

GENERAL PAPERS - POSTER SESSION
PRESENTED BEFORE THE DIVISION OF PETROLEUM CHEMISTRY, INC.
AMERICAN CHEMICAL SOCIETY
WASHINGTON, D. C. MEETING, AUGUST 28-SEPTEMBER 2, 1983

GUM AND DEPOSIT FORMATION FROM JET TURBINE AND DIESEL FUELS

By

F. R. Mayo and B. Y. Lan
SRI International, Menlo Park, California 94025

INTRODUCTION

The objective of this work is to determine the chemistry of deposit formation in hot parts of jet turbine and diesel engines and, thus, to predict and prevent deposit formation.

Previous work in the field has been extensive (1, 2), but a real understanding of deposit formation has been elusive. Work at SRI started on the basis that deposit formation from fuels must take place stepwise and is associated with autoxidation and the hydroperoxide produced (3). More recent work (4) showed that in the absence of dissolved oxygen, higher temperatures are required for deposit formation. Our recent report (5) indicated that gum and deposit formation proceed mainly through oxidation products of the parent hydrocarbon, coupling of these products to dimeric, trimeric and higher condensation products (partly or wholly by radicals from hydroperoxides) and precipitation of insoluble products. We know of no information on how these first precipitates are converted to the ultimate, very insoluble, carbonaceous materials that cause engine problems.

The present paper describes measurements of rates of oxidation and soluble gum formation in both pure hydrocarbons and mixed hydrocarbon fuels. Some patterns appear that can be largely explained on the basis of what is known about co-oxidations of hydrocarbon mixtures.

EXPERIMENTAL PROCEDURES

All of our hydrocarbons and fuels were distilled at about 10 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 all such cases, chromatography through acidic alumina resulted in faster oxidations at fairly steady rates.

All of our oxidations were carried out in an oil bath at 130°C, with shaking under air. At intervals, 70- μ L samples of gas were withdrawn and analyzed for oxygen/nitrogen ratio by gas chromatography on a 6' x 1/8" O. D. stainless steel column packed with 13X molecular sieve and attached to a thermal conductivity detector. Soluble gum was determined by evaporating a weighed 5-mL sample of fuel in a gentle stream of nitrogen at 160°C (without spattering). The residue (~0.1 mL) was then transferred with 1-2 mL of acetone to a tared aluminum dish weighing about 50 mg. This sample was then brought to constant weight (3-10 h) in a gentle stream of nitrogen in a furnace at 200°C. Weighings were made on a Perkin Elmer AD-22 electromicrobalance. This method gave results reproducible within 20% at low levels of gum, usually within 5% at higher levels.

Fuels A and C are very stable and very unstable jet turbine fuels supplied by NASA-Lewis Research Center. Fuels 1, 10, 13, 14 and 15 are diesel fuels supplied by the U. S. Army Fuels and Lubricants Research Laboratory.

RESULTS

Table I summarizes our work on pure hydrocarbons and several fuels; it shows that gum formation is closely associated with oxidation. Indene and N-methylpyrrole (NMP) are listed separately at the bottom of the table because they are special cases. The other materials are listed in the first column of figures according to decreasing rates of oxygen absorption under air at 130°C. There is a clear distinction between the pure compounds, which oxidize faster and the fuels, which oxidize slower. The second column of figures lists the same materials in order of decreasing rate of gum formation, which is nearly the same as the order for oxidation. The figures in the last column are the quotients of the rates for the indicated fuels in the previous columns. This column shows that the pure, fastest oxidizing compounds usually require the most oxygen to produce a milligram of gum, or that the fuels at the bottom of this column produce the most gum for the oxygen absorbed. The quotient is constant with time for Fuel A; similar information is lacking for other fuels.

TABLE I
 RATES OF OXIDATION, GUM FORMATION AND RATIOS OF
 OXYGEN ABSORBED TO GUM FORMED

	umole O ₂	Mg gum		100 umole O ₂	
	g fuel/hr	100 g fuel/hr		mg gum	
1-Phenylhexane	27.5	EtN	6.4	1-PH	40
Phenylcyclohexane	27.2	PCH	5.7	DOD	15
n-Dodecane	24.0	C	5.1	BCH	4.8
Bicyclohexyl	18.5	BCH	3.9	PCH	4.7
2-Ethyl-naphthalene	4.7	DOD	1.6		
		1-PH	.71	14	1.3
Fuel C	3.8			A	.80
Fuel 14	.78	14	.58	C	.75
Fuel 13	.20	13	.48	EtN	.73
Fuel 15	.17	15	.28	10	.65
Fuel 10	.09	1	.19	15	.59
Fuel 1	.06	10	.14	13	.42
Fuel A	.05	A	.05	1	.34
N-Methylpyrrole	97	IND	1282	NMP	.14
Indene	91	NMP	684	IND	.07

Table I shows that the rate of gum formation increases with the rate of oxygen absorption. Although the unstable Fuel C oxidizes and produces gum 80-100 times as fast as stable Fuel A, the oxygen required to make a milligram of gum is the same for the two fuels.

The special cases of indene and NMP are now considered. The other compounds and fuels in Table I apparently give mostly hydroperoxides as primary oxidation products. Other products are peroxide decomposition products and small yields of condensation products (gum). However, indene (6) and probably NMP copolymerize with oxygen to give alternating polyperoxides that are nonvolatile until they decompose thermally. The rates of oxygen absorption and gum formation are very high and more gum is left after decomposition of the polyperoxide and, therefore, less oxygen is required to produce this gum than for any other pure compound or fuel in Table I.

Study of the data in Table I gives rise to the question: Why do all the fuels oxidize slower than all the pure compounds, even though the fuels contain mostly compounds like the models? How does Fuel A differ from Fuel C? What are the important minor components in the fuels?

The classic work of Russell (7) on the co-oxidation of cumene and tetralin and the expansions by Mayo and coworkers (8) and Sajus (9) provide examples of rates of oxidation of hydrocarbon mixtures. Figure 1 is a plot of Russell's data on the rate of oxidation of cumene-tetralin mixtures at 90°C at a constant rate of chain initiation. Although tetralin alone oxidizes faster than cumene alone under these conditions, 4% of tetralin significantly retards the rate of oxidation of cumene. The high reactivity of pure tetralin with tetralylperoxy radicals can offset the high reactivity of tetralylperoxy radicals with each other (chain termination), but in dilute tetralin, which reacts with peroxy radicals much faster than cumene, the effect of fast chain termination predominates. Figure 1 shows that increasing proportions of tetralin may either decrease (at <4% tetralin) or increase (at >4% tetralin) the rate of oxidation of a mixture that is mostly cumene.

Figure 2 shows how these principles apply in mixtures of indene (which oxidizes much faster) and dodecane. At the lowest concentrations of indene, rates of oxidation are lower than for either pure hydrocarbon, at least until the indene is depleted, but with 1 M indene in dodecane, the rate of oxidation is faster than for dodecane alone and approaches the rate for indene in an inert solvent. NMP has a similar effect. The curves in Figure 3 show that the oxidation of Fuel A is so slow that it is not clear whether the initial oxidation is retarded by a little NMP. But the rate of oxidation increases as more NMP is added. These results are qualitatively satisfying, but they cannot be treated quantitatively. The Russell treatment (6) requires a constant rate of chain initiation, which is uncontrolled in our experiments. Our results do not suggest any catalytic effects of impurities or additives; as far as we can tell, these accelerators and retarders are consumed when they produce effects.

Several of our distilled fuels have been passed through acidic alumina to remove minor polar components, which have sometimes been returned to chromatographed fuel to reconstitute the original fuel. Figure 4 shows triplicate experiments with Fuel 10. The chromatographed fuel oxidizes faster initially than the distilled fuel (the usual situation) and the reconstituted fuel behaves

like the distilled fuel. Figure 4 shows the reproducibility of both the oxygen absorption and gum measurements (numbers at final points on curves). There is a close parallel in Figure 4 between the oxygen absorbed and the gum found.

The data in Tables II and III provide a comparison of Fuel A with Fuel C. By H/C ratio, Fuel C contains more aromatic material than Fuel A. Both fuels were examined by field ionization mass spectroscopy by Dr. S. E. Buttrill, Jr. and Mr. G. A. St. John, with the results shown in Table III. The instrument used could not distinguish between paraffins and alkylnaphthalenes, but to be consistent with the differences in H/C ratios in Table II, Fuel C must be higher in alkylnaphthalenes.

TABLE II
ANALYSES OF FUELS

	%C	%H	%N	%S	% (diff.)	H/C
Fuel A	86.4	13.3	<0.02	<0.02	<0.36	1.83
Gum from A + NMP	68.0	5.9	6.2	19.9	O + S	1.03
NMP, calc	74.3	7.1	17.3	0	0	1.40
Fuel C	87.6	11.9	<0.02	0.03	<0.19	1.63

TABLE III
CLASSES OF HYDROCARBONS BY MOLE % IN FUELS A AND C

Hydrocarbon Class →	Alkanes +C ₁₀ H ₇ R	Ring or C=C			PhR	Indanes, Tetralins	\bar{M}_n
		1	2	3			
Fuel A	20.0	16.9	15.7	5.0	28.3	14.1	151
Fuel C	45.4	10.3	6.9	2.9	19.3	15.2	159

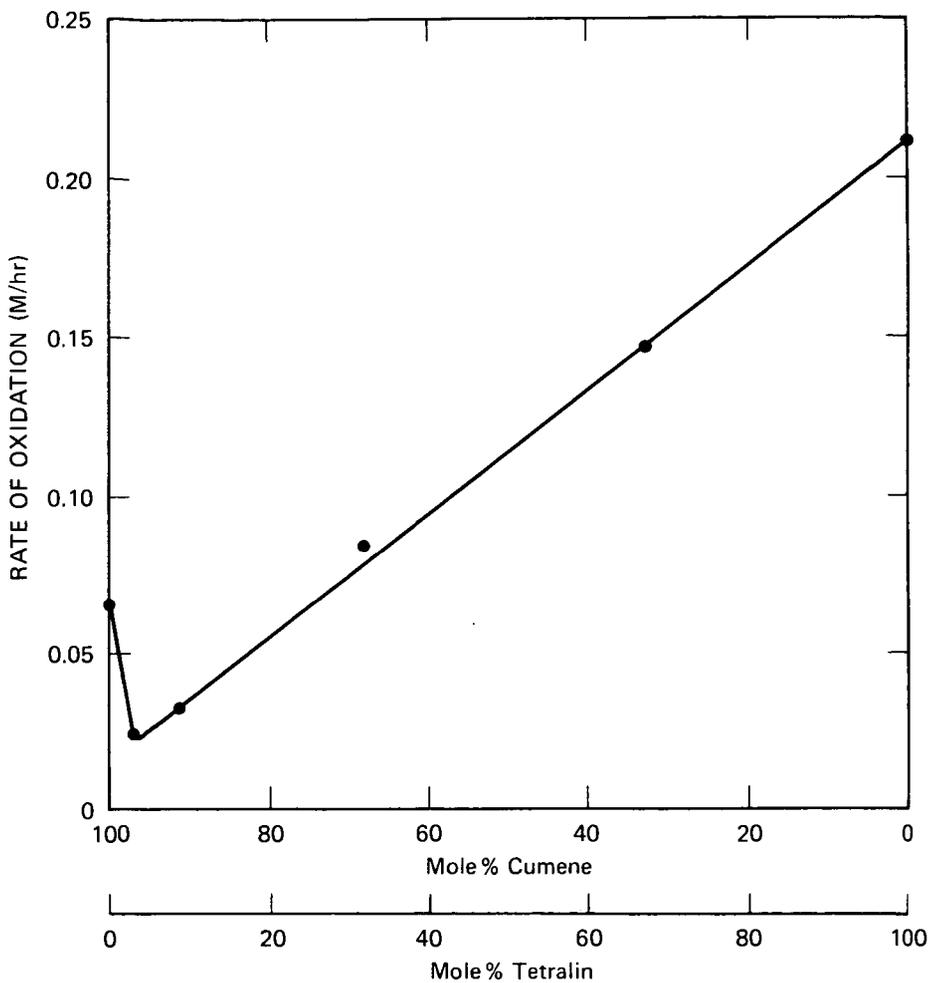
Table IV lists analyses of polar concentrates from three fuels. The polar concentrates contain more oxygen, nitrogen and sulfur than Fuels A and C and two of them are especially high in oxygen, suggesting that the fuels had undergone some oxidation before they reached us. The polar components of Fuels 10 and 13 were also analyzed by gas chromatography/mass spectroscopy. The Fuel 10 residues were rich in fluorene and phenanthracene/anthracene and their alkyl derivatives. Fuel 13 contained a wider range of products, in which carbazole and alkylcarbazoles were identified.

TABLE IV
ANALYSES OF POLAR CONCENTRATES

	%C	%H	%N	%S	% (diff.)	H/C
Fuel C	74.9	6.0	0.20	18.9	O + S	0.98
Fuel 10	85.8	8.5	0.94	1.87	2.85	1.18
Fuel 13	80.0	9.1	1.14	0.85	9.0	1.35

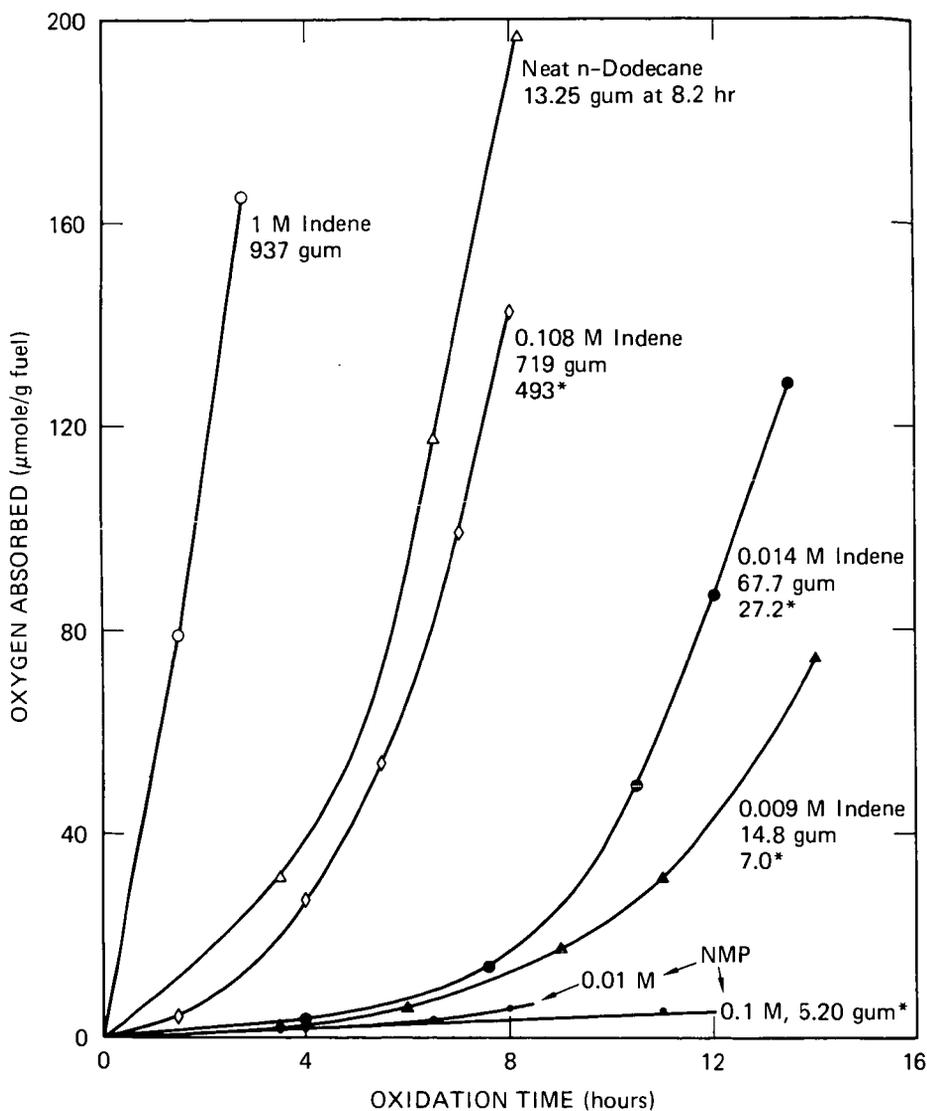
CONCLUSIONS

Our present working hypothesis is that deposits on hot engine parts come mostly from soluble gum formed on storage but maybe partly during heating of the fuel in the engine. The compounds that copolymerize with oxygen to give polyperoxides require the least oxygen to give a milligram of gum, but among other pure hydrocarbons and fuels, the rates of gum formation and oxygen absorption decrease together. It appears that the coupling of fuels and their primary oxidation products to form products of higher molecular weight, soluble gum and deposits is a small part of the chain termination reaction in which some of the free radicals that are involved in oxidation couple (terminate) instead of propagating. The faster the oxidation, the more coupling occurs. The dependence of rate of oxidation on rate constants for initiation, propagation and termination is expressed by the well known equation,



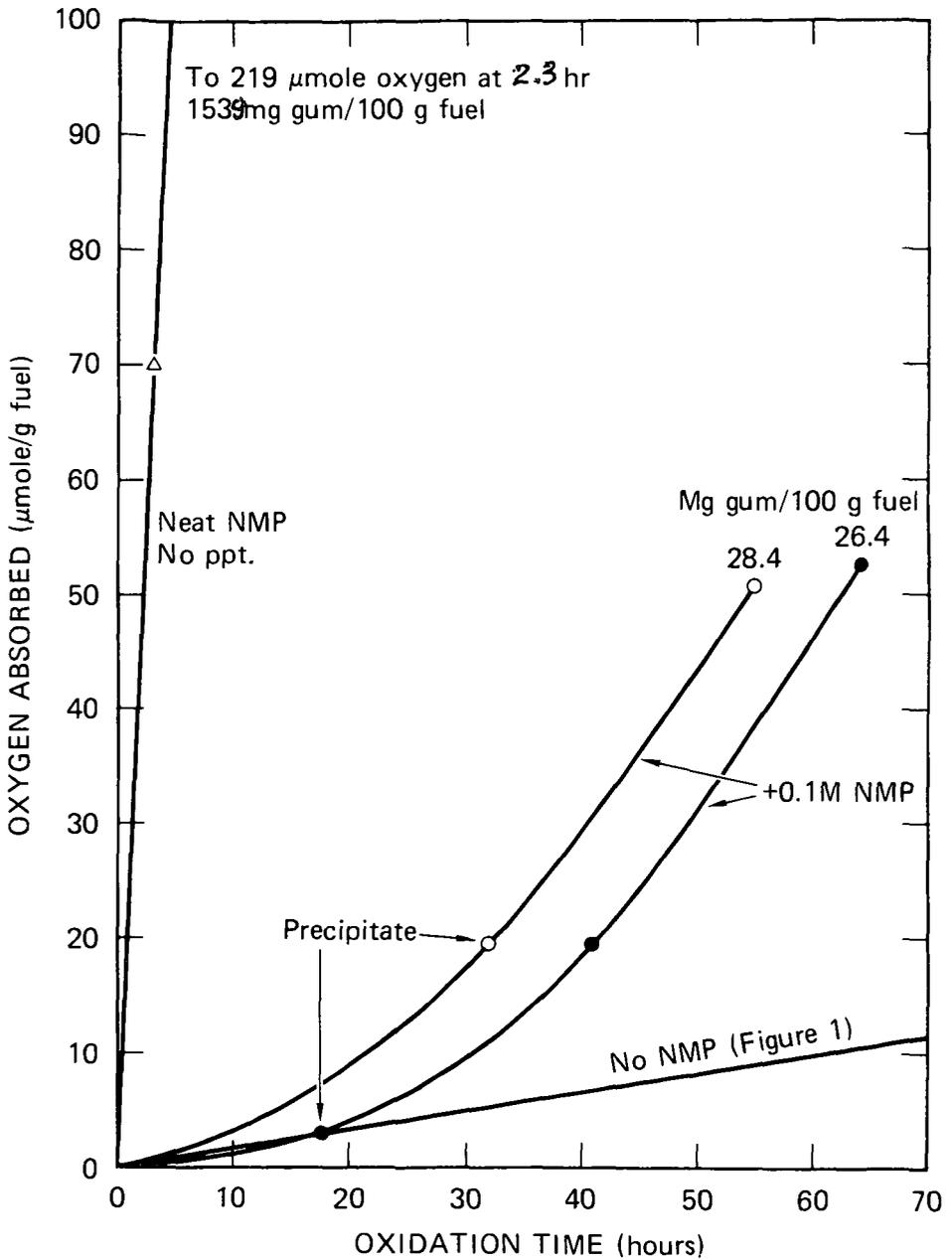
JA-2115-18

FIGURE 1 COOXIDATION OF CUMENE AND TETRALIN WITH 0.02 M $t\text{-BuO}_2\text{Bz}$ AT 90°C
Data of G. A. Russell (ref. 6)



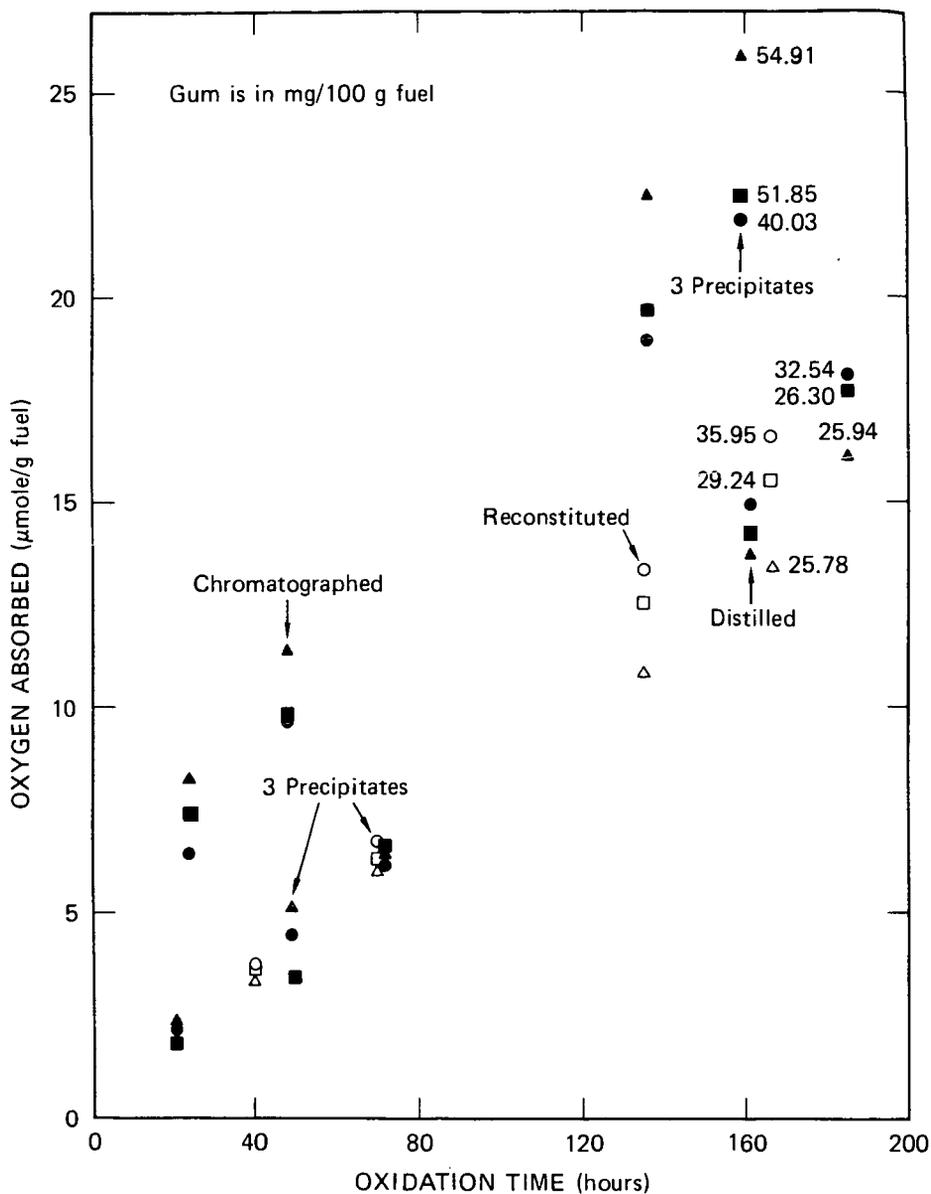
JA-2115-16A

FIGURE 2 OXIDATIONS OF n-DODECANE WITH INDENE AND NMP AT 130°C
 Gum is in mg/100 g fuel, determined at 100°C except when marked * for 200°C.



JA-2115-22

FIGURE 3 OXIDATION OF FUEL A AND NMP AT 130°C



JA-1924-16

FIGURE 4 OXIDATION OF FUEL 10 IN AIR AT 130°C

$$R_O = (k_i/k_t)^{1/2} k_p [RH]$$

For fuels that contain mostly paraffins, naphthenes and alkylbenzenes, the k_p s should be quite similar. We think that k_t is the most susceptible of the three constants to the effect of other fuel components, which may explain why nearly all the fuels oxidize and produce gum slower than the pure hydrocarbons. Although k_i can be affected moderately by minor components, any effect on increasing the rate of peroxide decomposition will be offset by a decrease in the steady state concentration of peroxides. It is known that polynuclear aromatic hydrocarbons and their alkyl derivatives are very reactive toward peroxy radicals and that their chain termination constants in oxidation vary over a wide range (10).

Although a non-radical condensation mechanism has not been excluded and although details of a radical condensation mechanism are lacking, it appears to us now that the most fruitful approach to understanding and reducing gum and deposit formation in fuels is through the effects of condensed aromatic and heterocyclic compounds on the rates of oxidation of fuels.

Other factors that appear to be critical in gum and deposit formation are the effects of oxygen concentration and metals and the mechanism by which soluble gum evolves into insoluble deposits. Our conclusions based on oxidation at 130°C should eventually be confirmed by tests at storage temperatures, although the relative stabilities of fuels appear not to change much between 40 and 150°C (11).

ACKNOWLEDGMENT

This research was supported by the U. S. Army Research Office and NASA-Lewis Research Center.

LITERATURE CITED

- (1) Nixon, A. C., Chapter 17 in *Autoxidation and Antioxidants*, W. O. Lundberg, ed., Wiley Interscience, NY (1962).
- (2) CRC Literature Survey on the Thermal Oxidation Stability of Jet Fuel, Report No. 509 of Coordinating Research Council, Inc., Atlanta (1979).
- (3) Mayo, F. R., Richardson, H. and Mayorga, G. D., *PREPRINTS*, Div. of Petrol. Chem., ACS, 20 (1), 33 (1975).
- (4) (2), pg. 71.
- (5) Mayo, F. R., Buttrill, S. E., Jr., Lan, B., St. John, G. A. and Dulin, D., *Preprints*, Div. of Fuel Chem., 27 (2), 76 (1982).
- (6) Russell, G. A., *J. Amer. Chem. Soc.*, 78, 1035, 1041 (1956).
- (7) *Ibid.*, 77, 4583 (1955).
- (8) Mayo, F. R., Syz, M. G., Mill, T. and Castleman, J. K., *Adv. Chem. Series*, 75, 38 (1968).
- (9) Sajus, L., *Adv. Chem. Series*, 75, 59 (1968).
- (10) Huntington, J. G., Mayo, F. R. and Kirschen, N. A., *Fuel*, 58, 31 (1979).
- (11) Stavinocha, L. L., Westbrook, S. R. and Brinkman, D. W., DOE/BC/10043-12 (1980).