 1232 mg/100 g PCH but no more than 14% of the NMP appears as gum.

6.6. Fuel A + NMP

The experiment with Fuel A in Table VIII shows that its oxidation is slow and becomes slower with time. Addition of 0.2 M NMP results in increasingly faster oxidation and early formation of a precipitate. Again, the gum formed is considerably less than the NMP added.

Elemental analyses of Fuel A, NMP gum (not deposits) from Expt. D94, and NMP alone indicate that the gum consists of 36% NMT, 44% of an Aromatic portion of Fuel A, and 20% oxygen:

	<u>%C</u>	<u>%H</u>	<u>%N</u>	<u>%S</u>	<u>%O, diff.</u>	<u>H/C</u>
Fuel A	86.37	13.27	<0.02	<0.02	0.32	1.83
Gum from oxidn. of A + NMP	68.04	5.90	6.17	~ 0	19.9	1.03
NMP, calculated	74.30	7.06	17.27	0	0	1.40
Gum without NMP, calculated	64.54	5.26	0	~ 0	30.2	0.97

The gum contain 2.8 O atoms/NMP. These data are further evidence for our generalization that the additives or impurities that most affect oxidation and gum formation are most reactive and are consumed rapidly.

7. OXIDATIONS AT LOW OXYGEN PRESSURES

These experiments used blends of air, nitrogen, and oxygen at a total pressure of one atmosphere, measured at 23-25°C. Changes in O/N ratio were measured by our usual GC method except for the last Fuel C experiment starting with 465 torr of oxygen. Here, the decrease in total pressure corresponded closely to the consumption of oxygen and so this experiment deserves inclusion in Table X.

Table X summarizes valid experiments with Fuels C and A, and DOD containing ~10 mole % TET, at initial partial pressures of oxygen of 16 to 465 torr in oxidations at 130°C without added initiator. The data

are calculated on a consistent basis from the initial atmospheric pressures and the experimental O/N ratios from GC. Each set of data usually represents one oxidation and shows how the oxygen concentration changed with time.

7.1. 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 important conclusion is that R_g/R_0 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_0 ; 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.

7.2. Fuel A

Fuel A is one of our slowest oxidizers and gum formers, and in any experiment R_0 and presumably R_g decrease steadily from the beginning of

the oxidation, as shown in the last two Fuel A experiments in Table X. This Table summarizes three experiments at initial oxygen pressures of 16 to 20 torr. All showed similar initial R_0 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 total average R_g values are divided by earlier R_0 values and all the ratios are lower than in the 158 torr experiment. Apparently the R_g values are small because both R_0 and R_g decreased with time; thus, ratios based on early R_0 values are too high. However, in the first two Fuel A experiments 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 at 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. Slight 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_0 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_g/R_0 values agree

fairly well with each other and with other data for Fuel A. Low pressure oxidations with $t\text{-Ru}_2\text{O}_2$ at 100° are expected to improve reproducibility.

7.3. 10 Mole % of TET in DOD

Two experiments with TET/DOD mixtures are listed in Table X. In air, the reactions are fast and autocatalytic. With an initial 20 torr of oxygen, the reaction starts at about the same rate, but this rate decreases steadily until it approaches zero at 5 torr of oxygen.

8. SUMMARY AND CONCLUSIONS

Most previous work on fuel stability has emphasized solid deposits, but this work deals mostly with soluble gum. Gum is always formed before deposits and usually in greater quantity. Section 3.1 provides good evidence that deposits come from soluble gum, and we suspect that hard deposits on hot engine parts arise mostly from gum in solution in the fuel. None of our pure hydrocarbons gave deposits at 100° or 130°C and none of our fuels gave deposits in γ -initiated oxidations at 56°C (Figure 9).

Both our own and previous work (Taylor, 1974, and many others) show that oxidation is essential for the formation of gum and deposits, except at pyrolysis temperatures. In the present work, there is a close relation between the rates of oxygen absorption and gum formation at 130°C (see Figure 10 and some examples in Table VIII where gum was

determined at more than one conversion). The relation is even insensitive to oxygen pressure (Table X) and both reactions stop when the oxygen pressure is reduced to 10-15 torr.

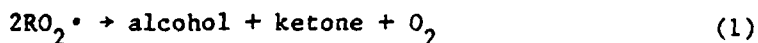
Table IX shows that all of our pure hydrocarbons absorb oxygen at 130°C faster than all our fuels, except Fuel B. Most of the hydrocarbons also form gum faster than most of the fuels, because they absorb oxygen so much faster. However, most of the fuels give much more gum for the oxygen absorbed (high R_g/R_o ratio) than most of the hydrocarbons, which give the least gum for the oxygen absorbed, especially DOD. As noted in Section 5, IND and NMP are special cases.

The R_g/R_o values in Tables VIII and IX provide a basis for explaining the gum and deposit problem. From the definitions of R_g and R_o and the 8% oxygen content of Fuel 14 gum, the percent of the oxygen absorbed in the C28 oxidation that appears in the final gum = $2.5 R_g/R_o$ = 1%. EtN and Fuels A, 10, 13, and 14B have R_g/R_o ratios up to 10 times that of Fuel 14 (0.4), and if their gums have comparable oxygen contents, then they contain up to 10% of the oxygen absorbed. Further, the R_g 's in Tables 8 and 9 are taken after a heating period in which up to two-thirds of the evaporated residue has been lost. They therefore represent minimum R_g/R_o ratios.

Our oxidation work in progress with $t\text{-Bu}_2\text{O}_2$ as initiator at 100°C indicates that the number of molecules oxidized per $t\text{-BuO}^\bullet$ radical is in the hundreds with the most reactive hydrocarbons but not far from one with the least reactive fuels. Thus, gum formation during oxidation appears to be associated mostly with the chain termination reaction, not with the chain propagation reaction.

Our work with oxidations of mixtures shows how small proportions of the more reactive component may either accelerate or retard oxidation of the less reactive component, but only by being consumed itself. We have seen no indication of any truly catalytic effect of any organic compound on the rates of oxidation or gum formation. We propose that the low rates of oxidation of fuels illustrate the minimum rates of oxidation of some mixtures according to Section 6.1 and the retarding effects of alkylnaphthalenes and their oxidation products.

The close relation between R_o and R_g for single fuels and a general background in the oxidation of hydrocarbons suggests a new mechanism for gum and deposit formation. The basic mechanism for converting monomeric to polymeric fuel units is proposed to be part of the chain termination mechanism. In most oxidation reactions, chain termination is bimolecular and involves two radicals:



Reaction 1 contributes nothing to the required condensation reactions except to provide oxygen compounds that are more reactive in oxidation than hydrocarbons. Reactions 3 and 4 are significant only at low oxygen pressures where R_o and R_g approach zero (Section 7). Thus Reaction 2 has to be responsible for most of the coupling of monomer to dimer. The peroxide formed is probably stable up to 80-100°C but not at higher

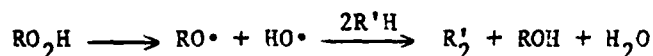
temperatures. When the dialkyl peroxide decomposes in solution, it just reinitiates oxidation, but when it decomposes in a viscous medium during severe heating in the gum analysis, most of the resulting radicals attack the surrounding molecules and do not escape, as shown by experiments with indene polyperoxide (Section 6.1 and Russell 1956) and styrene polyperoxide (Mayo, Miller, 1956). Thus the dialkyl peroxides made at low temperature survive to participate in gum formation during gum determinations but those made at high temperatures do not. The proportions of Reactions 1 and 2 depend on temperature and the fuel, permitting considerable latitude in the yields of gum on the oxygen absorbed and suggesting an explanation for relating gum tests at various temperatures.

However, by itself, Reaction 2 can only produce dimer. To make higher molecular weight products, the chain propagation Reaction 5 must be considered:



For growth of the dimer, some of the RH reacting with peroxy radicals must be polymers produced in Reaction 2 and thus able to oxidize and grow further. The high oxygen contents of gums show that oxidized monomers and polymers are more reactive than hydrocarbons in Reaction 5 (Section 3.2). This scheme requires that R_g/R_o should increase with conversion unless dimer contributes heavily to gum. It also neglects the possibility that some polynuclear aromatic hydrocarbons have first order termination reactions and are autoretarding.

An older mechanism for gum formation is condensation by radicals from pyrolysis of hydroperoxides (Mayo et al., 1976):



This mechanism is supported by the good yields of dimer obtained when the hydroperoxide of EtN was heated with EtN or when EtN was heated with *t*-Bu₂ O₂, both at 150° in the absence of oxygen. However, in the presence of oxygen, this C-C coupling is superseded by the oxidative coupling mechanism above.

Still another mechanism is aldol-type condensations and esterifications of oxidation products (Mayo et al., 1976). Again gum formation should be proportional to the concentration of accumulated oxidation products, not to the rate of oxygen absorption. We have no evidence for this mechanism at this writing.

A widely held view is that small proportions of reactive nitrogen- and sulfur-containing compounds are largely responsible for formation of gum and deposits (CRC Report No. 509, p.53, and many others). This explanation must apply to many fuels; when it does, the fuel stability should be improved as the reactive components are consumed, and examples have been reported (Bowden, Brinkman, 1980; Stavinoha, Brinkman, 1981). Some nitrogen and sulfur compounds increase deposit formation and some do not (Frankenfeld et al., 1983). The considerable recent literature on deposits from 2,5-dimethylpyrrole in fuels shows mostly that this compound is unusually reactive in oxidation and that its oxidation product is unusually insoluble. However, the present paper and also Malhotra et al. (1984) show that pure alkyl naphthalenes and other polynuclear aromatic hydrocarbons are also important sources of

gum and that some of the least stable fuels have the highest proportions of these hydrocarbons (Section 2.1). Instability from this source will not change much with aging time.

Chromatography of fuels over alumina usually has some effect on rate of oxygen absorption, but not much on R_g/R_o . Chromatography apparently removes some trace impurities that may accelerate or retard oxidation, as noted previously. As long as they are trace impurities, they cannot contribute much to gum formation except through their effect on R_o .

Although oxidations at 130°C proceed at a convenient rate and are fairly reproducible, their relations to reactions at ambient temperatures are uncertain. Indications are that the relative stabilities of various fuels do not change much with temperature. However, we are now trying to bridge the gap in fuel oxidations between 43° and 130°C with $t\text{-Bu}_2\text{O}_2$ -initiated oxidations at 100° and in longer experiments at 60°C. These experiments will be presented in future papers, which are directed toward a simple and reliable test for fuel stability.

This section concludes with a discussion of the largest and most diverse effort we know about on fuel stability, carried out by the Bureau of Mines in Bartlesville with support from the Western Petroleum Refiners Association (Smith et al., 1958). Results were published in two volumes. Volume 1 surveys gum and deposit formation from 34 distillate fuels and 250 blends at 43.3°C for 39 weeks in vented bottles, with and without added materials. The second volume, "Studies Relating to Causes of Instability", was probably intended to solve the gum and deposit problem for good, but it did not.

This work resembles some of our own. In retrospect, some of the Smith techniques were faulty, but there is no indication that the faults were recognized, or even that any experiment was repeated. All the fuels should have been distilled before they were used, to minimize differences in the previous histories and initial gum contents of the fuels. Further, apparent uncertainties in gum determinations are greater than the differences among stable fuels.

Oxygen absorption was usually measured for 48 hours at 65.6°C (150°F). All the fuels were thoroughly degassed before use; oxygen absorption was then rapid for 1 to 4 hours before the rates became steady and slow. To compare fuels, these slow rates were extrapolated to zero time, thus obscuring possible interesting differences among initial rates of fuels. The 1 to 4 hours required to reach the steady rate suggest rate differences during this period and that oxygen dispersion was inadequate.

Nine fuels were chromatographed over silica and alumina. Most of the resulting fuels oxidized faster, but one oxidized slower. The recovered polar compounds contain more N, S, and O, and less H/C than the fuels. Two reconstituted fuels oxidized faster than the originals, and six, slower. The effects of chromatography on gum formation are erratic, often large. Thus, as measured by rate of oxidation, fuels are permanently altered by chromatography.

Our own results with chromatographed fuels are consistent with those of Smith et al., which we consider reasonable. However, our R_g/R_o ratios are usually nearly constant for a single fuel at a single temperature. Thus, this fundamental ratio is largely unaffected by

trace components in fuels while changes in rates of oxidation alone may be confusing.

Smith et al. also resolved nine whole fuels into polar, saturate, monocyclic, and polycyclic aromatic fractions and compared their rates of oxidation and gum formation in 48 hours at 65.6°C. We conclude that the fractionations were not meaningful. Oxygen absorption rates for saturated fractions vary 60-fold, for monocyclic aromatic fractions by about 400-fold. However, we endorse some of the conclusions of Smith et al: oxygen absorptions by the saturated fractions were steady; by the polycyclic aromatic fractions were initially fast but then decreased steadily; by the monocyclic aromatic fractions were slowest and became slower; polycyclic aromatic fractions gave the most gum for the oxygen absorbed.

The results above and in our Table IX show that rates of oxidation alone with unknown rates of initiation are a poor guide to an understanding of gum and deposit formation, but that simultaneous measure of oxygen consumption and gum formation provides considerable insight. Our next paper will show that such measurements at known rates of initiation permits still further progress.

We now propose a basic conclusion about tests for fuel stability. In the absence of a known initiator, rates of oxygen absorption and gum formation in hydrocarbon fuels depend on peroxides already present or generated by light, traces of metals, or the initial slow oxidation. The result is an induction period until the rates become large enough to measure. This induction period will be long and poorly reproducible below ~ 80°C because it will depend on unmeasurable differences among

supposedly identical samples. Above 120°C the induction period is so compressed that the less measurable differences among fuel samples become unimportant and a fairly fairly reproducible rate is soon attained. This argument implies that devising a test for use below 50°, maybe below 80°, for fuel stability that can be reproduced in different laboratories is impractical until the differences among induction periods can be eliminated. One solution is to perform the test at a known rate of initiation (by peroxide, azo compound, or radiation). Another route is to provide just enough initiation or radiation to eliminate most of the induction period and then measure fuel stability. A third route is to count aging time from when the sample gives a measurable rate of oxidation and/or gum formation after a previous period of radiation at test temperature or thermal initiation at a higher temperature. A fourth route is to measure the eventual steady rate of oxygen absorption at test temperature and give little attention to the time elapsed before this rate is attained. Whether any of these versions will be more useful than the present uninitiated tests will have to be determined by experiment.

Acknowledgements

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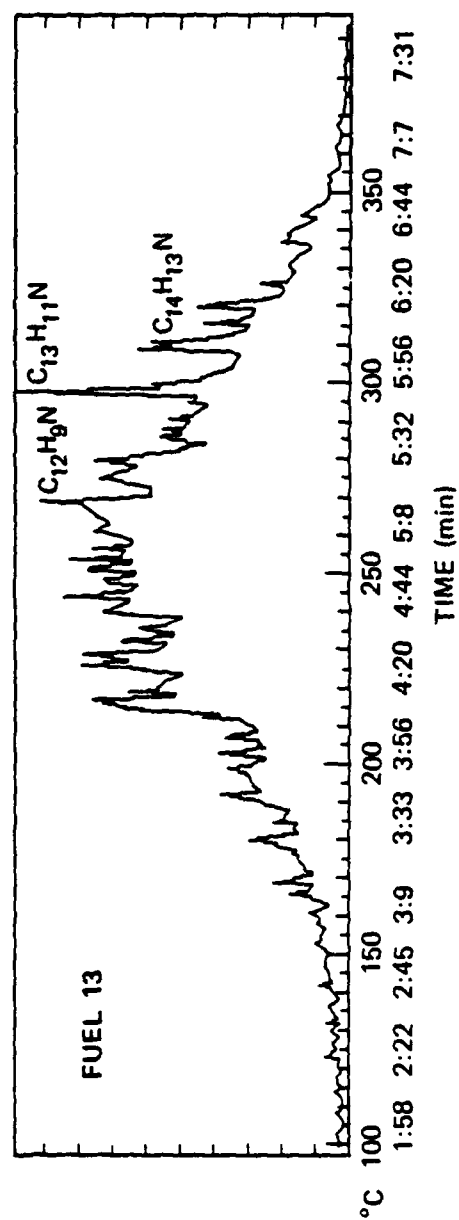
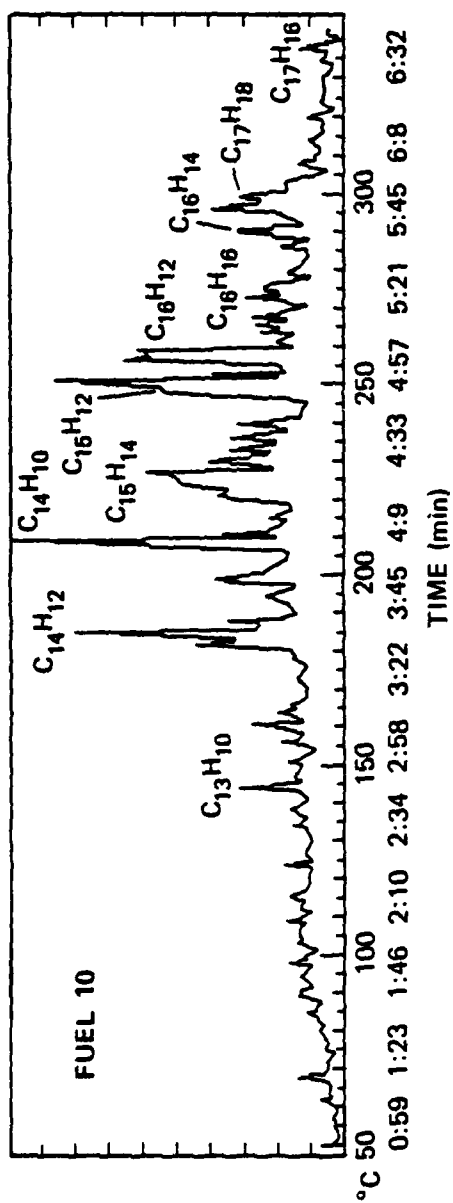
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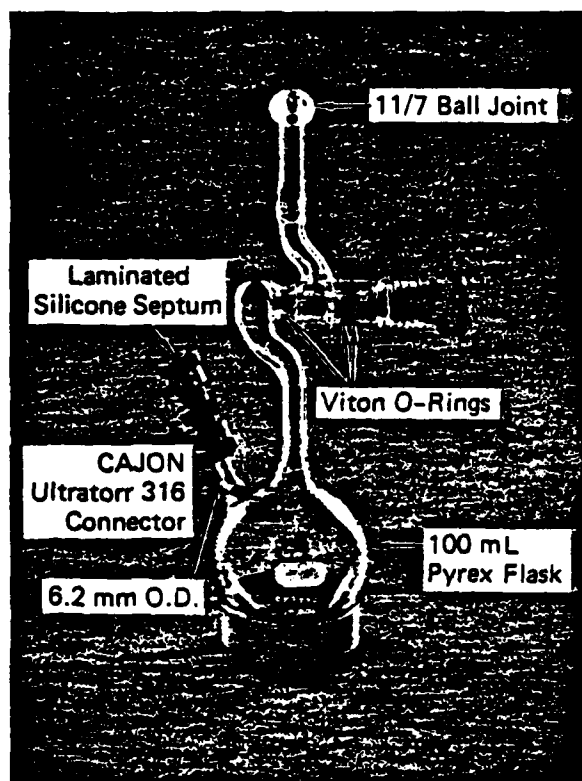
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- Figure 1 GC Polar Components of Fuels 10 and 13
- Figure 2 Reaction Flask for Oxidations
- Figure 3 Evaporation Bottle for Gum Determinations
- Figure 4 Molecular Weight Profile of Distilled but Unoxidized Fuel C
- Figure 5 FI Mass Spectrum of the Deposit Precursors Isolated from Vacuum-Distilled, Unoxidized Fuel C
- Figure 6 FI Mass Spectrum of the Deposit Precursors Formed in Fuel C after Oxidation for 4.25 Hours at 130°C
- Figure 7 FI Mass Spectrum of the Deposit Precursors Formed in Fuel C after Oxidation for 7.17 Hours at 130°C
- Figure 8 FI Mass Spectrum of the Deposit Precursors Remaining in Fuel C after Oxidation for 11.7 Hours at 130°C
- Figure 9 Oxygen Consumption by Fuels at 130°C
- Figure 10 Oxidation of Fuel 10 in Air at 130°C
- Figure 11 Oxidation of Reconstituted Fuel 10 at 130°C in Air with 0.1, 1, and 10 Times Original Proportion Polar Compounds
- Figure 12 Oxidations of n-Dodecane with Indene at 130°C Gum is in mg/100 g fuel, determined at 100°C except when marked* for 200°C
- Figure 13 Cooxidations of n-Dodecane with 1-PH and EtN at 130°C
- Figure 14 Oxidations of n-Dodecane and Additives at 130°C



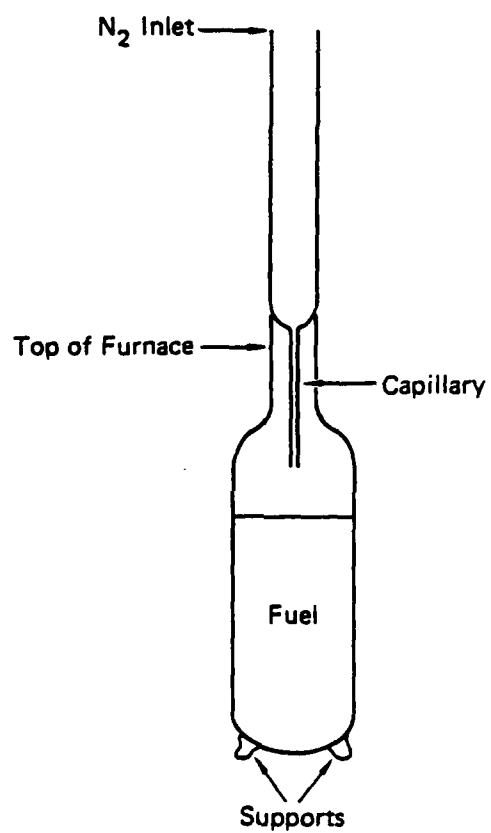
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FIGURE 1 GC OF POLAR COMPONENTS OF FUELS 10 AND 13



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FIGURE 2 REACTION FLASK FOR OXIDATIONS



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FIGURE 3 EVAPORATION BOTTLE FOR GUM DETERMINATIONS

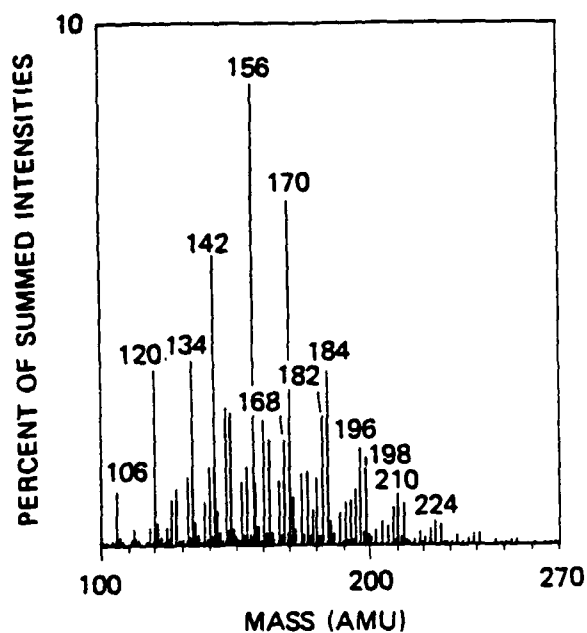


FIGURE 4 MOLECULAR WEIGHT PROFILE OF DISTILLED BUT UNOXIDIZED FUEL C

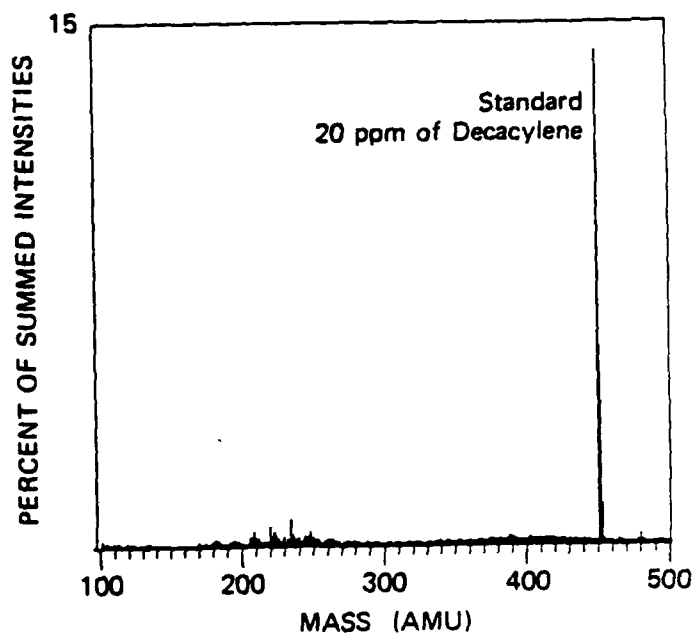


FIGURE 5 F1 MASS SPECTRUM OF THE DEPOSIT PRECURSORS ISOLATED FROM VACUUM-DISTILLED, UNOXIDIZED FUEL C

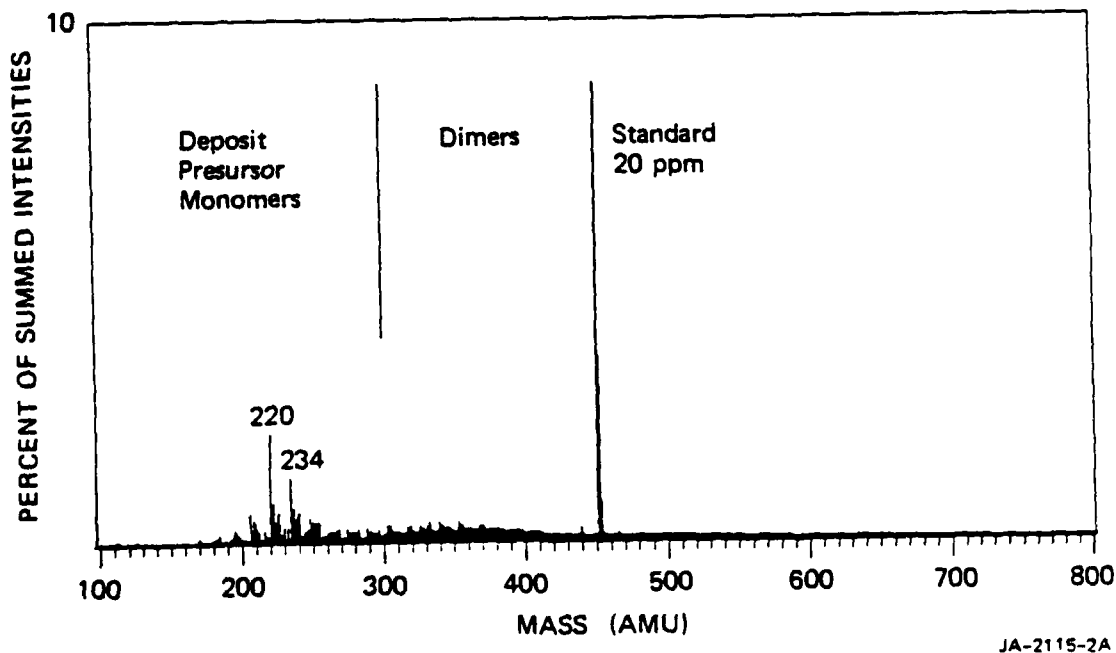


FIGURE 6 F1 MASS SPECTRUM OF THE DEPOSIT PRECURSORS FORMED IN FUEL C AFTER OXIDATION FOR 4.25 HOURS AT 130°C

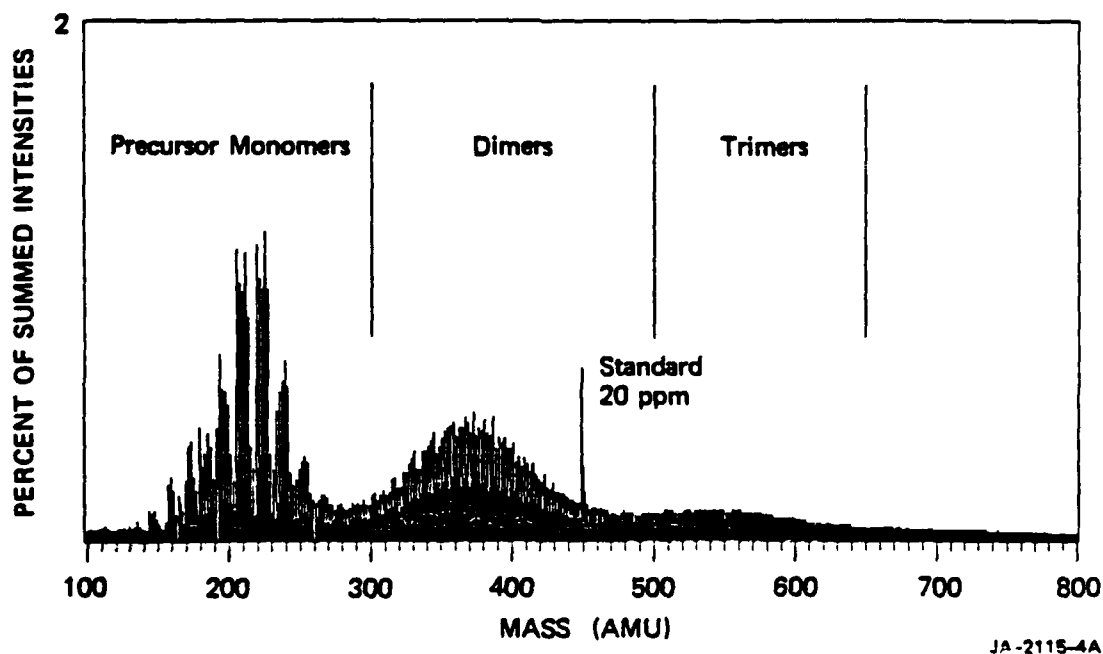


FIGURE 7 F1 MASS SPECTRUM OF THE DEPOSIT PRECURSORS FORMED IN FUEL C AFTER OXIDATION FOR 7.17 HOURS AT 130°C

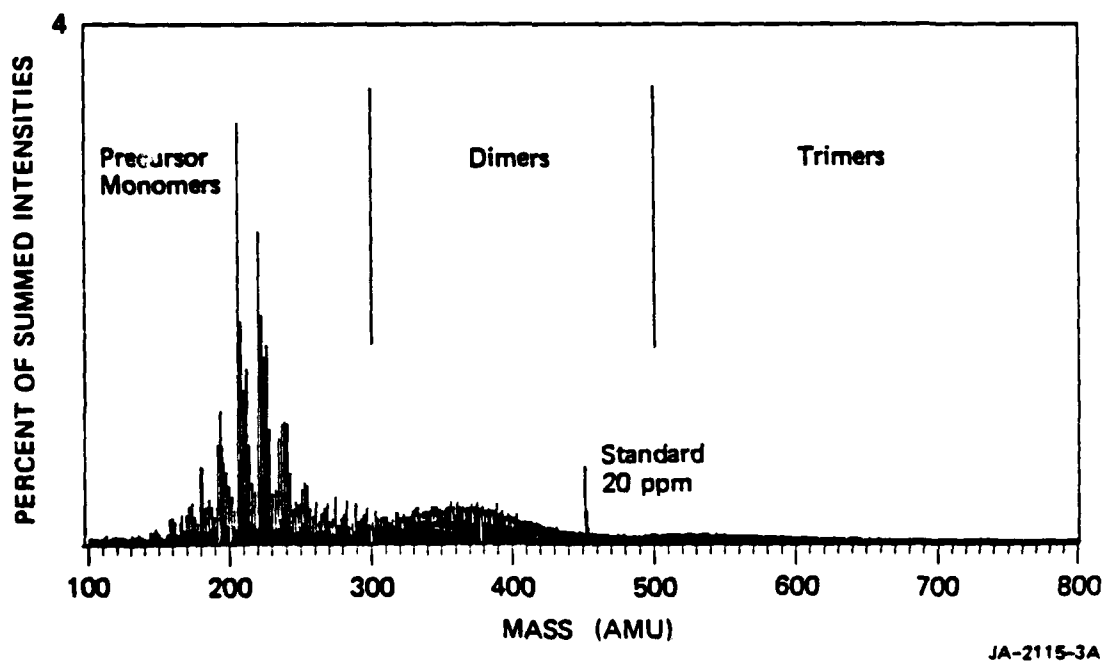


FIGURE 8 F1 MASS SPECTRUM OF THE DEPOSIT PRECURSORS REMAINING IN FUEL C AFTER OXIDATION FOR 11.7 HOURS AT 130°C

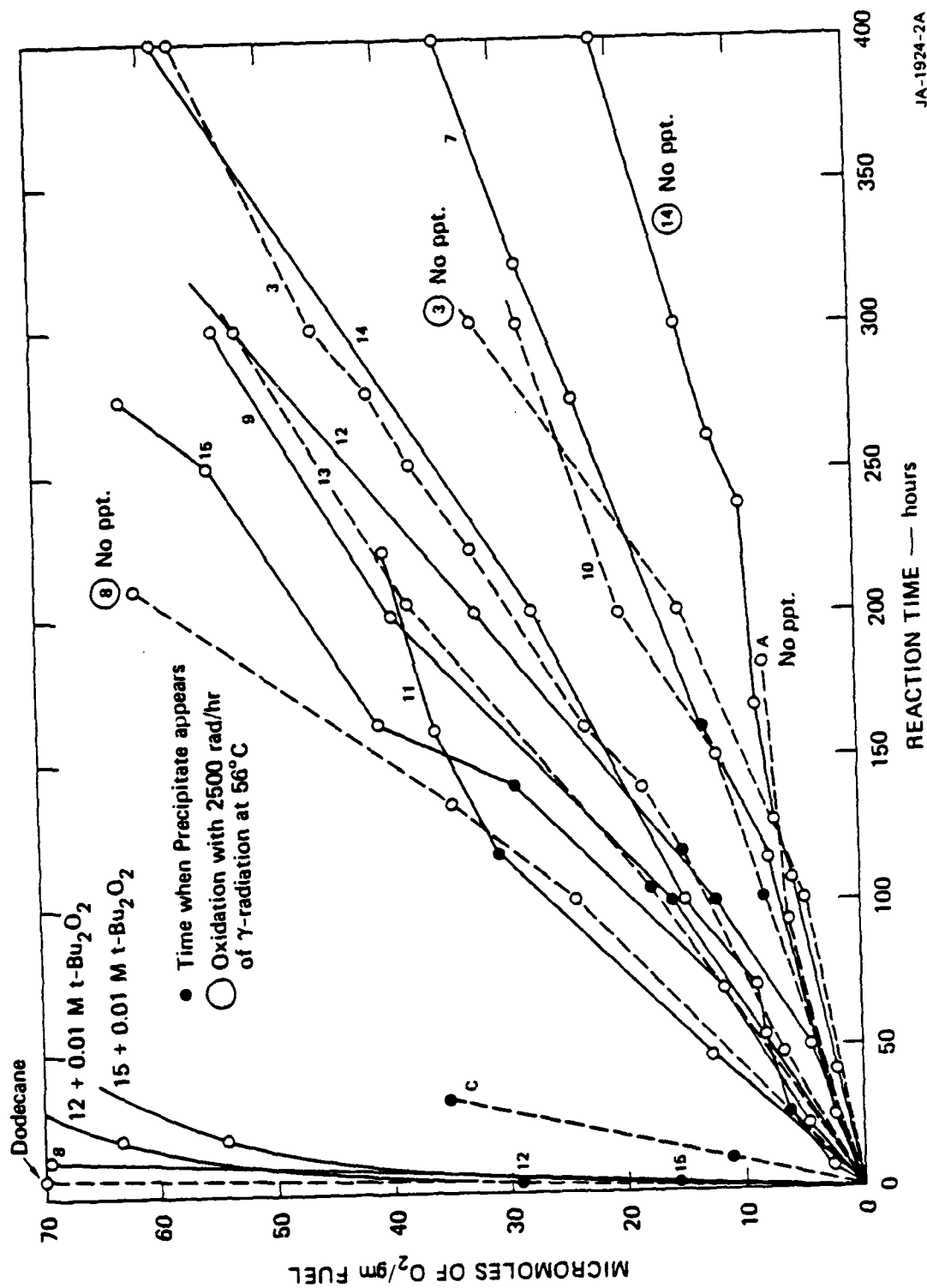
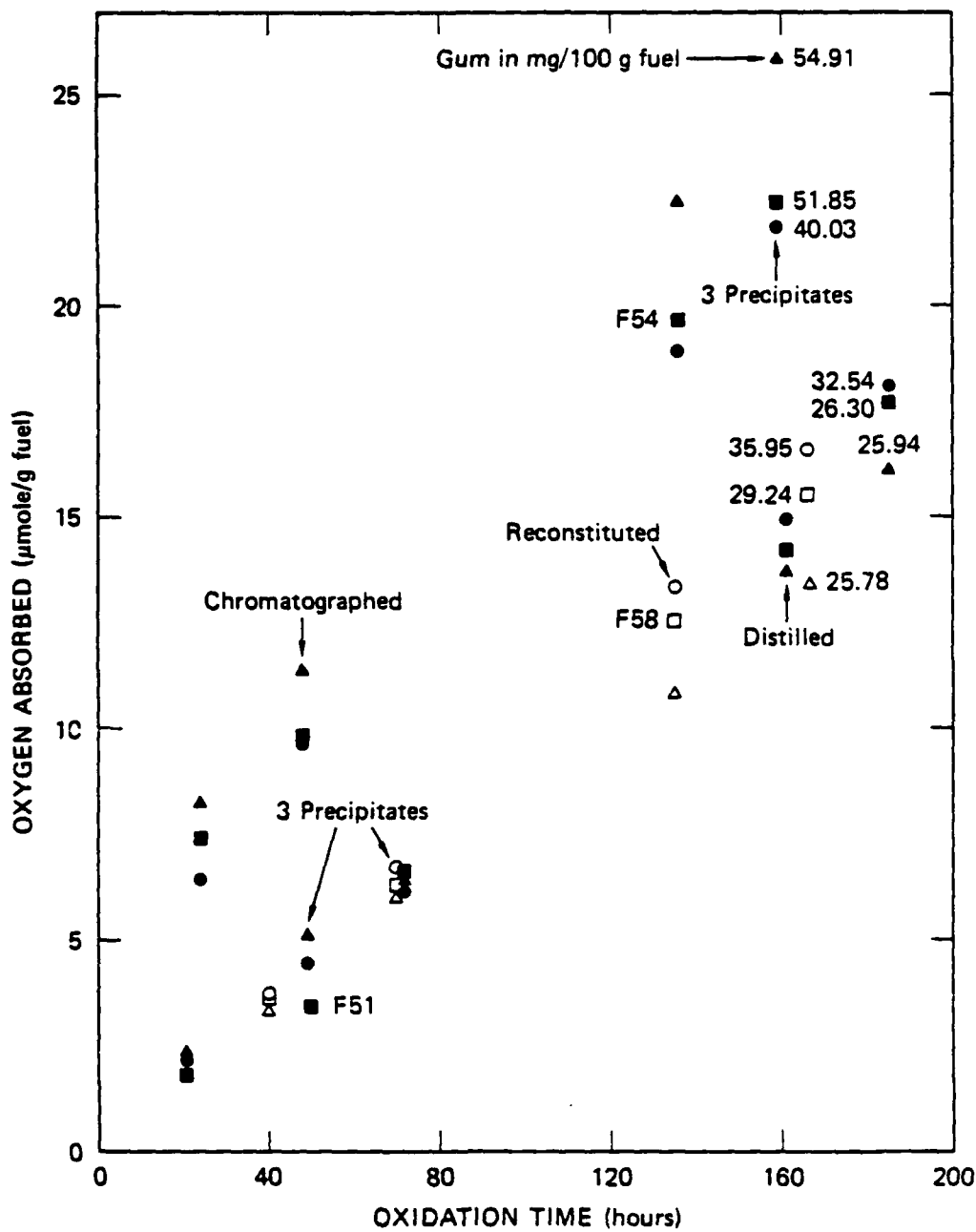


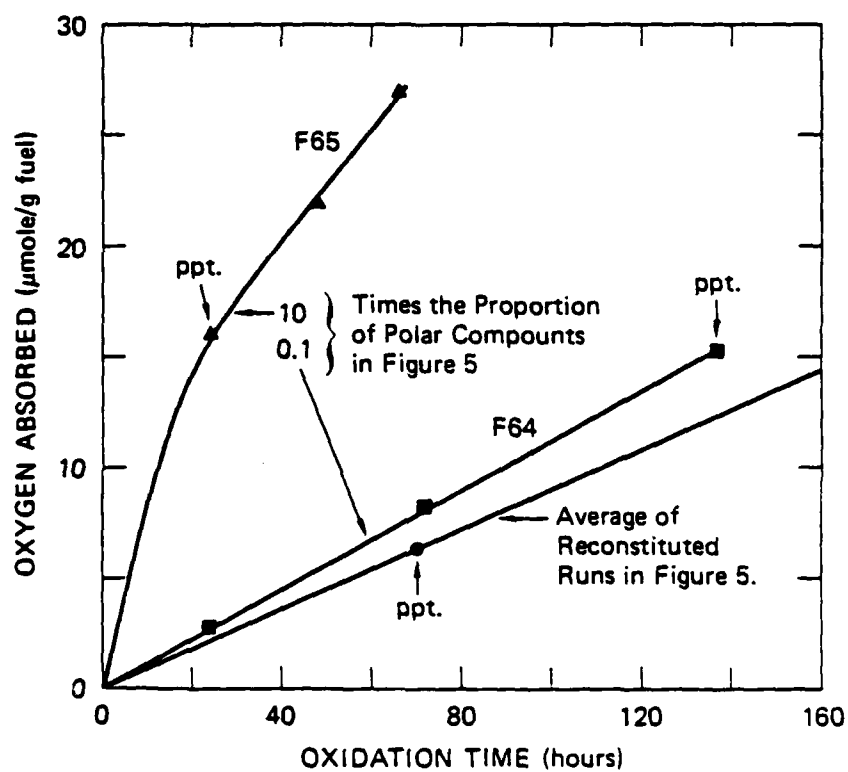
FIGURE 9 OXYGEN CONSUMPTION BY FUELS AT $130^\circ C$

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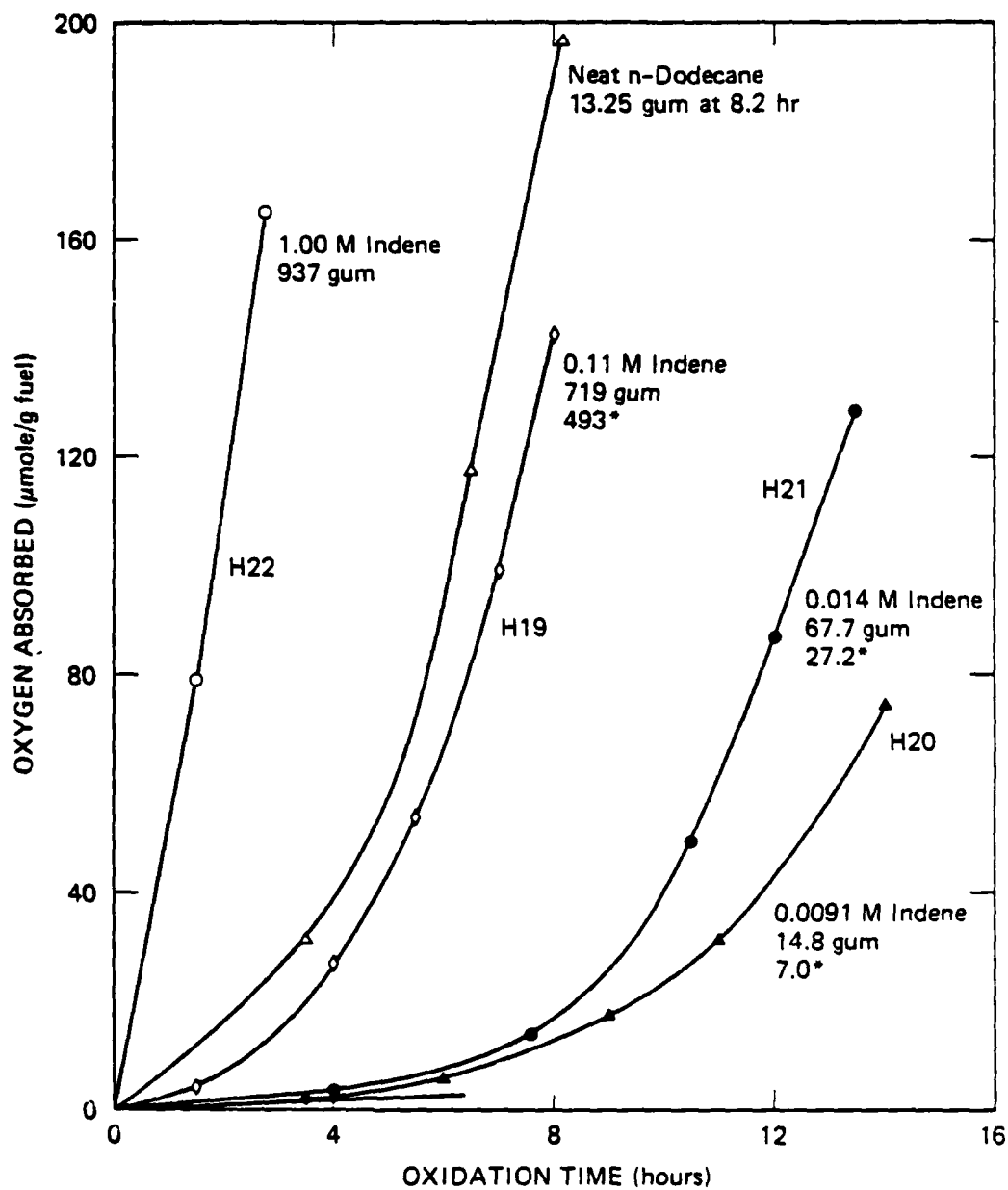
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FIGURE 10 OXIDATION OF FUEL 10 IN AIR AT 130°C



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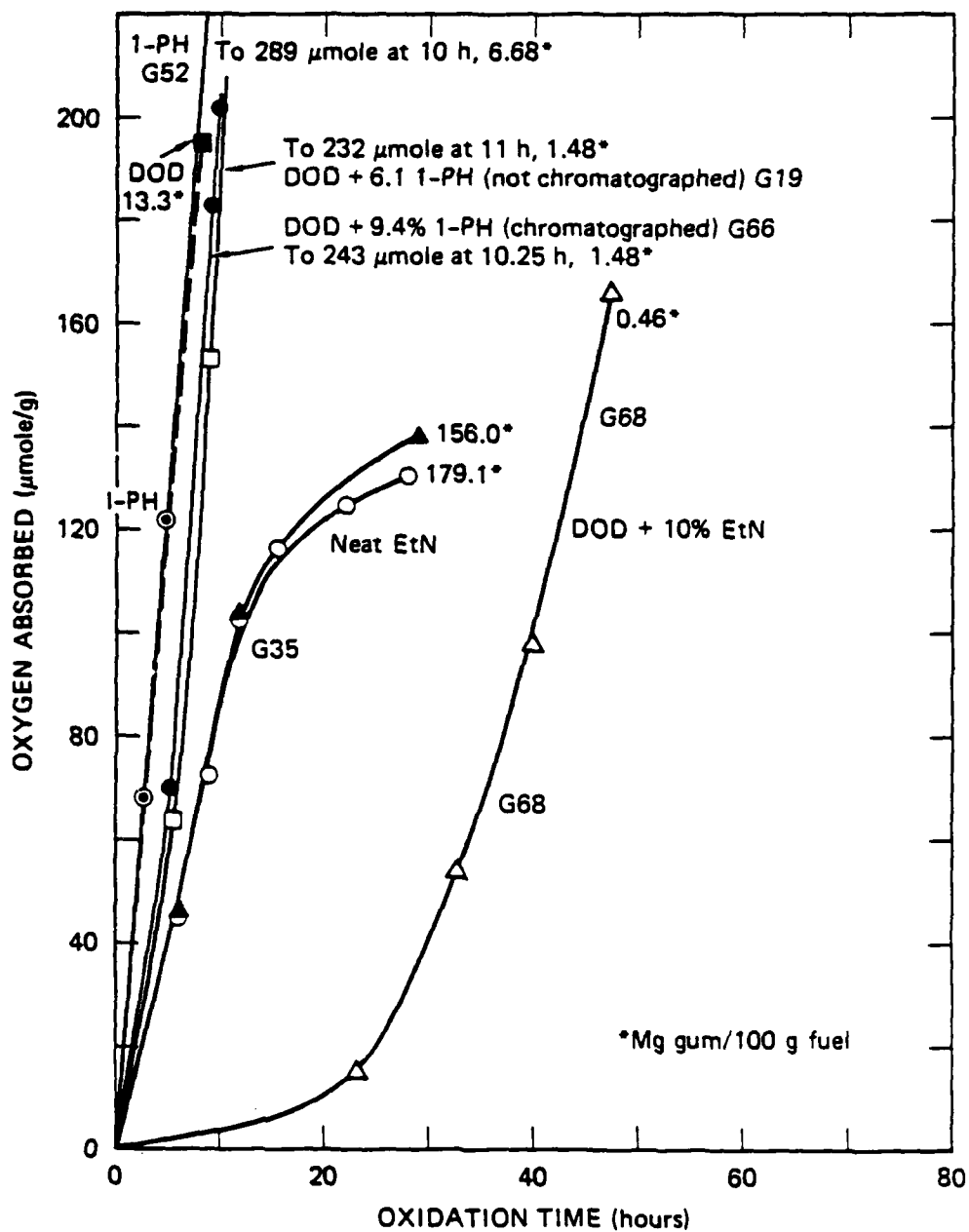
FIGURE 11 OXIDATION OF RECONSTITUTED FUEL 10 AT 130°C IN AIR WITH 0.1, 1, AND 10 TIMES ORIGINAL PROPORTION OF POLAR COMPOUNDS



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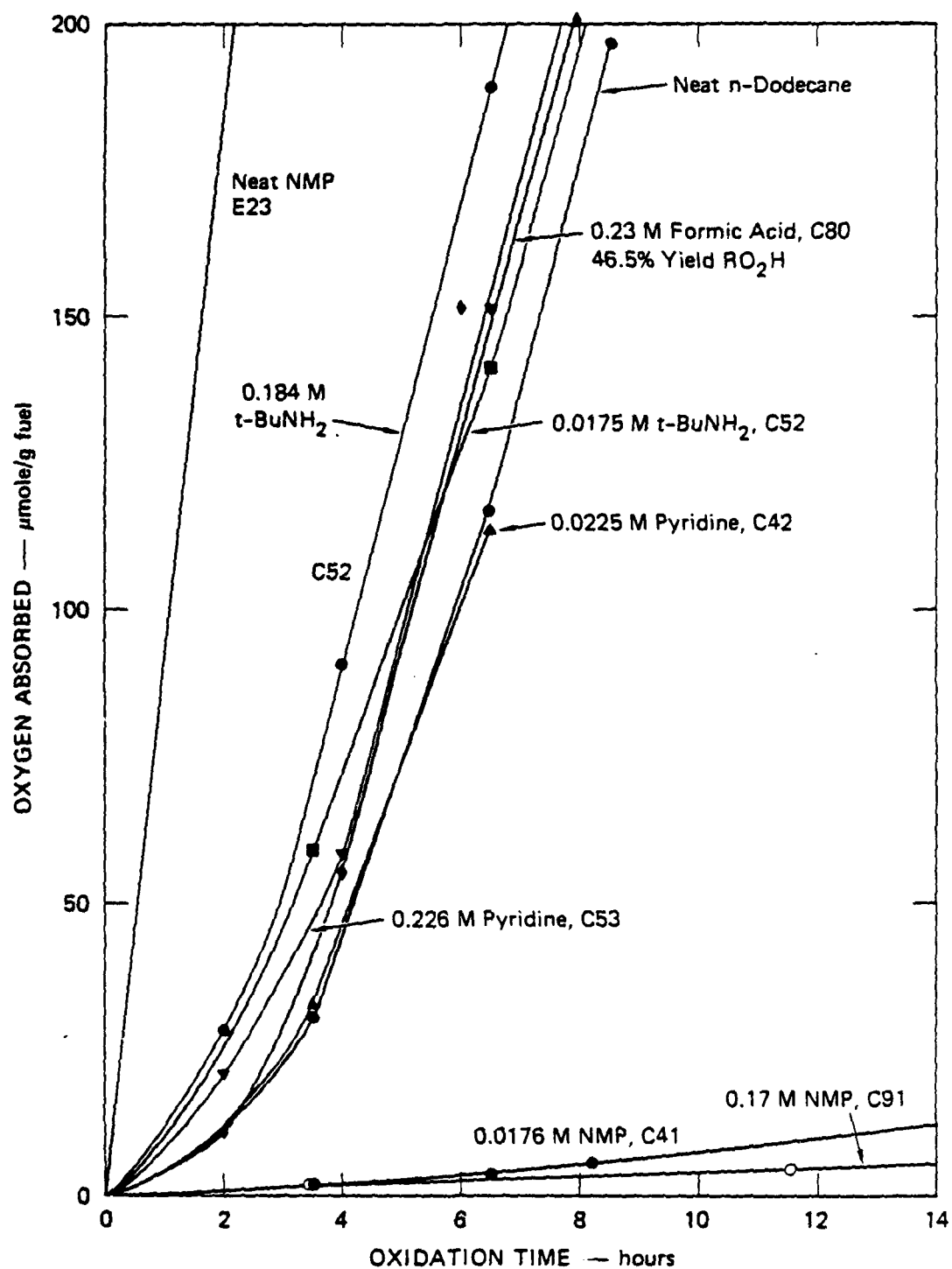
FIGURE 12 OXIDATIONS OF n-DODECANE WITH INDENE AT 130°C

Gum is in mg/100 g fuel, determined at 100°C except when marked * for 200°C.



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FIGURE 13 COOXIDATIONS OF n-DODECANE WITH 1-PH AND EtN AT 130°C



JA-1924-5A

FIGURE 14 OXIDATIONS OF n-DODECANE AND ADDITIVES AT 130°C

Table I
DISTILLATION RANGES OF FUELS

Fuel	Boiling Point (°C)		Description
	Pressure (torr)	Initial Final	
A	5	48 90	Stable jet turbine fuel
B	4	45 90	Intermediate stability
C ^a	5	30 110	Very unstable
1	6	55 95	50/50 mixture of No. 2 diesel truck and tank fuels
10 ^a	6	55 109	Gulf Oil Company diesel
13 ^a	6	55 110	Chevron straight run Northslope diesel
14	15	53 250	50/50 Mixture of No. 2 diesel fuels from Anniston Army Depot. 14B was 6% of 14.
14A	15	53 200	
14B	14	200 234	
15	12	55 145	No. 2 diesel from Marine Fuel Storage Program

^aRedistilled to reduce color.

Table II
ELEMENTAL ANALYSES OF FUELS AND FRACTIONS

Sample	%C	%H	%N	%S	%O ^a	H/C
Crystals from DOD/TET	73.2	7.3	0		19.5	1.18
Oil	65.5	6.3	0		28.2	1.15
Fuel A	86.4	13.3	<0.02	<0.03	< 0.36	1.83
Fuel B	86.5	12.9	0.65		~0	1.78
Fuel C	87.6	11.9	<0.02	0.03	0.17	1.62
Distln. residue, unoxidized	85.5	8.2	1.37		4.9	1.12
Polar concentrate	74.9	6.0	0.20		18.9	0.98
Fuel 1	85.9	13.7	0		0.4	1.89
Fuel 4, pyridine-sol. wall deposit, 1127 h	73.2	4.9	0.35		21.5	0.80
Fuel 10	85.7	13.15	0.73		0.40	1.83
Polar fraction	86.6	8.6	0.94	2.01	1.98	1.18
Gum, 185 h	72.8	5.90	1.01		20.3	0.97
Wall deposit, 185 h	66.9	4.78	0.98		27.4	0.85
Fuel 13	84.6	12.8	0		2.7	1.80
Polar fraction	80.0	9.1	1.14	9.0	0.85	1.35
Gum, 368 h	72.1	6.1	0.99		20.8	1.01
Wall deposit, 368 h	71.5	5.1	0.86		22.6	0.84
AcMe-insol. deposit	73.0	5.1	0.86		21.0	0.84
Fuel 14	87.0	13.0	0		~0	1.77
Distillation residue	87.1	11.8	0.09		1.06	1.61
Fuel 14A	85.9	11.9	0.43		1.7	1.66
Final sol. gum L4A	84.1	6.3	0		9.6	0.89
Fuel 14B	87.1	11.4	0		0.9	1.56
Fuel 15	86.9	13.1	0		~0	1.80

^aO and O + S by difference

Table 'II

Compositions of Fuels in Mole % by FIMS

Fuel	z-Number										
	+2	0	-2	-4	-6	-8	-10	-12	-14	-16	-18
A ^a	26	38	25		11						
B ^a	27	24	15		26			8			
C ^a	6	4	3		16	15		55	1		
1	18	15	12	1	13	14	3	18	4	1	1
10	13	10	10	4	19	16	3	24	1		
14A	13	11	9	1	16	18	3	24	4	1	0.4
14B	7	3	2	4	5	5	5	7	13	13	23 ^b
15	14	13	9		19	17	1	22	2	2	1

^aProportions of major components only.

^bAlso 6% of Z = -20 and 8% of either z = -26 (C₁₇H₈, C₁₈H₁₀, and C₁₉H₁₂) or some dibenzothiophenes with 2-4 C in alkyl substituents. The latter seem more probable.

Table IV

RESULTS OF THE OXIDATION OF VACUUM-DISTILLED FUEL C

Time at 130°C (h)	0	4.25	7.17	11.7
O ₂ consumed (μmol/g)	0	5.46	10.9	26.9
μmol/g · h ^a	0	1.28	1.87	3.52
Deposit Precursor Properties				
Concentration (ppm) ^b	74	132	2540	2600
Number av. mol. wt., $\overline{M}_n$	435	388	355	318
Weight av. mol. wt., $\overline{M}_w$	496	440	419	381

^aDuring preceding interval^bBased on total materials found by FIMS

Table V
PRINCIPAL IONS FROM 3-DODECANOL, 2-DODECANONE,
AND OXIDATION PRODUCTS OF n-DODECANE

Ranking	No Oxidation		First Oxidation	
	3-Do-decanol	2-Do-decanone	Untreated	Heated To 180°
1	169	184	183	169
2	157 ^a	185	169	185
3	168	182	199	199
4	131	122	185	203
5	184	183	184	184
6	185	150	217	201
7	171 ^a	155	182	217
8	373	370	201	183
9	186	186	216	198
10	183	136	197	373
11	182	156	198	159
12	198	108	370	186

Suggested identifications of ions above.

131	$C_8H_{17}OH_2^a$	182	dodecenone	198	C_{12} diketone
157	$C_{10}H_{21}O^a$	183	↑	199	↑
159	$C_{10}H_{21}OH_2^a$ or $C_9H_{19}O_2^a$	184	dodecanone	201	↓
168	dodecene ^a	185	dodecyl-O	203	dodecanediol + H
169	dodecyl	186	dodecanol	216	dodecanetriol or hydroxyhydroperoxide
170	dodesane				
171	$C_{11}H_{23}O^a$	197	C_{12} diketone-H	217	dodecanetriol + H

^a From specific cleavages of 3-dodecanol.

Table VI
FIMS FROM OXIDATIONS OF OTHER HYDROCARBONS AT 130°C

Hydrocarbon	1-PH	PCH(Expt. C50)	TET	EtN	
Mol. wt. of parent RH	162	160	132	156	
Dimer, R ₂	322	318	262	310	
Reaction time, h	2.0	5.5	2.0	4.0	
O ₂ absorbed, μ mole/g	49.3	135	36.6	119	
			4.5	29	
Rank of Peak Intensities					
1	R ⁺	RH	R ⁺	R ⁺	ketone
2	RH	ROH	RH	ROH	RH+2 O
					- C ₂ H ₄
3	ketone	R ⁺	RH+2 O	RH+2 O	ROH
	ROH	RH+2 O	ROH	ketone	RH-2H
					RH+O-C ₂ H ₄
5	RH+2 O	ketone	ketone	R ₂ +2 O	parent
					RH+2 O-2H
6	unsat. ketone	R ₂	OH ketone	OH ketone	dimer + O
					RH + O
7			R ₂ ketone	dimer ketone	dimer+ 2 O
					-C ₂ H ₆
8			R ₂ + O	RO•	dimer
9			OH ketone + H	RH-3H	dimer + 2 O
					-2C ₂ H ₄

Table VII

PRINCIPAL IONS FROM OXIDATION PRODUCTS OF N-DODECANE
OF MASS NUMBER >337

<u>Ranking</u>	<u>Untreated</u>	<u>Heated</u>
1	370	373
2	385	385
3	399	399
4	371	371
5	401	355
6	386	367
7	400	353
8	387	337
9	383	350
10	415	369
11	368	374
12	369	386

Suggested identifications of ions above, neglecting carbon loss.

337	Dimer - H	374	
338 ^a	Dimer C ₂₄ H ₅₀	383	Dimer triol -3 H
350	Dimer ketone - 2H	385	- H
353	Dimer + O - H	386	+ H
355	Dimer + O + H	387	
367	Dimer diketone + H	399	Dimer + 4 O - 3 H
368	↑	400	↑
369	↓	401	↓
370		402 ^a	Dimer + 4 O
371	Dimer diol + H	415	Dimer + 5 O - 3 H
373		506 ^a	Trimer, C ₃₆ H ₇₄

^aNot enough for ranking.

Table VIII

Oxidations of Hydrocarbons and Fuels in Air at 130°

Expt. No.	Remarks ^a	Oxidn. Time, h	Ppt., h	R ₀ , $\frac{\mu\text{mol O}_2}{\text{g fuel}\cdot\text{h}}$	R _g , $\frac{\text{mg gum}}{100\text{g fuel}\cdot\text{h}}$	R _g /R ₀
n-Dodecane (DOD)						
K80	H ₂ SO ₄ washed, distilled	2.0		7.6 ^c	1.16	0.152
		4.0		13.0	0.38	0.029
		6.0*		14.7 ^c	0.27	0.018
Dodecane Mixtures (see also IND, NMP)						
C42	0.0225 M pyridine	3.5		9.3		
		8.2		26		
53	0.226 M pyridine	2.0		10.5		
		6.5		23		
43	0.175 M t-BuNH ₂	3.5		17		
		8.2		36		
52	0.184 M t-BuNH ₂	2.0		14		
		8.3		32	1.31	0.042
80	0.23 M HCO ₂ H	2.0		5.6		
		8.0		25	0.77	0.030
H34	11.8% TET in DOD	2.0		20		
		6.1		46 ^b	0.185	0.0041
G19	8.1% 1-PH	5.5		11.7		
		11.0		21	0.13	0.0062
66	9.4% chromat. 1-PH	3.0		7.7		
		10.3		23.7	0.14	0.0061
31	9.1% EtN	2.0		1.37		
		62.0		1.49		
68	9.9% chromat. EtN	3.0		0.29		
		46.5		3.6	0.010	0.00028
Tetralin (TET)						
K81	Chromat., distld.	0.57		75 ^d	6.4	0.076
		0.93*		69 ^d	6.9	0.010
Bicyclohexyl (BCH)						
C59		26		0.12		
		517		0.73	0.185	0.26
74		22		0.203		
95	Chromatographed	83		1.81		
96	Chromat., then distilled	1.0		1.49		
		9.0*		18.9	3.9	0.21
1-Phenylhexane (1-PH)						
G70		1.5		0.70 ^a		
		2.5		10	0.56	0.056
G23		3.5		24		
		5.0		28		
		9.0*		28	0.75	0.027
52	Chromatographed	3.5		19		
		5.5		22		
		10		29	0.67	0.023

Table VIII (Continued)

Expt. No.	Remarks ^a	Oxidn. Time, h	Ppt., h	R _o ,	R _g ,	R _g /R _o
				μmol O ₂ g fuel·h	mg gum 100g fuel·h	
Phenylcyclohexane (PCH)						
F15	Chromatographed	2.25		28		
		11.0*		27	5.7	0.21
C73	0.119 M t-BuNH ₂	2.0		20	9.6	0.48
		4.0	4	29	15.2	0.53
F 9	0.139 M NMP	2.0		2.5		
		18.0		6.4	4.7	0.71
38	Chromatographed +	3.0		2.5		
	0.140 M NMP	29.0	29	8.5	6.2	0.72
10	0.224 M pyridine	2.0		28		
		7.0		31	6.2	0.20
16	Chromatographed +	2.5		22		
	0.211 M pyridine	10.0		28	7.8	0.29
2-Ethyl-naphthalene (EtN)						
G3		2		0.92		
		62		0.33		
35	Chromat. (dup.)	6		7.6		
		28		4.7	6.4	1.37
J44	Fractionally	0.94		89	68	0.76
K86	Distilled	0.5		65 ^e	22	0.34
		1.0*		64 ^e	42	0.66
		2.0		42 ^e	42	1.00
Indene (IND)						
G44	Neat, 14.7 M	3.0*		91	1280	14.1
H20	0.0091 M in DOD	14		5.3	0.50	0.094
21	0.0145 M in DOD	13.5		9.5	2.01	0.21
19	0.108 M in DOD	8		18	62	3.45
22	1.00 M in DOD	2.75		60	340	5.6
N-Methylpyrrole (NMP)						
E23	Neat, 11.3 M	2.25*		97	684	7.1
C41	0.0176 M NMP	3.5		0.40		
	in DOD	50		5.7		
91	0.169 M NMP	4		0.54		
	in DOD (dup.)	27		0.50	0.20	0.38
Fuel A ^b						
D70		21.0		0.092		
		182		0.044		
71		24.0		0.087	0.053	0.61
D95		24		0.20	0.050 gum	1.92
		399	262	0.037	+0.021 deposit	
E16		48.0		0.082		
		448*	448	0.038	0.055	1.45
D94	0.206M NMP ^a (dup.)	17.5	17	0.24		
		64.0		0.82	0.44	0.54

Table VIII (Continued)

Expt. No.	Remarks ^a	Oxidn. Time, h	Ppt., h	R _o , $\mu\text{mol O}_2$ g fuel·h	R _g , mg gum 100g fuel·h	R _g /R _o
Fuel B						
H35		29.2 40	29	6.05 10.9 ^f	6.4	0.59
36		15.5 23*	17	5.0 22 ^f	13.0	0.59
66	Chromat. once	8.0 16.3		8.4 23.2	16.7	0.72
73	Chromat. twice	5 17.6		4.4 14.5	11.4	0.78
Fuel C ^b						
E 7		10		3.13	11.0	3.6
5		12		5.3	22	4.2
6	Reconstituted	10		2.8	27	9.6
25		28.3*	28	3.8	5.0	1.33
26	Chromatographed	16.5	15	6.5	11	1.75
27	Reconstituted	16.5	15	7.0	14	1.96
D87	465 torr O ₂	15.5		3.8	21	5.4
E 2	+4.5 wt% SS316 turnings	13.5		3.5	11.9 +0.5 deposit on SS	3.5
Fuel 1						
F23		187*	150	0.063	0.19	3.03
23	Chromatographed	418	220	0.105	0.21	2.00
26	Reconstituted (dup.)	76	30	0.24	0.35	1.45
Fuel 10						
F51		185*	48	0.096	0.142	1.47
54	Chromatographed	159	159	0.14	0.33	2.33
58	Reconstituted	166	70	0.094	0.18	1.89
64	10% reconstituted	24 236	137	0.12 0.13	0.21	1.56
65	10X reconstituted	24 118	24	0.67 0.47	0.77	1.64
G92	14.9% SS316 turnings	17 227	40	0.52 0.16	0.50 gum +0.13 ppt. + 0.11 on SS316	4.6
Fuel 13						
F 3		66 167*	115	0.19 0.20	0.49 gum +0.37 deposit	4.2
8	Chromatographed	52 309	309	0.059 0.048	0.073	1.52
59	Reconstituted	49 185	49	0.25 0.18	0.46	2.5
G17		48	48	0.23		1.30
53		95 827	589	0.085 0.138	0.20 gum +0.20 ppt	2.9

Table VIII (Concluded)

Expt. No.	Remarks ^a	Oxidn. Time, h	Ppt., h	R _o , μmol O ₂	R _g , mg gum	R _g /R _o
				g fuel·h	100g fuel·h	
Fuel 14						
G17		48	48	0.23	0.29	1.30
53	Chromatographed	95		0.085		
		827	600	0.138	0.40	2.94
C28		29.3	7	0.49		
		58*		0.77	0.30	0.38
G62	Chromatographed	115		0.19		
		230		0.20		
Fuel 14A						
L4A	Distilled	72	72	0.220		
	next	164		0.164	0.51 gum	
	total	236		0.181	0.29 deposit	4.3
Fuel 14B						
L4B	Distilled	72	72	0.42		
	next	66		0.50	3.96 soluble	
	total	138		0.46	0.94 deposit	10.6
Fuel 15						
F66		24		0.48		
		167*	50	0.17	0.28	1.69
67	Chromatographed	28		0.71		
		96	40	0.52	1.12	2.17
68	Reconstituted	28		0.21		
		194	140	0.18	0.31	1.72

*Data used in Table 9.

^aPercentages are in mole % for pure hydrocarbons, weight % for fuel mixtures.

^bSee also Section 3.1 for details on Fuel C, also Section 7 for oxidations at low O_2 pressure

^{c,d,e,f}yields of hydroperoxide in % on O_2 absorbed, respectively, for each group of experiments: ^c50, 60; ^d~100, ~100; ^e63, 60, 77; ^f5, 2.

Table IX

COMPARISON OF RATES OF OXIDATION AND GUM FORMATION AT 130°C^a

Fuel	R _o	Fuel	R _g	Fuel	R _g /R _o
NMP	97	IND	1280	DOD	0.018
IND	91	NMP	680	1-PH	0.027
TET	69	EtN	42	TET	0.10
EtN	64	B	13	BCH	0.21
1-PH	28	TET	6.9	PCH	0.21
PCH	27	PCH	5.7	14	0.38
B	22	C	5.0	B	0.59
BCH	19	BCH	3.0	EtN	0.66
DOD	15	13	0.85	C	1.33
C	3.8	1-PH	0.75	A	1.45
14	0.77	14	0.30	10	1.47
13	0.20	15	0.28	15	1.69
15	0.17	DOD	0.27	1	3.0
10	0.096	1	0.19	13	4.2
1	0.063	10	0.14	NMP	7.1
A	0.038	A	0.055	IND	14.1

^aR_o and R_g are defined in Table 8.

Table X
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 _g /R _o	Notes ^b
FUEL C					
0	18.0				
19	12.4	0.20			Nearly stopped at 43 h,
160	7.53	0.044	0.18	4.1	9.2 torr O ₂
0	30.3				
43	16.2	0.22	1.22	5.5	
134	11.0	0.11	0.31	2.8	Nearly stopped at 69 h,
					14.2 torr
0	152.3				
3	150.0	0.51			
17	72.2	3.1			
17	152.1				Air change
23.8	101.7	3.7			
23.8	152.6				Air change
28.8	124.7	3.8	5.0	1.32	
0	153.9				Chromatographed
3	127.0	6.4			
11.5	40.8	7.0			
11.5	152.6				Air change
16.5	130.2	5.9	11.3	1.91	
0	464.8				Used oxygen analyzer
4.5	433.2	3.2			
14.0	301.2	7.7	21	2.7	
FUEL A					
0	20				
44	18.5	0.016			
162			0.017	1.1	[O ₂] increased
0	18.7				
43	17.5	0.0203			
286			0.0122	0.6	[O ₂] increased
0	16.5				
21	11.4	0.18			
50	12.6		0.044	0.24	[O ₂] increased
0	158.0				Expr. D95
24	143.7	19.7			
262	114.9	0.0451			
262	154.7				Air change
399	119.3	0.037	0.050	1.92	
			0.021	deposit	
10 Mole % TET in DOD					
0	20.1				9.15 mol% TET in DOD
1.5	6.53	6.4			
2.5	5.36	4.1			Nearly stopped at 2.5 h,
5.0	5.00	2.2	0.21	0.095	5.4 torr
0	152.0				11.8 mol% TET
2	95.6	20.3			
2	133.5				Air change
4	46.7	24.0 (interval)			
6.1	65.1	42.4	0.125	0.0029	After 2 more air 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."

Appendix B

GUM AND DEPOSIT FORMATION FROM JET TURBINE
AND DIESEL FUELS AT 100°C

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GUM AND DEPOSIT FORMATION FROM JET
TURBINE AND DIESEL FUELS AT 100°C

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ABSTRACT

Rates of oxidation and gum formation for six hydrocarbons, three jet turbine fuels, and three diesel fuels have been measured at 100°C in the presence of $t\text{-Bu}_2\text{O}_2$ as initiator. Four of the six fuels oxidize faster at 100° than in previous work at 130° without initiator. For several substrates, the amount of gum produced for the oxygen absorbed is similar at 100 and 130°, even with large changes in rates and $t\text{-Bu}_2\text{O}_2$ concentrations. Thus, one mechanism of gum formation is intimately associated with oxidation. The effects of $t\text{-Bu}_2\text{O}_2$ concentration on rates of oxygen absorption and gum formation suggest that gum formation is associated with chain termination by two peroxy radicals. The pure hydrocarbons have long kinetic chains and give good yields of hydroperoxides. The fuels give short kinetic chains and produce little hydroperoxide but more gum for the oxygen absorbed. A second mechanism of gum formation is the coupling of substrates by peroxides in the absence of oxygen. A third mechanism, condensation of oxidation products from alkylnaphthalenes, is also proposed.

1. INTRODUCTION

Our previous paper on gum and deposit formation (Mayo, Lan, 1986) described rates of oxidation and gum formation from pure hydrocarbons and fuels in air at 130°. (All temperatures are Centigrade.) The pure hydrocarbons oxidized faster than the fuels but the fuels gave more gum and deposits for the oxygen absorbed. Cooxidations of fuels with additives showed that only those that were most reactive in oxidation had much effect (positive or negative) on the rates of oxidation and that such additives were soon consumed. Evidence with Fuel C showed that soluble oxidation products and gum are the first products formed and that as gum accumulates, it eventually precipitates. However, no precipitate was obtained from oxidation of any pure hydrocarbon. 2-Ethyl-naphthalene, which gave the most gum of any hydrocarbon, is apparently a good solvent for gum.

The present Paper describes similar experiments at 100° in the presence of di-*t*-butyl peroxide ($t\text{-Bu}_2\text{O}_2$). We had several motives in this work. We want to bring our experimental work closer to the temperature range of practical fuel stability problems; we expect to need chain initiators to obtain convenient rates of oxidation at lower temperatures; and we want to determine the effect of rate of initiation on rates of oxidation and gum formation.

2. EXPERIMENTAL

2.1. Fuels

The fuels used were described previously (Mayo, Lan, 1986). Fuel A was a stable jet turbine fuel; C was an unstable No. 2 home heating oil; the others were diesel fuels. Fuel 14B was the highest boiling 6% of Fuel 14; Fuel 14A was the remainder of 14.

2.2. Oxidation Procedures

Oxidations were run on 10-mL samples of fuels in the presence of about 100 mL of air. Depletion of oxygen was measured by gas chromatography at 50°C as described earlier (Mayo, Lan, 1986). $t\text{-Bu}_2\text{O}_2$ (ICN Pharmaceutical, 97% by the HCl method of Mair and Graupner 1964) was initially weighed in the reactor for each run and later delivered by syringe ($D = 0.798$). Hydroperoxides were determined by their refluxing NaI-i-PrOH method.

2.3. Gum Determination

Most of the peroxide survived the oxidations and so we did not use our previous evaporation technique in a nitrogen stream at atmospheric pressure; decomposing peroxide might cause at least some coupling of fuels to dimers. In some runs, the peroxide was removed by adding about 50% of dodecane and distilling at 15 torr. (Dodecane boils higher than the peroxide but below most fuels.)

The procedure adopted is the following. A weighed 4-mL sample of oxidized fuel was put into a 25-mL flask with a short neck and a glass ball joint 23 mm in diameter to hold a Viton O-ring. The other part of the joint was attached with a clamp to 30 cm of 10-mm Pyrex tubing, bent at a 135° angle 12 cm above the joint. The bend led to a 25 mL distilling flask, used as receiver. The fuel was then distilled at ~1 torr with a very small flame until the pot was nearly dry. The 12 cm of vertical tubing provided some reflux and returned "bumped" liquid. The clamp was then removed (for space considerations) and the pot and vertical part of the distilling setup, still at 1 torr, were immersed in a glass bath 6 cm in diameter and 20 cm high. This bath was nearly full of a mixture of ~80% ethylene glycol and 20% water. It was heated to smooth and gentle boiling with a gas flame. The boiling temperature was maintained at 130° by occasional replacement of the evaporated water. The distilling set-up was left at this temperature for five minutes to

provide a reproducible point for completing the gum determination. The set-up was then removed from the bath, clamped, cooled, and eventually opened to air. The side arm was rinsed with reagent acetone to separate this hold-up from the rest of the fuel. The hold-up in the formerly vertical tube and the residue in the pot were then transferred with several portions of reagent acetone (total ~ 2mL) to 50 mg aluminum weighing pans from which the solvent was evaporated on a warm hot plate. These pans were then heated for 20 h at 200°C in a slow stream of nitrogen and then weighed on a microbalance.

Although the absolute values of our gum determinations are of dubious significance, the gum contents are assumed to provide valid comparisons. By use of data for oxidation, Experiment K89A with Fuel 14 during 28 days at 100°C, some educated guesses can be made about the extent of gum formation. Fuel 14, normalized to 100 g, absorbed 1.65 mmoles, 52.8 mg of oxygen and gave about 90 mg of dimers and higher oligomers (evaporation residue) and then 32.4 mg of "gum" after heating for 20 hours at 200°C. By carbon analysis, this "gum" contains 0.03% of the original carbon in the fuel and (by differences from C + H + N) about 8% oxygen, 2.67 mg, 5.1% of the oxygen absorbed. This experiment also yielded a black film on the Pyrex flask. The film was thoroughly rinsed with hexane and then extracted with an acetone/ethanol/benzene mixture. After evaporation of this solution and drying at 1 torr, the deposit weighed 32.24 mg; it was not heated. That 5% of all the oxygen absorbed appeared in the film gum and probably another 5% in the deposit, even after significant losses at 200°, was surprising. This situation is discussed further in Section 3.3.

Our evaporation technique in gum determination has been tested by using the oxidized Fuel 14A from Experiment L4A. Four pairs of evaporations were performed with 2-3.5 g samples of fuel: (1) evaporation to a 6-mm circle of liquid, (2) evaporation to dryness (residue would not flow), (3) evaporation to dryness and then for 10 minutes longer, and (4) by vacuum distillation. In the last procedure, the fuel was concentrated almost to dryness at 1 torr. A cold finger containing dry

ice was then inserted and the distillation was continued to dryness, all parts of the distilling flask being heated to about 100°C. This procedure is expected to remove physically all the monomeric products from the higher boiling products. The latter were then transferred to the usual aluminum dish with reagent acetone. Although the first weights of the four dishes before heating varied considerably, the final weights of the residues after 20 hours of heating all fell between 118.6 and 124.7 mg/100 g fuel and averaged 121.2. Thus, for large residues (4 mg on the dishes), the differences among these evaporation procedures are insignificant and reproducibility is excellent.

3. RESULTS AND DISCUSSION

3.1. Oxidation and Gum Formation

Our data on rates of oxidation (R_o) and gum formation (R_g) are summarized in Table I. Most of the headings need no explanation. The abbreviations for the pure hydrocarbons used correspond, respectively, to n-dodecane, tetralin, 2-ethylnaphthalene, 2-methylnaphthalene, phenylcyclohexane, and 1-phenylhexane. When several oxidation periods are indicated for one run number, fresh air was usually supplied for each. Rates for intervals illustrate the reproducibility of our results and how the rates change with time. Runs in which >78% of the oxygen was consumed in any period are omitted because of possible effects on rates. The highest consumptions of oxygen in runs in Table I are: for H55, Fuel B, 78%; L18, EtN, 75%; F87, DOD, 70%; and J37A, DOD, 66%.

Only three recent TET runs are included. For these, the TET had been washed with 2M NaOH and water and then distilled at 18 torr, with rejection of the first and last portions. Even with efforts to exclude oxygen and and to store at low temperatures, the rates of oxidation were independent of how much $t\text{-Bu}_2\text{O}_2$ was present, and the TET accumulated titratable peroxide. Aldrich EtN, fractionally distilled in vacuum in a good column at NASA, oxidized faster than Aldrich material distilled here with a poor column. MeN oxidized much slower than EtN. It appears

that the rates of oxidation of alkylnaphthalenes depend on the formation of hydroperoxides, their conversion into naphthol inhibitors, and the efficacy of the latter (Larsen et al. 1942).

The oxidations of DOD and Fuels B and C are autocatalytic; oxidations of the alkylnaphthalenes and all the other fuels are self-retarding. With other pure hydrocarbons, trends are not clear. No precipitate was obtained from any pure hydrocarbon but most of the fuels gave adherent precipitates (as well as soluble gum) as uniform films on the parts of the flasks in contact with liquid.

In oxidations of Fuel 14, there were no other solids at reaction temperature, but a faint cloudiness appeared on cooling the reaction mixtures. We interpret this cloudiness to decreasing solubility of the deposit in fuel and we count it as soluble gum. We think that the continuous gentle shaking of our reactor causes all the deposits to grow on the surface films. The ratio of insoluble/soluble gum with $t\text{-Bu}_2\text{O}_2$ in Experiment K89A, ~ 1 , is the largest that we have seen at SRI.

As indicated in Section 2.1, Fuel 14 was fractionated into lower (14A) and high boiling (14B) fractions. The higher-boiling 14B absorbed oxygen somewhat faster than 14A at 0.01 M $t\text{-Bu}_2\text{O}_2$ and gave gum deposits about twice as fast.

Table I shows a wide range of rates of oxidation and gum formation and their ratios. They are summarized in Table II.

Table I gives some yields of hydroperoxides on the oxygen absorbed. The best yields are associated with the fastest oxidations. Some titration of TET hydroperoxide showed more peroxide than the oxygen absorbed. Such results are ascribed to unmeasured oxidation at room temperature before titration.

3.2. Comparison of Results at 100 and 130°C

Rates of oxidation, gum formation, and their ratios in oxidations at 100 and 130° are compared in Table II. Values at 130°C are taken from our previous paper (Mayo and Lan, 1986) and are listed in order of

decreasing magnitude in the R_o and R_g columns and in order of increasing magnitude in the R_g/R_o column. Values at 100° come from runs marked with asterisks in Table I and are listed immediately to the right of the 130° values without respect to the 100° rank. With 0.03-0.04 M t-Bu₂O₂ at 100°C, differences among hydrocarbons and fuels are much smaller than at 130° without initiator. The rankings for R_o for and above Fuel C are similar at the two temperatures; the rates at 130° are 1-6 times those at 100°C. However, MeN and Fuels A, 10 and 13 oxidize faster at 100° than at 130°C. Thus, these fuels have less ability to initiate and maintain their own oxidations and have shorter kinetic chain lengths than the other and faster oxidizing fuels; they are self-retarding in oxidations.

Use of t-Bu₂O₂ at 100° also narrows the range of R_g . Again, the faster oxidizers give gum faster at 130 than at 100°; the reverse applies to the slow oxidizers.

The R_g/R_o ratios tell us the relative amounts of gum formed for the oxygen absorbed. If the mixture of mechanisms for gum formation is the same at 100 and 130°, then the ratios of R_g/R_o for the two temperatures should be the same. The last column of Table II shows that 5 of the 12 ratios are between 0.5 and 2, 7 between 0.3 and 3, even with large differences in R_o and R_g alone. The experimental error in measuring low rates of oxygen absorption and gum formation may contribute to the larger discrepancies.

This section shows that a controlled rate of initiation is important to understand gum formation and that it will be important at lower temperatures where reactions are much slower.

3.3. Effects of Concentration of t-Bu₂O₂

Table III summarizes effects of changes in t-Bu₂O₂ concentrations from three-fold to 76-fold for each of several fuels on R_o , R_g , and their ratios. The smaller effects of t-Bu₂O₂ are associated with the hydrocarbons and fuels that oxidize fastest at 100° without t-Bu₂O₂. However, the R_g/R_o ratios for a single fuel are little affected by the

changes in R_o and R_g , showing that the mechanism of gum formation is intimately related to the mechanism of oxidation. The last two columns give the apparent orders (n) of R_o and R_g on the initial concentration of $t\text{-Bu}_2\text{O}_2$, calculated from the relation:

$$\text{Ratio of } R_o \text{ (or } R_g) \text{ values} = \text{ratio of } [t\text{-Bu}_2\text{O}_2]^n.$$

In conventional long chain oxidations, $n = 0.5$ but as the kinetic chain length approaches zero, n approaches 1. $n = 1$ is also characteristic of inhibited or self-retarding oxidations. The fastest (longest chain) oxidizers, DOD and EtN, have n values of < 0.3 in Table III. These low values are consistent with their fairly fast oxidations without $t\text{-Bu}_2\text{O}_2$ and neglect of autocatalysis or self-retardation. The other, slower oxidizing fuels have n values closer to 1, corresponding to short chains and/or self retardation. The orders for R_o and R_g are nearly parallel.

Table IV presents the same basic data in another manner. The first two columns of data give the μ moles of oxygen absorbed and $t\text{-Bu}_2\text{O}_2$ decomposed in the whole reaction mixtures. Details for each experiment are given in Table I. The $t\text{-Bu}_2\text{O}_2$ decomposed is calculated from the equation (Raley et al., 1948):

$$\log \frac{\text{initial } t\text{-Bu}_2\text{O}_2}{\text{final } t\text{-Bu}_2\text{O}_2} = 0.002143 t \text{ (in hours)}$$

The kinetic chain length (number of molecules of oxygen absorbed in chain propagation for each $t\text{-BuO}\cdot$ radical produced) is equal to $(\Delta O_2 / 2\Delta t\text{-Bu}_2\text{O}_2) - 1/2$, where the 1 is the net oxygen absorbed in chain termination for radicals of two alkylperoxy radicals. The kinetic chain lengths range up to 130 with the pure hydrocarbons (except MeN) and are substantially higher with low $t\text{-Bu}_2\text{O}_2$ concentrations and long times than with high peroxide concentrations. The oxygen absorbed at long reaction times probably includes contributions from autocatalysis, which is neglected in the calculations. The fastest oxidizing Fuels B and C also

give significant chain lengths, but the other fuels give little chain propagation and therefore little hydroperoxide.

The last two columns of figures in Table IV give the mg of gum formed in the listed experiments and the mg of gum per mmole of $t\text{-Bu}_2\text{O}_2$ decomposed. For most single fuels, this ratio changes only moderately with the amount of $t\text{-Bu}_2\text{O}_2$ decomposed. As with chain lengths, the highest yields of gum tend to occur at the lowest concentrations of $t\text{-Bu}_2\text{O}_2$ (Table I) and the longest reaction times where autocatalysis would distort results the most. Autocatalysis may account for the deviations in gum yields with DOD and EtN. The yields of gum are in the range 3 to 2000 mg/mmole $t\text{-Bu}_2\text{O}_2$ decomposed. Variations in the yields of gum with different fuels correspond to difference efficiencies in the coupling reaction. On this basis, EtN is the most efficient gum former, followed by 14B, 14A, PCH, 1-PH, TET, 13, 10, B, C, and A. MeN and DOD are the least efficient gum formers. This order agrees poorly with those for R_g and R_g/R_o in Table II, which have different bases.

3.4. Mechanisms of Gum Formation

This section presents three mechanisms for formation of soluble gum in air at and below 130°C , which requires hours. They are probably related to the mechanisms of deposit formation on heated metal tubes in a Jet Fuel Thermal Oxidation Tester (JFTOT, ASTM, 1975), where a stream of n -dodecane containing dissolved oxygen was exposed to a hot tube for 28 seconds at various temperatures between 190 and 538°C (Hazlett et al. 1977). However, the deposits, which are more practically important, are mostly insoluble and higher in N, S, and aromatics than the gums and the fuels. In the Hazlett work (1977) the concentration of hydroperoxides reached a maximum when the dissolved oxygen was exhausted at 282°C . Between 282 and 385°C , the peroxides decomposed, mostly to alcohols, but partly to ketones, and initiated pyrolysis to CO and smaller alkanes and alkenes. A later paper (Hazlett 1980) shows that deposits start to form during the oxidation, but that most of them appear during the decomposition of peroxides. He concludes that the deposits are formed

at high free radical concentrations.

Our previous paper (Mayo, Lan 1986) proposed that gum formation starts with coupling of two alkylperoxy radicals in the chain termination of oxidation and that growth beyond dimer depends on converting dimer to peroxy radicals by chain propagation. Tables 3 and 4 are consistent with these proposals, which we have no reason to change. The Tables do not resolve the questions of the relative contributions of propagation and termination to gum formation because the orders on $t\text{-Bu}_2\text{O}_2$ are parallel. Tables 3 and 4 show that autocatalysis in fast oxidations obscures the effect of $t\text{-Bu}_2\text{O}_2$, but that most fuels have short kinetic chain lengths and a small range for $\text{mg gum}/\Delta t\text{-Bu}_2\text{O}_2$.

The second mechanism is the coupling of fuel molecules and their oxidation products in the absence of oxygen. We have two new examples. In one experiment, 10.3 g of oxidation product L18 containing 5.80 mg gum and 0.853 mmole of hydroperoxide was heated for 24 h at 135-150° in an evacuated tube. The usual gum determination then gave 258 mg of yellow oil and white crystals after distillation at 1 torr, and 84.1 mg of "gum" after 20 h heating at 200°, an increase of 78.3 mg, 13.5 times the gum formed in the oxidation step. If the additional material is all dimer ($\text{C}_{24}\text{H}_{22}$), 0.252 mmole was produced by 0.853 mmole of hydroperoxide, a yield of 30% after (and 95% before) the 20-h heating at 200°.

In another experiment, 9.86 g, 63.1 mmole, of EtN and 1.486 g, 9.84 mmole, of 97.6% $t\text{-Bu}_2\text{O}_2$ was heated in a sealed evacuated tube at 150°. An aliquot was then concentrated at 1 torr, finally for 5 min at 130°. The residue corresponded to 2.084 g, 6.71 mmole, of mostly crystalline, white dimer, a yield of 68.2% on the peroxide used.

Thus the coupling of hydrocarbons by peroxides in the absence of oxygen produces dimers (and presumably some oligomers) in good yield without incorporation of oxygen (except possibly from the peroxide). Oxygen prevents this direct coupling and gives gums containing several percent of oxygen. The yield of coupling products in oxidation are very

low but vary greatly (Section 3.3) and the products contain oxygen. The oxygen pressure at which one coupling reaction replaces the other is unknown.

The extraordinarily high yields of gum for the $t\text{-Bu}_2\text{O}_2$ decomposed from the best NASA EtN in Experiments J44B and L18 suggests that another mechanism of gum formation is involved. This mechanism has not yet been investigated, but it might involve some reaction like the condensation of naphthaldehyde and naphthol; both are possible secondary products from the oxidation of EtN.

4. SUMMARY AND CONCLUSIONS

This paper extends our previous work (Mayo and Lan, 1986) on oxidation and gum formation in pure hydrocarbons, jet turbine, and diesel fuels at 130°C without added initiator to 100° with added $t\text{-Bu}_2\text{O}_2$. Three of the six fuels and MeN oxidize faster at 100° than at 130° . These fuels have short kinetic chain lengths in oxidation and do not produce much hydroperoxide. Thus, comparison of individual rates of oxidation and gum formation for various fuels at unknown rates of initiation is of dubious significance. However, for any single substrate, the amount of gum produced for the oxygen absorbed (R_g/R_o) tends to be similar at 100° and 130° , even with large changes in rates of oxidation and gum formation and $t\text{-Bu}_2\text{O}_2$ concentration. Thus, one mechanism of gum formation is intimately associated with ongoing oxidation.

The effects of $t\text{-Bu}_2\text{O}_2$ concentration on rates of oxygen absorption and gum formation show that the kinetic orders of these reactions range from 0.25 to 1.0 but have a similar magnitude for each hydrocarbon or fuel. In general, the pure hydrocarbons have small kinetic orders and long kinetic chains and give good yields of hydroperoxides and low yields of gum for the oxygen absorbed. Most of the fuels have kinetic orders approaching one and short kinetic chain lengths and produce little hydroperoxide but much gum for the oxygen absorbed.

Another mechanism of gum formation is the coupling of substrates by peroxides in the absence of oxygen. This is an efficient mechanism for coupling and the products contain little or no oxygen if they are made from hydrocarbons. This mechanism is replaced by the oxidation termination mechanism when gaseous oxygen is present. The oxygen pressure at the transition is not yet known.

The last paragraph of Section 3.4 proposes that products of oxidation of EtN condense to give high yields of gum by a third mechanism. This is consistent with a report of Kiiko (1982) that a resin is the principal oxidation product of 1-methylnaphthalene and that much more naphthaldehyde than naphthoic acid is formed.

Gum formation by aldol condensations and esterification of oxidation products (Mayo, 1975) and by aldehyde-hydroperoxide interactions leading to polyesters (Sauer et al., 1958) have been proposed, but so far we have seen no need for these mechanisms.

ACKNOWLEDGEMENT

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Table I

OXIDATIONS OF PURE HYDROCARBONS AND FUELS AT 100°C

Expt. Number	Fuel ^a	t-Bu ₂ O ₂ , M	Reaction Time, h ^b	R ₀ ^c	R _g ^d	R _g /R ₀	Peroxide ^e
F86	DOD	0.010	102.5	1.50 ^f	0.027	0.018	
F87	DOD	0.10	54.5	2.80 ^c	0.063	0.022	
J37A	DOD ^{f*}	0.038	16	2.73			
			next 24	3.46 ^f			
			Total 40	3.15	0.29	0.092	
J37B	DOD + 3 mole % anthracene	0.051	16	1.02 ^f			
			next 24	1.36 ^f			
			Total 40	1.08	0.30	0.28	
K92A	DOD	0	52	0.28	0.066	0.111	
			next 49	0.92 ^f			
			Total 101	0.59	0.066	0.111	
K92C	DOD	0.041	23	2.6	0.26	0.10	
L15A	DOD	0.010	28	1.69	0.28	0.17	77
L15B	DOD	0.100	10	3.2			
			next 12	3.6 ^f			
			Total 22	3.4	0.42	0.12	77
L27B	TET	0	1.00	33			
L55A	TET [*]	0.010	0.5	37	6.23	0.19	>90
			next 1.5	29			
			Total 2.0	31	15	0.47	>90
L55B	TET [*]	0.10	0.5	50			
			next 1.5	28			
			Total 2.0	32	11	0.33	>90
J5 } J6 }	EtN	0.066	9	10 ^d	3.6	0.37	31.8
L39A } L27C }	Aldrich wash NaOH	0.57	7	29 ^d	15.5	0.54	11.0
J44B } L18 }	EtN, NASA	0.010	2	8.3	3.6	0.44	>90
		9	3	17	5.0	0.29	65
		0.034	1.03	36	19	0.53	>90
		0.106	1.00	18			
			next 1.00	21			
			next 1.00	20			
			next 1.10	28			
			next 1.07	18			
			Total 5.17	21	11	0.51	75

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GUM AND DEPOSIT FORMATION IN DIESEL FUELS(U) SRI
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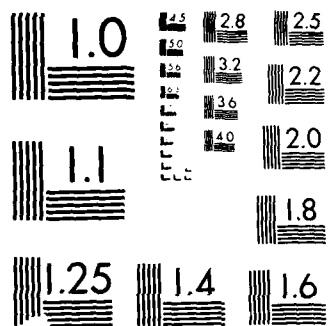
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UTION TEST CHART

Table I

OXIDATIONS OF PURE HYDROCARBONS AND FUELS AT 100°C (Continued)

Expt. Number	Fuel ^a	t-Bu ₂ O ₂ , M	Reaction Time, h ^b	R _g ^c	R _g ^d	R _g /R _o	Peroxide ^e
J23A	MeN	0.039	3 next 7 next 12 next 26 Total 48	0.33 0.23 0.25 0.19 ^d 0.22	0.87	4.0	
J23B	MeN Chromat.	0.039	3 next 7 next 12 next 26 Total 48	0.84 0.61 0.28 0.27 ^d 0.36	1.42	4.0	
L14	MeN, recrystal- ized	0.012	16.6 next 72 Total 88.6	0.42 0.14 ^d 0.19	0.47	2.5	22
G37	PCH [*]	0.030	7 next 8 next 6 Total 21	8.9 9.0 5.6 7.6	0.90	0.12	
L21A	1-PH [*]	0.037	7	5.0	1.91	0.39	
H63	Fuel A	0	255	0.0059 ^d	0.0054	0.91	
H64	Fuel A	0.0045	277(136)	0.054 ^d	0.051	0.95	
H57	Fuel A [*]	0.036	140	0.30 ^d	0.28	0.95	~0
H77	Fuel A	0.34	19	5.18 ^d	3.02	0.58	3
H55	Fuel B [*]	0.042	40.5	3.60 ¹	0.542	0.151	13
H54	Fuel C [*]	0.037	52(31)	3.20 ¹	0.42	0.130	2.4
F81	Fuel 10	0	209	0.013 ^d	0.016	1.19	
F84	Fuel 10 [*]	0.010	113(113)	0.094 ^d	0.141	1.49	
F79	Fuel 10 [*]	0.10	60(48)	0.915 ^c	1.354	1.48	

Table I
OXIDATIONS OF PURE HYDROCARBONS AND FUELS AT 100°C (Concluded)

Expt. Number	Fuel ^a	t-Bu ₂ O ₂ M	Reaction Time, h ^b	R _g ^c	R _g ^d	R _g /R ₀	Peroxide ^e
F82	Fuel 13	0	209(120)	0.070 ^d	0.105	1.49	
F83	Fuel 13	0.010	113(113)	0.11 ^d	0.15	1.34	
F78	Fuel 13	0.10	60(48)	0.50	1.64	3.25	
G54	Fuel 13 Chrom.	0	1510	0.0069 ^d	0.0097	1.41	
G59	Fuel 13*	0.029	144(144)	0.44 ^d	0.42	0.95	~0
K89A	Fuel 14	0	28 days (28d)	0.025 ^d	0.048		
K89B	Fuel 14*	0.037	20 days (7d)	0.22 ^d	0.48p 0.62	3.8 2.8	~0
L4C	Fuel 14A	0.010	10 days (72)	0.105 ^d	0.31	4.3	
L4D	Fuel 14A	0.101	140(72)	0.763 ^d	0.141p 2.51 0.89p		<30
L22A	Fuel 14B	0.010	72 next 68 Total 140	0.204 0.067 ^d			8
L22K	Fuel 14B	0.16	72	0.14 0.69	1.18 4.9	8.6 7.0	<30 8

* Experiments included in Table II.

^a Vacuum distilled except as noted.

^b The number in parentheses is the time when deposit formation was first noted.

^c In this column, i, c, d indicate increasing, constant or decreasing rates with time.

^d R₀ = rate of O₂ absorption in μ moles O₂/g fuel $\cdot$ h.

^e R_g = rate of gum formation in mg gum/100 g fuel $\cdot$ h. Numbers are for formation of soluble gum except when marked p for precipitate; R_g/R₀ includes both.

^e Yield of hydroperoxide on oxygen absorbed.

Table II

COMPARISON OF RATES OF OXIDATION AND GUM FORMATION AT 100° AND 130°C^a

R _O		R _O 130°		R _O 100°		R _O 130°		R _O 100°		R _O 130°		R _O 100°		R _O 130°		R _O 100°	
Fuel	130°	100°	R _O 130°	R _O 100°	Fuel	130°	100°	R _O 130°	R _O 100°	Fuel	130°	100°	R _O 130°	R _O 100°	Fuel	130°	100°
TET	69	31 ^b	2.2	2.2	EtN	42	19	2.2	2.2	DOD	0.018	0.092	0.20	0.20			
EtN	64	36	1.8	1.8	B	13	0.54	24	24	1-PH	0.027	0.39	0.07	0.07			
1-PH	28	5.0	5.6	5.6	TET	6.9	13 ^b	0.53	0.53	TET	0.10	0.39 ^b	0.26	0.26			
PCH	27	7.6	3.6	3.6	PCH	5.7	0.90	6.3	6.3	PCH	0.21	0.12	1.8	1.8			
B	22	3.6	6.1	6.1	C	5.0	0.42	12	12	14	0.38	2.8	0.014	0.014			
DOD	15	3.2	4.8	4.8	13	0.85	0.42	2.0	2.0	B	0.59	0.15	3.9	3.9			
C	3.8	3.2	1.2	1.2	1-PH	0.75	1.9	0.39	0.39	EtN	0.66	0.53	1.3	1.3			
14	0.77	0.22	3.5	3.5	14	0.30	0.62	0.31	0.31	C	1.33	0.13	10	10			
13	0.20	0.44	0.45	0.45	DOD	0.27	0.29	0.93	0.93	A	1.45	0.95	1.5	1.5			
MeN	0.098	0.22	0.45	0.45	MeN	0.16	0.87	5.4	5.4	10	1.47	1.5 ^b	0.98	0.98			
10	0.096	0.29 ^b	0.33	0.33	10	0.14	0.44 ^b	0.32	0.32	MeN	1.65	1.4	2.4	2.4			
A	0.038	0.30	0.13	0.13	A	0.055	0.28	0.20	0.20	13	4.2	0.95	4.4	4.4			
Spread ^c	1816	164	47	47	764	83	68	233	30	63							

^aRates of 130° were measured without added initiator; rates at 100° were measured with 0.03-0.04 M t-Bu₂O₂. 100° data are from experiments marked with * in Table I.

^bGeometric mean of 0.01 and 0.10M t-Bu₂O₂ rates.

^cRatios of highest to lowest value in each column.

Table III
EFFECT OF $[t\text{-Bu}_2\text{O}_2]_0$ on R_0 and R_g at 100°C

Fuel	Experiment Numbers ^a	Ratios at Higher/Lower $[t\text{-Bu}_2\text{O}_2]$				Apparent Order on $t\text{-Bu}_2\text{O}_2$	
		$t\text{-Bu}_2\text{O}_2$	R_0	R_g	R_g/R_0	R_0	R_g
DOD	F86, 87	10	1.87	2.3	1.22	0.27	0.36
	L15A, B	10	2.02	1.47	0.73	0.29	0.17
EtN	J5, 6	8.63	2.97	4.31	1.45	0.50	0.68
	J44, L18	3.21	1.71	1.73	1.04	0.25	0.25
Fuel A	H64, 77	75.6	96	59	0.61	1.05	0.94
Fuel 10	F79, 84	10	9.73	9.6	0.99	0.98	0.98
Fuel 13	F78, 83	10	4.39	10.8	2.42	0.64	1.03
Fuel 14A	L4C, D	10.1	7.27	7.54	1.05	0.86	0.87
Fuel 14B	L22A, B	10.0	5.05	4.2	0.81	0.70	0.62

^aDetails in Table I.

Table IV

RELATIONS OF $t\text{-Bu}_2\text{O}_2$ DECOMPOSED TO KINETIC CHAIN LENGTHS
AND GUM YIELDS

Substrate	Expt. Number	ΔO_2 , Millimoles	$\Delta t\text{-Bu}_2\text{O}_2^a$	Kinetic Chain Length ^b	Gum, mg	$\frac{\text{Mg Gum}}{\Delta t\text{-Bu}_2\text{O}_2^a}$
DOD	F86	1.334	0.046	14	0.24	5.3
	F87	1.241	0.254	2	0.72	2.83
	J37A	0.942	0.066	6.7	0.8	13.3
	L15A	0.351	0.013	13	0.59	46
	L15B	0.561	0.103	2.2	0.68	6.6
	J37B ^c	0.330	0.092	1.3	0.9	9.6
TET	H96	1.427	0.0092	77	0.50	54
EtN	J5	0.278	0.0088	15	1.03	117
	J6	0.650	0.065	4.5	3.5	54
	J44B	0.363	0.0017	106	1.92	1130
	L18	2.209	0.0053	130	11.3	2120
MeN	L14	0.170	0.0421	1.5	0.476	11.3
PCH	G37	1.476	0.028	26	1.76	63
1-PH	L21A	0.296	0.011	13	0.664	60
A	H64	0.121	0.0325	1.3	1.15	35
	H57	0.335	0.1755	0.46	3.18	18.1
	H77	0.796	0.296	0.85	4.64	15.7
B	H55	1.174	0.0732	7.5	1.77	24
C	H54	1.389	0.081	8.0	1.80	22
10	F84	0.1165	0.0540	0.6	1.74	32
	F79	0.0899	0.281	~0	7.8	28
13	F83	0.146	0.055	0.82	1.95	35
	G59	0.400	0.213	0.54	7.7	36
	F78	0.0513	0.237	~0	7.9	42
14	K89B	0.902	0.333	0.80	2.5	75
14A	L4C	0.212	0.069	1.0	6.7	97
	L4D	0.919	0.505	0.4	41	81
14B	L22A	0.298	0.050	3.1	14.5	293
	L22B	0.439	0.30	0.24	31	104

^a Mmoles $t\text{-Bu}_2\text{O}_2$ decomposed during oxidation.^b Kinetic chain length = $(\Delta\text{O}_2/2 \Delta t\text{-Bu}_2\text{O}_2) - 1/2$.^c Contained ~3 mole% anthracene.

Appendix C

SOURCE OF JFTOT DEPOSITS FROM AN
OXIDIZED JP-8 FUEL

Source of Jet Fuel Thermal Oxidation Tester Deposits from an Oxidized JP-8 Fuel

The object of this research was to determine what components of an oxidized fuel are most responsible for deposits on hot engine parts. A 5-deg boiling range cut of a JP-8 fuel was oxidized with air at 100 °C and then fractionally distilled at 25- and 5-Torr pressure into (essentially) recovered fuel, a high boiling fraction (containing monomeric oxidation products), and a residue (containing bifunctional and polymeric materials). Restoration of polymeric oxidation products to the original or recovered fuels greatly increased deposit formation in the jet fuel thermal oxidation tester (JFTOT), ASTM D 3241, but restoration of monomeric oxidation products had little effect. An explanation is proposed.

1. Introduction

The jet fuel thermal oxidation test (JFTOT), ASTM D 3241, is one of the best measures of the tendency of middle distillates to give deposits on hot engine parts. For control of these deposits, the fractions of an oxidized fuel that cause most of these deposits should be known. In the work described here, a narrow-boiling fraction of JP-8 fuel was oxidized with air at about 100 °C and then cut by fractional distillation into the main fraction (mostly unoxidized fuel), the monomeric oxidation products of higher boiling point (mostly hydroperoxides, alcohols, and ketones), and the undistillable residue. The best data on primary oxidation products of alkanes come from the papers by Jensen and co-workers (Jensen et al., 1979; Korcek et al., 1987) on the oxidation of *n*-hexadecane in a flow microreactor at 160 °C with a few minutes average residence time and 119 Torr of oxygen: 48.5 mol % hydroperoxides, 38% alcohols, 0.5% ketones, 8% diols (after reduction), 0.3% cyclic ethers, and also 4.5% cleavage products (Jensen et al., 1981), mostly acids and ketones. Longer oxidations give more alcohols, ketones, and cleavage products from decompositions of hydroperoxides. Formation of bifunctional products is favored by higher oxygen pressures and formation of cyclic ethers by lower oxygen pressures. At 120 °C, the C₁₆ products were 73.5% monofunctional, 25.2% difunctional, and 1.3% trifunctional (Jensen et al., 1979). Thus, the undistillable residue from oxidation of our JP-8 fuel may contain bifunctional products amounting to perhaps one-third of the amount of monofunctional oxidation products.

2. Experimental Part

Four gallons of JP-8 fuel (coded AL-12780-F) was supplied by Southwest Research Institute. Its boiling range by D 86 (10–90%) was 161–172 °C. Table I shows its boiling range in a packed column at atmospheric pressure and in a 1-m Vigreux column at 25 Torr. In two series of distillations at 25 Torr, 34.5 wt % material (fraction 77) was cut out with a 5-deg boiling range. By GC, it consisted of C₉ and C₁₀ hydrocarbons. Two liters of this fraction in a 3-L flask was oxidized with good stirring in a slow stream of air at an average temperature of 100 °C, controlled by the voltage on a mantle. The exit gas was tested occasionally for oxygen content; the lowest O/N ratio found was 0.16. For a half-life of 140 h at 100 °C, about 90% of the initial 0.01 M *t*-Bu₂O₂ decomposed in 19 days. More

Table I. Oxidation of JP-8

boiling range at 760 mmHg = 137–188 °C	
boiling range at 25 mmHg = 50–86 °C	
11 950 g of JP-8 cut into 4125 g of fraction 77 (boiling range at 25 mmHg = 67–72 °C)	
2 L of fraction 77 (1545 g) oxidized in air with 0.01 M <i>t</i> -Bu ₂ O ₂ for 19 days at ~100 °C to give 1495 g of product 84A (D 25 0.7718)	
	moles of ROOH ^a
product 84A distilled at 25 torr yielded	
1359 g of 84C, boiling range 58–80 °C, mostly recovered fuel with some cleaved oxidation products	0.119
123 g of 84D, distillation residue	0.006
2 g of H ₂ O	0.085
11-g loss by decomposition during distillation	0.028 (24%)
121 g of 84D distilled in 3 lots at 5 Torr yielded	
60 g of 87A, boiling range 50–80 °C, mostly <54 °C, monomeric oxidation products	0.003
51 g of 87B, distillation residue, bifunctional monomeric and polymeric products (1 g of deposit on reactor added to 87B; >95% dissolved)	0.057
10 g of H ₂ O and loss	0.025 (30%)

^a By Hercules method I (Mair and Graupner, 1964).

Table II. Compositions of Fuels in JFTOT's^a

expt	fraction			87B bifunctional and polymeric
	77 unoxidized	84C recovered	87A monomeric	
1	100			
2	100			
3	95.8		4.2%	
4	96.6			3.4%
5(reconstituted oxidized fuel)		92.8	4.0%	3.2%
6		96.8		3.25%
7		96.0	4.0%	

^a Weight percent in 605-mL samples.

details are given in Table I. Table I summarizes the oxidation of this fraction to the whole liquid product (84A) and further fractional distillation of the latter at 25 Torr into mostly unreacted fuel and cleavage products (84C) and the first distillation residue (84D). Because peroxides are concentrated and less stable in this residue, it was distilled

Table III. Results of Jet Fuel Thermal Oxidation Test (JFTOT), ASTM D 3241

	change in pressure, mmHg ^a	TDR spun deposit rating ^b	visual rating ^c	max thickness by DMD, ^d cm × 10 ⁻⁷	vol of deposit by DMD, ^d cm ³ × 10 ⁻⁷
1	0	8 at 51	1	7 at 36	25
2	0	10 at 51	1	9 at 44	30
3	0	11 at 51	3 (spot)	9 at 50	28
4	125 in 46 min	30 at 32	<3P	664 at 32	1105
5	125 in 54 min	22 at 32	<3P	319 at 18	572
6	125 in 64 min	22 at 32	<3P	575 at 32	1012
7	0	12 at 51	1	18 at 34	33

^a At filter. ^b Highest rating observed on heating tube at indicated distance (mm) from cool fuel inlet end. ^c P = peacock variety of colors. ^d Deposit measuring device, which utilizes dielectric breakdown voltage to define deposit thickness (Stavinoha et al., 1986). The last number on each line is the position on the heating tube, as in b.

in three portions at 5 Torr and separated into distillate (87A, monomeric oxidation products) and a residue (87B) which could not be safely concentrated further.

Fuel samples of 605 mL were made up as shown in Table II. The original 84A contained 4.1 wt % 87A and 3.5 wt % 87B, but the quantities of these materials available were not quite sufficient to make these proportions in the experiments listed in Table II. The blends were evaluated by the JFTOT, ASTM D 3241, with previous aeration of the samples with a mixture of 10% oxygen and 90% nitrogen. The test was run at 282 °C, which gave a reasonable deposit with the neat JP-8.

For gum preparation and analysis, 25 mL, 19.35 g of fraction 77 was oxidized with 0.1 M *t*-Bu₂O₂ for 168 h at 100 °C; 11.16 mmol of O₂ was absorbed. The product was concentrated up to a liquid temperature of 85 °C, leaving 0.594 g of concentrated gum, a yield of 4.0 wt % fraction 77. This gum was miscible with hexane, even on chilling, and no precipitate could be separated. Analyses were as follows: fraction 77, 85.70% C, 14.02% H, 0.25% N, 0.40% S, 100.37% total; concentrated gum, 70.70% C, 9.14% H, 0.80% N, 0.44% S, 18.92% O by difference. The H/C ratio decreased from 1.95 in the fuel to 1.54 in the gum concentrate, with significant concentration of nitrogen and possibly some concentration of S in the gum.

3. Results and Discussion

Table III shows that experiments 4–6, which contain polymeric and some polyfunctional monomeric oxidation products, consistently give the most deposits. The differences are most impressive with the deposit thicknesses and volumes determined by the deposit measuring device of Stavinoha et al. (1986). The most deposit is obtained from the polymeric oxidation product blended into unoxidized fuel (experiment 4). The next most deposit is obtained from the same oxidation product in recovered oxidized fuel. Addition of monomeric oxidation product to fuel does not contribute to deposit formation; it even reduces the amount of deposit obtained with the polymeric oxidation product.

These results are consistent with the following explanation of deposit formation. Deposits come mostly from decomposition of peroxides (Hazlett, 1980) at or near the surface of the hot metal, but to form deposits, some products must be adsorbed (deposited) on the surface. The data indicate that monomeric decomposition products are

not readily adsorbed but the polymeric and polyfunctional ones are. The presence of some low-boiling polar products in the oxidized fuel and the addition of monomeric oxidation products apparently enhance the solubility of the polymeric decomposition products enough so that fewer of them are absorbed. It should follow that addition to fuels of small proportions of good solvents for gum should discourage deposit formation. Thus, the practical effect of "detergents" in reducing deposit formation may be due mostly to their solvent properties.

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