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THE CHEMISTRY OF FUEL DEPOSITS AND THEIR PRECURSORS

Frank R. Mayo, et al

Stanford Research Institute

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December 1972

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Final Report

(1 October to 27 December 1972)

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By

F R. MAYO
N. KIRSHEN
H. RICHARDSON
R STRINGHAM

Prepared under Contract N00019-72-C-0161

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NAVAL AIR SYSTEMS COMMAND
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13. ABSTRACT

The ultimate objective of the work described in this Report is to determine the chemistry of deposit formation in jet turbine fuel systems. The immediate objective is to determine the nature and method of formation of deposit precursors that should have higher molecular weights and polarities than the fuels. Three approaches have been tried. (1) Oxidations of refluxing n-decane at 155°C with limited supplies of oxygen gave no indication of higher molecular weight products and suggested the need for higher reaction temperatures. (2) Comparison of distillation residues of a standard fuel that had, and had not, been thermally stressed in a JFTOT Coker Test indicated that most of these residues were due to additives or slow reactions during storage and that this approach should employ clean fuel of narrow boiling range. (3) Our principal and most successful effort used such a fuel and separated higher molecular weight products from other oxidation products by precipitation from pentane at -78°. Products have been obtained with molecular weights up to 1200, with up to 5% oxygen, and capable of resinifying on heating. The present status of the jet fuel deposit problem is summarized.

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CONTENTS

THE CHEMISTRY OF FUEL DEPOSITS AND THEIR PRECURSORS

1. OBJECTIVE

The ultimate objective of the work described here is to determine the chemistry of deposit formation in jet turbine fuel systems so that it can be predicted and minimized or prevented. Because the deposits are so insoluble and refractory and because they are formed in very small proportions, the immediate objective of this research is to determine the nature and method of formation of deposit precursors, which are presumably simpler and formed in much larger quantities.

2. SUMMARY AND CONCLUSIONS

Work in this report has been directed first toward finding conditions to maximize the yields of deposit precursors, and then toward determining the nature of some relatively insoluble oxidation products. Our first oxidations of refluxing n-decane at 155° with limited air supply gave alcohol, ketone, and ester oxidation products, but no evidence of high molecular weight products that might be deposit precursors. This work is presented in Section 5 and summarized in Section 5.1.

Our next effort, which is discussed in Section 6 and summarized in Section 6.1, was to compare residues from distillations of a standard jet fuel of broad boiling range that had, and had not, been thermally stressed in a JFTOT coker test. Since both samples gave qualitatively similar residues, we concluded that the later were at least partly due to additives or formed in storage. We concluded also that use of a fuel of narrow boiling range would facilitate separation of fuel and oxidation products.

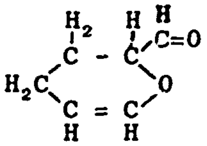
Our principal and most successful effort used a fuel of narrow boiling range; we separated higher molecular weight oxidation products by precipitation from pentane at low temperatures. This work is presented in Section 4 and summarized in Section 4.1. Section 7 gives our opinions of the present status of the jet fuel deposit problem and the most promising directions for further research.

3. BACKGROUND

Little is known about deposits from gas turbine fuels except that they contain more nitrogen, sulfur, and oxygen than the original fuel, that they contain a variety of carbonyl and hydroxyl groups, with considerable hydrogen bonding, and that some are partly soluble in N-dimethylformamide or aqueous caustic solution. The following kinds of organic products might have these properties:

(1) Bifunctional oxygen compounds of a few hundred molecular weight containing carboxyl and alcohol groups. Sulfonic acids and salts of acids are also possibilities.

(2) High molecular weight compounds of moderate polarity; i.e., polymers of either the vinyl or condensation type. The polar groups might be carboxyl, salt, amide, ester, alcohol, or nitrogen or sulfur compounds. The polymer must have enough of these groups to make it insoluble in fuel, but the fuel and its primary oxidation product can hardly have a high enough concentration of polar groups to yield a high polymer that is highly polar. Aldol condensation products that retain their hydroxyl groups might have the necessary polarity, and their formation would be catalyzed by strong acids. Higher molecular weight compounds also could be produced by peroxide crosslinking of lower molecular weight compounds. The Diels-Alder dimer of acrolein,



with both a vinylene ether and an aldehyde group, polymerizes readily to insoluble products of complicated structure; its homologs and analogs might cause trouble in fuels.

(3) Some metal chelates are very insoluble. Many fuels may contain enough trace metals and nitrogen compounds and accumulate enough oxygen to produce such products.

An unfortunate but real possibility is that several of these kinds of precursors, and perhaps others, contribute to a very complicated baked deposit.

In initiating ressearch on the chemistry of deposit formation, we have recognized that oxidations of pure hydrocarbons, even under mild conditions, can give high-boiling and intractable compounds. We must also recognize that fuels from different suppliers may give different deposits with different chemistries and precursors, and that the extent and nature of the walls of the reaction vessel and the free oxygen contents of the fuels may also affect the reactions being investigated. These last two variables, however, should be fixed in a standard coking test.

We now consider the question: How can such products be made in hot wing tanks? Some liquid phase,[1*] at least a little oxygen,[1] and heat are required. Deposit formation is accelerated by sulfides and disulfides,[2,3] by some metals, particularly vanadium and copper,[4] and by polymer coatings[5] that might protect the metals. The rate of deposit formation increases with temperature, with an apparent activation energy of 10 kcal/mole, up to a cut-off temperature, which varies in the apparatus used[1] from 190° to 245°C, depending on the fuel. Here, the rate of deposit formation decreases or levels off.

The deposits originate in the liquid phase as soft spheres.[6] They accumulate on surfaces and agglomerate to hard and less soluble deposits.

In the same apparatus in which deposits were obtained from jet fuels,[1,2,4,5] deposits were also obtained from pure alkanes.[3,7] Lighter

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*References are listed at the end of this report.

alkanes gave more deposits than heavier ones, and n-dodecane gave more than 2,2,5-trimethyl-hexane.[3] Thus, in the range 100° to 250°C, n-decane gave about four times as much deposit on a Ti strip as n-hexadecane. This result seems reasonable only if some gas-phase as well as liquid-phase reaction is involved or if there is some solubility effect; i.e., the oxygenated products of the light hydrocarbon are less soluble in the light hydrocarbon.

Although pure deoxygenated hydrocarbons leave deposits on stainless steel tubes at 600°C[3], some oxidation of hydrocarbons seen necessary to produce the polar groups that are required to produce deposits in the 200° to 300°C range with which we are most concerned. Oxidation is also required to produce products that can condense or polymerize. Peroxides formed by oxidation may also be important in condensing either starting hydrocarbon or oxidation products:

$$\mathrm{ROOH} \rightarrow \mathrm{RO}\cdot + \mathrm{HO}\cdot \tag{1}$$

$$2\mathrm{R'H} + \mathrm{RO}\cdot + \mathrm{HO}\cdot \rightarrow \mathrm{R'_2} + \mathrm{ROH} + \mathrm{H_2O} \tag{2}$$

The radicals produced in reaction (1) will give the most coupling in (2) and the least oxidation when oxygen pressures are low.

4. FIRST OXIDATIONS AND PRECIPITATIONS OF STANDARD JET FUEL RAF-177YX-63*

4.1. Introduction and Summary

Our oxidation results with Standard Fuel RAF-177YX-63 are presented first because they have been most fruitful. The narrow boiling range of this fuel, 186° to 202°C, facilitates separation of the fuel and its oxidation products; all of our experiments with relatively insoluble oxidation products have been carried out with this fuel.

The fuel was first distilled to remove additives and materials accumulated in storage; about 0.05% of residue was rejected. Several 50-ml samples were then oxidized for 24 to 44 hours at reflux (192°) at different low rates of oxygen or air supply, but the differences among them seemed to be neither notable nor reproducible. The products were mostly alcohols, ketones, and esters. All the products were therefore combined; the oxidation products (higher-boiling) were concentrated, diluted with pentane, and fractionally precipitated at -78° into nine fractions which differed in their solubilities in the original fuel.

The most and least soluble of these fractions were investigated in more detail. Both contained small proportions of acids and esters but most of the material was neutral alcohols and ketones. From molecular weights and elementary analyses, the least and most soluble fractions average $C_{30.7}H_{44.2}O_{5.0}$ and $C_{27.9}H_{40.1}O_{3.63}$ as compared with $C_{13.7}H_{26.7}$ for the original fuel. The average molecular weights of the fuels have more than doubled and material with molecular weight as high as of 1200 has been detected. The C/H ratios show that aromatic groups have been

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*Experimental work by H. Richardson

concentrated in these fractions. Their oxygen contents show that the least soluble fraction has the most (five) functional groups per average molecule. Heating these fractions in air or an inert atmosphere at 200° gave charred and still less soluble products.

A reoxidation of recovered fuel gave about as much oxidation products as the original oxidation, indicating that one oxidation had little effect on the ability of the fuel to oxidize further.

4.2. Oxidation and Analytical Techniques

Two liters of jet fuel RAF-177YX-63 were distilled through a 30-cm vigreux column at ambient pressure. The boiling range corresponded to the specified narrow boiling range, 186° to 202°C, with about 1 g of residue left in the pot. The distilled jet fuel was stored in the dark under a nitrogen atmosphere. The narrow boiling range should minimize the overlap in boiling points of the hydrocarbons and their oxidation products.

In a typical oxidation run, 50 ml of distilled fuel was placed in a 100-ml round-bottom flask with two or three boiling chips. The flask was fitted with an air condenser through which an adjustable capillary passed for introducing air or oxygen. The fuel was heated to reflux (191°) with a mantle, and gas was introduced for the duration of the experiment at 6.5 ml/min.

After the experiment was completed, a 25-g aliquot was taken for vacuum distillation at 12 torr. The distillation flask was calibrated so that a nearly constant amount of residue remained. On completion of distillation, the residues were adjusted to nearly constant weight (± 50 mg) by addition of distillate. The residues were analyzed by ir (calibrated with dinonylmethyl carbinol and 2-undecanone) and their molecular weights determined by vapor-phase osmometry.

The distillate from each experiment was treated with bromine in carbon tetrachloride and back titrated to determine the amount of unsaturation present after correcting for the competing substitution reaction.[8,9]

4.3. Results of Oxidations

Results of eleven oxidations of distilled fuel are compared in Table I. First we consider the introduction of air into the refluxing sample. Experiment I, in which the air was introduced at the top boundary of the refluxing vapor in the condenser, gave the least alcohol + carbonyl. Experiment IV, in which the air was introduced just above the liquid, gave gave 3.4 times as much of these products, and Expt. V, in which the air was introduced near the bottom of the liquid layer, gave 5.2 times as much oxidation products. In all experiments, more alcohol than carbonyl groups were formed, and the least secondary oxidation of alcohol occurred in Expt. I, where air was least available. Experiments VII and VIII, with oxygen, showed more oxidation but less dependence on where it was introduced. Experiment VIII, where oxygen was introduced into the vapor phase, gave the highest concentration of unsaturation in any whole product and is possibly the only experiment that gave an important increase in olefin.

Experiments IV and III show the effect of increasing reaction time from 24 to 44 hours. The combined yield of alcohol plus carbonyl is 2.45 times as great in a period 1.83 times as long. These relations suggest some autocatalysis, and the carbonyl/alcohol ratios suggest increasing oxidation of alcohols to carbonyls with increasing time. Comparison of Experiments V and II (with reaction times of 24 and 29 hours) suggests that reproducibility of our results is not particularly good. This is not surprising if the oxygen concentration depends on the reflux rate.

Experiments IV and VI indicate that a titanium strip, about half in the liquid and half in the gas, results in formation of less total alcohol and carbonyl (an unexpected result) but less carbonyl/alcohol.

Comparison of Expts. VII and VIII with V and IV shows that introduction of O_2 instead of air results in more formation of alcohol + carbonyl but no consistent trend in carbonyl/alcohol ratio.

4.4. Precipitation of Individual Oxidation Products

The lack of any clear trend in oxidation products with oxygen supply, and the realization that there is not necessarily much connection between the formation of alcohol and carbonyl groups on the one hand and the formation of deposits and precursors on the other, led us to look for difficultly soluble precursors of deposits in the distillation residues of the oxidations on Table I. We therefore treated 0.2 ml of one residue with 0.8 ml of pentane (to keep the mixture mobile) and cooled the mixture to -78°C. Considerable gummy precipitate formed, which only partially redissolved at 0°.

Accordingly, each of the distillation residues in Table I was diluted with three volumes of pentane and chilled in a dry-ice-acetone bath to yield a precipitate. The solutions were warmed to 0°C, and the supernatant solutions were decanted off the gummy precipitates (Table I). The largest of these precipitates (VII) was examined carefully. Vapor phase osmometry (VPO) indicated $\bar{M}_n = 400$ as compared with $\bar{M}_n = 192$ for the starting fuel and $\bar{M}_n = 225$ for the residue. Titration with dilute aqueous base found a neutralization equivalent of ~1200, although the technique had not been optimized. Gel permeation chromatography revealed material of molecular weight as high as 1200.

Table I

OXIDATIONS OF REFLUXING RAF-177YX-63 at 191°

Experiment	I	II	III	IV	V	VII	VIII	VI[a]	XI[a]	IX[a]	X[a]	Original F-II
Time, hr	29.0	29.0	44.0	24.0	24.0	24.0	24.0	24.0	24.0	24.0	24.0	
Oxidant	Air Vapor[b]	Air Liquid	Air Vapor[c]	Air Vapor[c]	Air Liquid	O_2 Liquid	O_2 Vapor[c]	Air Vapor[c]	Air Liquid	O_2 Vapor[c]	O_2 Liquid	
Distilate, g	24.0757	23.5312	23.76[d]	23.7597	23.9717	22.1065	23.5275	24.1553	24.2999	21.9099	23.2334	23.9378
Residue, g	0.7782	0.7624	0.771[d]	0.8159	0.7679	1.0650[e]	1.3501[e]	0.7665	0.6707	2.6984[e]	1.4796[e]	0.7999
C-C$_1$ in distillate, mmoles/g	0.148	0.130	0.134	0.137	0.169	0.162	0.213	0.174	0.095	0.181	0.139	0.162
$\bar{M}_n$ of residue, g/mole	199	251	252	239	247	225	260	209	238	200	272	192
Products in residue, by ir												
Alcohol, M	0.19	0.51	0.70	0.44	0.79	0.73	0.65	0.26	0.48	0.57	0.83	0
Carbonyl, M	0.03	0.37	0.63	0.27	0.35	0.55	0.34	0.13	0.27	0.32	0.60	0
Carbonyl/Alcohol	0.157	0.726	0.900	0.618	0.443	0.753	0.523	0.500	0.562	0.561	0.723	
Moles in residue, x 10^3[f]												
Alcohol	0.21	0.54	1.04	0.50	0.85	1.08	1.22	0.28	0.45	2.11	1.70	
Carbonyl	0.10	0.37	0.93	0.31	0.38	0.82	0.97	0.14	0.25	1.18	1.24	
Sum	0.31	0.91	1.97	0.81	1.23	1.90	2.19	0.42	0.70	3.29	2.94	
Precipitates from residue												
Wt. of precipitate, mg[g]	----	31.9	50.1	32.0	23.3	147.4	62.7	19.9	21.9	86.9	103.7	
Wt.% of residue	----	4.0	6.5	3.9	3.0	7.1	4.6	2.6	----	3.2	7.0	
Wt.% of fuel	----	0.13	0.20	0.13	0.093	0.56	0.25	0.080	0.088	0.35	0.41	

[a] Ti strip.

[b] Air introduced in condenser near interface of air and refluxing vapor.

[c] Oxidant introduced ~6 mm above refluxing liquid.

[d] Actual weights, 33.4861 and 1.085 g, have been multiplied by 0.71 for easier comparison of results.

[e] Could not be concentrated as far as Expts. I-VI because of formation of more high-boiling products.

[f] Concentration of product in M x wt. of residue in g/density of fuel in g.

[g] Corrected for mechanical losses.

4.5. Precipitation of Combined Oxidation Products

Table I indicates that all residues had similar absorptions and that they were similar qualitatively but different quantitatively. Further, the yields of precipitates were probably not quantitatively reproducible. Because of these similarities and uncertainties, all the precipitates and liquors were blended in toluene, which was removed under aspirator vacuum at $100^{\circ}C$. The resulting mixture (~8 ml) was diluted with 30 ml of pentane. When the solution was chilled to 0°, it became cloudy, but no precipitate formed. Freezing in a dry-ice-acetone bath and then equilibration at 0° resulted in an oily precipitate. Six precipitates were obtained successively in this way. Two additional precipitates were obtained by centrifuging precipitates formed at -78° without warming to 0°, as shown in Table II.

The supernatant solution from precipitate 8 was stripped of pentane and distilled at 15.5 torr and 94° to $140^{\circ}C$ with a gradual increase in color and viscosity. The first distillate corresponds to the jet fuel added to the oxidation residues to make them up to constant weight. The second portion of the distillate, which was slightly colored, distilled at 95° to 160° at about 0.01 torr. Residue 9 (0.5689 g) had a $\bar{M}_n$ of 414 by vapor phase osmometry. After removal of the pentane the mixture was pale yellow and of the consistency of light mineral oil. As the distillation proceeded, the color intensified and the viscosity of the material in the pot increased. Residue 9 was dark reddish brown and very viscous, flowing only very slowly. These observations may be interpreted either as a simple concentration effect that would have occurred without heating or as a heat-induced chemical reaction in the pot, or as both.

Table II

PRECIPITATED FRACTIONS FROM COMBINED OXIDATION RESIDUES

Fraction No.	Pptn. Temp., °C	Weight, g	$\bar{M}_n$ by VPO
1	0°	0.4750	385
2	0°	0.2466	398
3	0°	0.1068	411
4	0°	0.2234	364
5	0°	0.0561	412
6	0°	0.0324	413
7	-78°	0.1927	340
8	-78°	0.3346	354
9	[a]	0.5689	414

[a] Residue from vacuum distillation of unprecipitated liquid.

All the fractions 1 to 9 have molecular weights about twice that of the fuel. Fractions 1 and 9 differ in their solubilities in the original fuel. Precipitate 1 is only partially (perhaps 50%) and slowly soluble in fuel, while residue 9 dissolves quickly and completely. Both are totally soluble in toluene and methanol and seem to be totally insoluble in water or dilute sodium hydroxide.

4.6. Analyses of Precipitates 1 - 8 and Residue 9

Residue 9 and Precipitate 1 were analyzed for various functional groups. Titration for carboxylic acids was carried out in a ternary solvent system. Approximately 15-mg samples were dissolved in a mixture of 4 ml absolute ethanol, 1 ml of water, and 1 ml of toluene. The homogeneous mixture was titrated with 0.01 N aq sodium hydroxide, using a pH meter to detect the endpoint. Phenolphthalein was tried, but the endpoint was not sharp enough to be useful. Neutralization equivalents for Precipitate 1 and Residue 9 were 2,140 and 17,200, respectively, indicating much more acid in the early precipitates relative to the soluble distillation residue. Saponification equivalents were determined by a variation of the method of Shriner, Fuson, and Curtin.[10] The sample was dissolved in a mixture of 1 ml reagent (3g KOH/50 ml diethylene glycol) and 1 ml toluene in a glass-stoppered flask. The mixture was shaken for 15 min at 100°C in an oil bath. Then 10 ml of water was added and the solution was titrated with 0.1 N HCl, using a p_H meter to detect the endpoint. The values found were 865 and 742 for Precipitate I and Residue 9, respectively, after correcting for acid present in the sample. These results indicate that the earlier precipitates contain slightly less ester than the soluble distillation residue.

The method of Jordan[11] was employed to determine alcohols as acetates in a complex mixture. In this method the sample is dissolved in a mixture of 4 ml 2 M acetic anhydride in ethyl acetate with perchloric acid catalyst and 1 ml n-hexane and allowd to stand 10 minutes; then 2 ml of water is added and mixed. After 2 minutes, 10 ml of 3:1 pyridine and water is added, and the mixture is allowed to stand for another 10 minutes. The acetic acid is titrated with 0.5 M alcoholic NaOH. The difference between the sample titer and the titer of the reagent corresponds to the alcohols present. Titration of 22 mg of Residue 9 by this technique found that it was not sensitive enough to reveal quantitatively the amount of alcohol present.

Precipitate 1 and Residue 9 were fractionated separately on the basis of solubility in dilute base or toluene. The toluene-soluble fraction was treated with the saponification technique to yield two additional fractions. Chart I summarizes the operations employed in the fractionations; Table III summarizes the results.

Chart I

FRACTIONATION OF RESIDUES

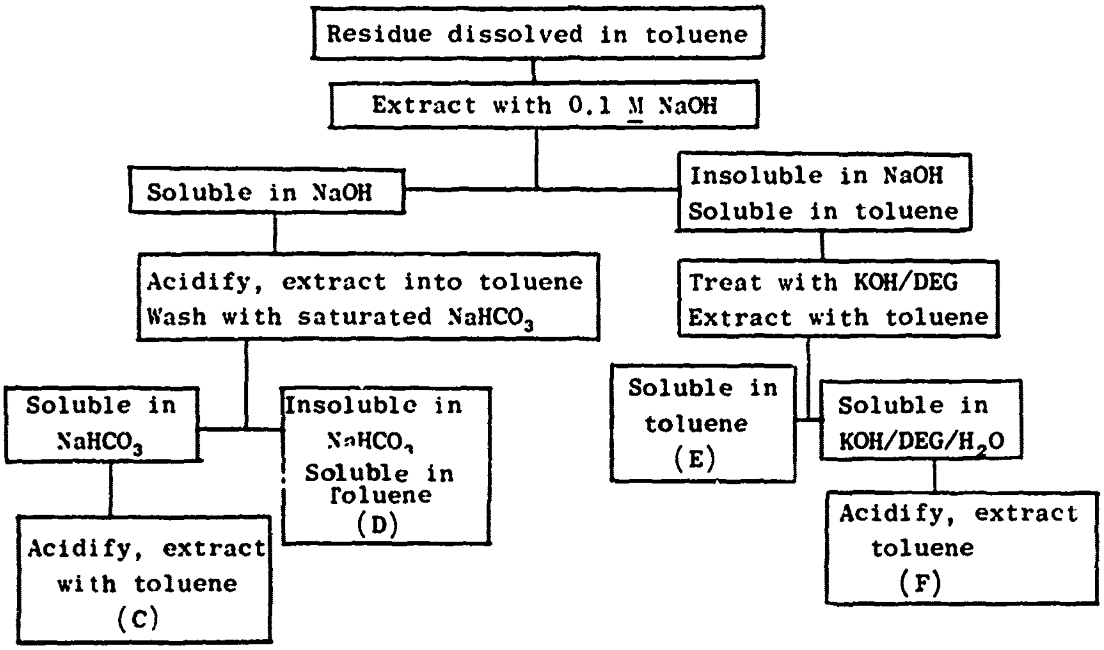

Table III

SUMMARY OF EXTRACTION RESULTS 1 AND 9

Fraction No.	Weight g	Mol Wt (VPO)	% of Total	Solubility
1[a]	0.1695	385	--	--
1C	0.0142	382	8.3_7	$NaHCO_3$[b]
1D	0.0143	353	8.4_4	NaOH[c]
1E	0.1139	497	67.1	Toluene[d]
1F	0.0271	357	16.0	NaOH[e]
9[a]	0.5689[e]	--	--	--
9C	0.0226	922	3.9_7	$NaHCO_3$[b]
9D	0.0456	482	8.0_2	NaOH[c]
9E	0.4650	434	81.7	Toluene[d]
9F	0.0357	397	6.2_8	NaOH[e]

a. Unfractionated.

b. Weak acid in original fraction.

c. Stronger acid in original fraction.

d. Neutral material that survived saponification.

e. Acids from saponification.

Fractions IE and 9E, the largest and neutral fractions, were analyzed for C and H: 1E: 74.39% C, 8.96% H, 16.65% O; 9E: 77.30% C, 9.30% H, 13.40% O.. These results, along with the VPO values for $\overline{M}_n$ in Table II, correspond to average empirical formulas of $C_{30.7}H_{44.2}O_{5.0}$ for 1E and $C_{27.9}H_{40.1}O_{3.63}$ for 9E. Qualitative infrared spectra of 1E and 9E indicated the presence of alcohol and ketone but no acid or ester groups. The average empirical formula of the original fuel is $C_{13.7}H_{26.7}$. Thus the atomic H/C ratio in the fuel, 1.95, has decreased to 1.44 in both 1E and 9E. Even if we count each oxygen atom as replacing 2H (as in a ketone), the H/C ratios in 1E and 9E are 1.77 and 1.70, respectively. It is difficult to escape the conclusion that these precipitated or concentrated oxidation products contain <u>more</u> than their share of aromatic groups and a considerable proportion of alcohol groups, contrary to the findings in Section 6 for whole oxidation products. To the extent that the oxygen is in alcohol or ether instead of carbonyl groups, the aromatic contents are higher than those calculated for ketones.

4.7. Formation of Solid Deposits by Heating Precipitates

To see what fractions of our oxidation products would form solid deposits and to provide a point of departure for later quantitative tests, we placed small amounts of Fractions 9C, 9D, 9E, and 9F as spots on a glass microscope slide, on a strip of titanium, and in a sealed tube with a CO_2 atomsphere, and then heated them in air at 200°C. All fractions formed dark, solid deposits under some conditions.

In 1 hour, 9F formed a solid deposit on both glass and titanium, 9D only on titanium. After 2 hours, 9E also gave a solid on titanium. At that time the other samples on glass and titanium were liquid and viscous but all solidified to black solids (looking like chars) on cooling to 25°. The sealed tube was heated for 4 hours at 200°C. All the fractions darkened and became more viscous, but they did not solidify even at 25°.

Solubilities were estimated by rinsing each spot, first with 1 ml of fresh fuel, then with 1 ml of toluene, and then with 1 ml of methyl ethyl ketone. Results are summarized in Table IV. In general the solubility properties of samples heated in air on glass or titanium were about the same, but the products formed under vacuum were often more soluble. All the products had a low solubility in fuel. The large, neutral fraction, 9E, was completely soluble in toluene, but none of the acidic fraction dissolved completely in that solvent. Methyl ethyl ketone was sometimes a better solvent.

Table IV

SOLUBILITIES OF DEPOSITS[a] FROM RAF-177YX-63

	Fractions			
Solvent	9C	9D	9E	9F
Fuel	~ 1/2	< 1/2	Slightly	Insoluble
	~ 1/2	< 1/2	Slightly	Insoluble
	~ 3/4	Slightly	Slightly	Insoluble
Toluene	Slight change	No change	Completely	Softens
	Slight change	Slight change	Completely	Softens, breaks up
	No change	~ 1/2	Completely	~ 1/2
AcEt	No change	Partly	b	Completely
	No change	No change	b	Mostly
	Completely	Completely	b	Completely

[a] Keys are in Chart I and Table III. In each group of three tests, the first result is after 2 hours on glass in air, the second is after 2 hours on Ti in air, and the third is after 4 hours on glass in a CO_2 atmosphere.

[b] Not tested since sample dissolved in toluene.

These experiments show that the gums that we can precipitate from oxidized fuel can be cured to black, insoluble deposits on subsequent heating in air at 200° and that the most polar (acidic) fractions give the most refractory deposits.

4.8. Reoxidation of RAF-1776YX-63

Distillates from Oxidations III, IV, and V were mixed, and 50 ml was oxidized with air passed into the refluxing liquid, as described in Section 4.2. The objective was to see if the second oxidation of the fuel gave about the same yield of oxidation products as the first distillation.

The reoxidation was carried out for 50 hours instead of the 29 or 24 hours used in Experiments II and V in Table I. The result was that about twice as much distillation residue (1.43 g) was formed in about twice as much time and that its molecular weight was 225 instead of 250 as in the other experiments. From these data we can conclude only that fuel recovered from an oxidation oxidizes about as fast as the original fuel; there is no good evidence that the first oxidation removes either an inhibitor or an especially reactive component.

4.9. Insolubilities of Deposits on Titanium Strips

Titanium strips from Oxidations IX, X, and XI were pumped at 10^{-6} torr at room temperature, to remove any volatiles, and weighed. Each of the strips was then immersed in 10 ml of RAF-177YX-63 and allowed to stand for a weekend. The strips were removed from the fuel, rinsed with pentane, and dried at 10^{-6} torr. Table V shows that weight changes were insignificant. There is an uncertainty of ± 0.1 mg in each weighing.

Table V

INSOLUBILITIES OF DEPOSITS ON TITANIUM STRIPS

Titanium Strip No.	Initial Weight, g	Final Weight, g	Δ, g
IX	2.1927	2.1923	-0.4 ± 0.2
X	2.1277	2.1275	-0.2 ± 0.2
IX	1.9961	1.9963	+0.2 ± 0.2

4.10. Sealed Ampoule Oxidations

The following experiments are intended to help us in optimizing conditions for formation of deposit precursors from our distilled sample (Section 4.1) of Standard Fuel RAF-177YX-63. We would like to use reaction times, temperatures, and oxygen pressures near those where precursors might be formed and then deposited in actual service. Our experiments show that nearly all the oxygen present is consumed in 15 minutes or less at 200°C.

RAF-177YX-63 was oxidized in sealed ampoules for various short periods of time. The fuel was placed in a glass flask with a breakseal, degassed, and a known amount of oxygen was added from a gas burette. The flask was then sealed and heated at 200°C. After the indicated reaction time, the flask was sealed onto the vacuum line and the remaining gases were analyzed by the procedure of Allara et al.[12] The entire fuel sample was distilled at 10 torr and 66° to 88°C to yield a distillation residue. The precipitation technique described in Section 4.5 was applied to the distillation residues.

The results of five oxidations are summarized in Table VI. In all runs virtually all oxygen added was consumed, in times as short as 15 minutes. The small distillation residues were pale yellow in color. The differences in weight are of little significance; the distillation was terminated only by estimating the volume of material remaining in the flask, which has little relationship to how volatile the residue actually is. Much error could occur due to drainage from the walls of the still.

Gel permeation chromatography of distillation residues III and IV through a series of 6 four-foot Porosil columns (2 x 60Å, 2 x 100Å, 1 x 250Å, and 1 x 500Å) with toluene as eluant indicated that these residues are nearly identical. The chromatogram indicated that there are two well-resolved components of these residues. An approximate calibration of the column set showed the first of these to have a molecular weight around 2000. The second component (much larger portion) corresponds to residual fuel, and has a molecular weight in the C_{15} range.

These results suggest that the highest molecular weight oxidation products are formed during the oxidation, which is fast, not during long subsequent heating when the oxygen supply is exhausted.

Table VI

OXIDATIONS OF 10 ml OF RAF-177YX-63 IN SEALED VESSELS AT 200°

	I	II	III	IV	V
Vessel vol, ml	31.4	25.5	29.0	23.8	42.5
ΔO_2, μmole[a]	820	330	393	304	638
Time, hr	0.25	1.0	1.0	24.0	1.0
Residue, g[b]	0.293	0.393	0.286	0.193	0.174
Max. mol. wt.[c]	~2000			~2000	

[a] <1μ mole of O_2 recovered.

[b] Because of poor control of holdups in distillation, weight differences are probably not significant.

[c] Earliest peak in glc.

5. OXIDATIONS OF n-DECANE

5.1. Introduction and Summary

The background discussion in Section 2 suggests that n-decane should be a simple, useful material for answering the questions: At what temperature, time, and oxygen concentration can the most products of high molecular weight and low solubility be obtained from n-decane? What kinds of decane oxidation products or mixtures are most easily condensed by reaction (2) on page 5?

Several oxidations of n-decane were carried out at reflux temperature, 155°C, and very slow streams of air. Although considerable quantities of alcohols, ketones, and esters were obtained, our control of the oxygen concentration was unsatisfactory; it would be inconvenient to extend the experiments to higher temperatures (superatmospheric pressure), and there was no indication that condensation products of 20 or more carbon atoms were being formed. These experiments were therefore abandoned. However, the experiments show that, at least after an induction period, most of the oxygen supplied is absorbed rapidly at 155°.

5.2. Experimental

Decane oxidations were carried out in a vertical cylindrical Pyrex reactor, 32 mm in diameter and 130 mm high, fitted at the bottom with a coarse fritted glass filter of the same diameter and at the top with a cold finger condenser. The glass filter serves as a gas inlet; the exhaust gas leaves the reactor at the top of the cold finger and then passes the probe of a Beckman 778 oxygen analyzer, which is wired to a 50-mV recorder.

In a representative decane run, 50 ml of decane (Phillips research grade, which has been passed through a column of SiO_2/Al_2O_3) is pipetted into the reactor. The air or oxygen flow is started and adjusted with a soap-bubble flow meter, and the reactor is lowered into a constant temperature oil bath at 155°C. Free space between the liquid and oxygen meter is minimized for early response of the oxygen meter. Throughout an air experiment the partial pressure of oxygen in the exit gas is recorded. After oxidation the product is fractionally distilled at 47 and then 7 torr and analyzed by vapor-phase osmometry, elemental analysis, ir, nmr, and mass spectrometry.

5.3. Results and Discussion*

Several decane oxidations were carried out, the first at 130° and the rest at 155°C. The first few oxidations (Runs 1 through 4) were performed in an apparatus similar to the one recently used but with a much larger condenser and consequently a large dead volume. The last few experiments (Runs 5 through 7) were performed in a new reactor with lower dead volume, which gives a faster response on oxygen concentration with time. Experimental conditions are shown in Table VII. At 130°C (Run 1) no detectable change was noted in oxygen partial pressure, although a little oxidation did occur as indicated by hydroperoxide formation. The data in Table VII indicate that considerable oxidation occurs at 155°C.

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*Experimental work by N. Kirshen and H. Richardson.

Table VII

OXIDATION OF n-DECANE FOR 10.5 HOURS AT 155°C

Run No.	Flow Rate, ml/min	O_2 Pressure, torr			Duration of Minimum Pressure, min
		Initial	Minimum	Final	
2	4.6	160(air)	70[a]	120	~ 60[a]
5	4.0	160(air)	18	33	~ 380
6	20.0	160(air)	53	105	~ 70
7	4.0	high	high	high	----

[a] This experiment used the high dead volume apparatus and is only roughly comparable to Runs 5 and 6.

The decane solutions from Runs 2, 5, 6, and 7 were distilled under reduced pressure from a small Claisen flask. The decane and any lower-boiling products distilled first. Additional fractions were collected by raising the bath temperature to about 140°C. Results of these distillations are summarized in Table VIII.

Table VIII

DISTILLATION OF n-DECANE OXIDATIONS

Run No.	Aliquot	Fraction I			Fraction II			Residue[a]	
		Wt, g	%	B.p.,[b]	Wt, g	%	B.p.,[b]	Wt, g	%
2	28.08	24.87	88.6	92[c]	0.65	2.3	90	0.92	3.3
5	33.72	31.45	93.3	58	0.75	2.2	88	1.58	4.7
6	31.84	27.69	87.0	58	1.83	5.8	92	1.39	4.3
7	36.76	29.60	80.5	58	1.28	3.5	90	1.74	4.7

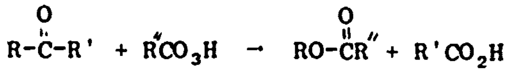
[a] At bath temperature of 140°C.

[b] End point at 10 torr pressure.

[c] End point at 47 torr.

Qualitative ir spectra were obtained for these fractions on the neat materials between salt plates. The spectra of the II fractions show strong ketone (1710-1720/cm) and alcohol (~ 3400/cm) absorptions and weak aldehyde absorption (2720/cm). The ir spectra of the residue shows these same absorptions, but the broader $>$C=O (1710-1740/cm) and -OH absorptions indicate also the presence, respectively, of esters and acids. The presence of esters in the residue is further borne out by the nmr spectra on CCl_4 solutions of Fraction II and the distillate of Run 2. A strong absorption at δ 5.05 is observed in the residue but not in the distillate nmr.

Some additional data obtained on Run 2 are summarized in Table IX. The molecular weights were determined by vapor-phase osmometry in a Mechrolab Model 302 apparatus with toluene as solvent. A rough mass spectrometric analysis on the residue showed a series of common fragments up to m/e = 241 and 243. A saturated C_{15} ester would have a molecular weight of 242.32 (before loss of a proton), and the series of fragments might correspond to a series of esters formed by the reaction,



$$R-\overset{O}{\overset{\|}{C}}-R' + R''CO_3H \rightarrow RO-\overset{O}{\overset{\|}{C}}R'' + R'CO_2H$$

where the peracid comes from oxidation of an aldehyde (formed by cleavage of an alkoxy radical). The mass spectrum shows no evidence of C_{20} compounds from coupling of C_{10} residues.

Table IX

OXIDATION RESIDUES FROM n-DECANE, RUN 2

Sample	Mol Wt	C,%	H,%	O,%	Empirical Formula
Fraction II	170	73.09	12.65	14.26	$C_{10.3}\ H_{21.3}\ O_{1.51}$
Residue	204	68.55	11.19	20.26	$C_{11.6}\ H_{22.6}\ O_{2.59}$
Decane (calc)	142.28	84.42	15.58	-	$C_{10}\ H_{22}$

6. COMPARISON OF THERMALLY STRESSED AND UNSTRESSED SAMPLES OF STANDARD FUEL RAF-178-64*

6.1. Introduction and Summary

Samples of a standard jet fuel, which had and had not been subjected to the JFTOT coker test, were concentrated by vacuum transfer and the very small residues were investigated. The residues were qualitatively similar, indicating that they were in the original fuel or were formed during storage. The residues contained less hydrogen and less aromatic groups than the original fuel; the increased oxygen content appears to be in ketone and ester, not in alcohol groups. Investigation by gas chromatography and mass spectrometry of the products with the longest retention times indicates that both hydrocarbons as well as oxygen compounds are among the highest boiling products. The oxygen compounds appear to be aliphatic and aromatic ketones and esters, but gel permeation chromatography gave no indication of coupling of fuel molecules to high molecular weight products. This work led us to concentrate our further efforts on a standard fuel of narrow boiling range, where separation of hydrocarbons and oxidation products should be easier (Section 4).

6.2. Origins of Samples and Fractions

Two samples of RAF-178-64 jet fuel, supplied by Dr. R. N. Hazlett, with a normal rather wide boiling range (184° to 267°C) were investigated. Sample U (unstressed) was simply deaerated and stored in an amber bottle under nitrogen. Sample S (thermally stressed) was put through the Alcor

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*Experimental work by H. Richardson, R. Stringham, and N. Kirshen.

JFTOT coker (490 ml in 4 hr) at a maximum tube temperature of 260° and filter pressure of 410 psi. The products were then fractionally distilled and analyzed as indicated below.

A 500 g aliquot of Sample S (or U) was transferred from a 1-liter bulb heated with a mantle to a cooled receiver by vaporization under high vacuum during about 4 hours in an all-pyrex apparatus. The results are summarized in Table X.

Table X

RESULTS OF VACUUM TRANSFER OF SAMPLES U AND S

Sample U			Sample S		
Fraction	Bath Temp., °C	Weight g	Fraction	Bath Temp., °C	Weight g
U_A	90	499	S_A	100	490
			S_B	100-115	10
			S_C	115	0.5
U_R	residue	0.25[a]	S_R	residue	0.14[a]

[a] May include some drainage of distillate from walls.

The stressed fuel S had a distinctive odor that might be associated with aliphatic aldehydes. On distillation, this odor appeared only in S_B; there was little difference between U, U_A, and S_A. Fractions U_R, S_R, and S_C had little odor.

6.3, Infrared Absorptions

Infrared spectra of the neat liquids, U, S, and each fraction, were taken in a sodium chloride cell with a 0.098-mm path length. No differences were noted between U and S or between U_A and S_A. However, the absorptions at 1600/cm and a few absorptions at <1000/cm were weaker in U_A and S_A than in the original fuels, U and S. These observations seem to indicate lower contents of aromatics and oxygenated materials in these fractions. This result was surprising since only about 1 part in 1600 was removed (U versus U_A). However, since we are looking at a complex mixture of compounds, slight changes in the product mix could make large differences in the intensity of the absorption at 1600/cm if different substitution patterns in aromatic molecules change the intensity of this absorption greatly. These decreases in absorption were even pronounced in S_B and S_C. The absorptions that were diminished in U_A, S_A, S_B, and S_C were stronger in U_R and S_R than in the original fuels. Further, strong absorptions at 1710/cm and 1735/cm in S_R and U_R are attributed to carbonyl compounds, probably ketones and esters. No significant absorption by hydroxyl groups was noted. Qualitatively, S_R and U_R were identical; no quantitative conclusions could be drawn because the sizes of the fractions were different. However, ir data suggest that the residues are probably higher in aromatic content or character and are definately higher in oxygen content than the original fuels.

6.4. Elementary Analyses

The last conclusion above is verified by elemental analysis of the residues U_R and S_R. Table XI shows that both residues, and particularly that from the stressed fuel, are enriched in oxygen and depleted in hydrogen compared with the original fuels.

Table XI

ELEMENTAL ANALYSIS OF JET FUEL RESIDUES

Sample	C,%	H,%	O,% by diff.
U_R	85.92	13.09	0.99
S_R	86.09	12.45	1.46
U(original)	86.1	13.81	~ 0

6.5. High Speed Liquid Chromatography

Table XII, which summarizes results of high speed chromatography on fuel samples, leads to a somewhat different conclusion on the compositions of the residues. These analyses were carried out with a 4-foot Porosil 60 column, a reciprocating pump, and a Waters R-401 refractive index detector. Hexane was used as the mobile phase at a flow rate of 0.6 ml/min. The operation gives class separations of aliphatic hydrocarbons, benzenoid hydrocarbons, and naphthalene derivatives, but any and all oxygenated products are held up in the column. Table XII shows that by relative peak areas there are somewhat more aliphatic than benzenoid hydrocarbons in the original fuels, but that the predominance of aliphatic hydrocarbons is much greater in the residues. This result means that when all the oxygen-containing products are removed from residues, the residual high-boiling hydrocarbons are high in aliphatic content. It may then follow that there is more coupling and less oxidation of aliphatic than of aromatic (benzylic) radicals.

Table XII

LIQUID CHROMATOGRAPHIC PEAK AREA RATIOS

Sample	Peak Area Ratio Hydrocarbon/Aromatic + Naphthalene
U	1.35
S	1.39
U_R	4.50
S_R	4.32

6.6. Gas Chromatography-Mass Spectrometry

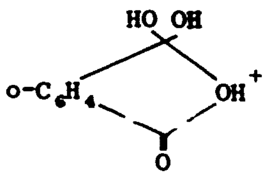
Gas chromatography and the ancilliary technique of gas chromatography-mass spectrometry (glc-ms) were applied to the residues U_R and S_R, using about 0.2 g of each. Two glc column packings applicable to the separation of the high boiling residue components were evaluated: (1) Carbowax 400/Porasil F (low K'), a Durapak from Waters Associates, and (2) 3% OV-1/Chromosorb W. With 6 ft by 1/8 in. stainless steel tubes at 200°C,both columns were found to be suitable for the residue analysis, although the OV-1 column gave somewhat better resolution.

Between 96 and 98% of the residues U_R and S_R elute within six minutes after injection. The remaining 2-4% comprises 17-20 peaks eluting in 6 to 65 minutes. The elution times of some known compounds were determined, and from these data it is apparent that the early-eluting materials are primarily hydrocarbon in nature whereas the later-eluting species are mainly higher boiling oxygenated compounds. No notable qualitative or quantitative differences were seen between U_R and S_R chromatograms, the same peaks occurring in both. This observation suggests that these compounds are present as traces in the original fuel or formed in storage, not in the coker test.

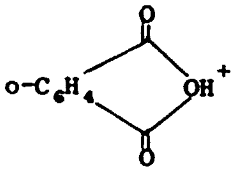
More information regarding the identity of the higher boiling species was sought by use of glc-ms and the Finnigan model 3000 gas chromatography peak identifier. The Carbowax 400/Porasil F column was chosen for this work,since it would be likely to have the lowest bleed. A number of the later-eluting compounds were scanned and the mass spectra evaluated. No attempt was made to positively identify a particular compound peak, but an attempt was made to determine the compound type, such as an ester, or ketone. This may be done by following general rules for predicting prominent peaks in a spectrum.[13,14] For instance, the major fragments of aliphatic ketones are those resulting from cleavage at the C-C bonds adjacent to a C=O group, the charge remaining with the oxygen-containing fragment giving rise to a series of mass units of 43 + 14n. With aryl alkyl ketones β-bond cleavage occurs, producing the characteristic $\text{Ph-}\overset{O}{C}^{+}$ fragment at m/3 = 105. With esters both R+ and $R\overset{O}{C}^{+}$ peaks (29 + 14n) are formed; there is also a prominent peak for the $^{+}\overset{O}{C}\text{-OR}$ fragment at m/e = 59, 73, or 87, etc. Furthermore, esters may give a "rearrangement" peak depending on the kind of ester, i.e., methyl, ethyl, propyl. This one fragment will occur at m/e = 74, with increments of 14 for members of a homologous series.

Following are the results of some of the peaks inspected:

(1) Compound elution time: 36 min (last peak on chromatgram). This mass spectrum exhibited a base peak at 149 and another strong peak 167 plus many other fragment peaks. These two peaks are probably the rearranged fragments



and



of phthalate esters.

(2) Compound elution time: 26 min. The base peak occurs at m/e 105, with peaks at 91, 117, 131, and 208. M/e 105 is attributable to the $Ph-\overset{\overset{O}{\|}}{C}{}^+$ fragment. A possible structure for this compound would be $Ph-CH=CH-\overset{\overset{O}{\|}}{C}-Ph$.

(3) Compound elution time: 18 min. This compound gives a base peak at 57 with alkyl and/or saturated carbonyl fragments up to 197. This 197 fragment is probably the $C_{14}H_{29}\overset{\overset{O}{\|}}{C}{}^+$ ion. Lacking any other clues. we suggest that this compound may be a long-chain aliphatic ketone.

(4) Compound elution time: 13 min. This compound, base peak at 57, also produced fragment ions attributable to saturated carbonyl ions up to 155, the $C_9H_{19}\overset{\overset{O}{\|}}{C}{}^+$ ion. The highest recognizable peak in the spectrum was at m/e 182, which could come from an unsaturated ketone, $C_9H_{19}\overset{\overset{O}{\|}}{C}-CH=CH_2$, which in turn could have come from "dehydration" of the corresponding hydroperoxide.

Thus it appears that the later-eluting oxidized species found in jet fuel residues are predominately long-chain carbonyl compounds, probably ketones and esters, the latter species seen in earlier nmr work. It also appears that some of these species could contain unsaturation, but there is no evidence of coupling of fuel molecules to higher molecular weight products.

6.7 Gel Permeation Chromatography of Liquid Fuel

The Waters GPC 200 was fitted with four Poragel columns (4 ft by 3/8 in.) in series: two with 60 Å pore size, one 250 Å, and one 500 Å. This combination of columns, with toluene as solvent and a flow of 1 ml/min, should provide size separation of components of the jet fuel residues in the molecular weight range of 100 to above 3000.

Elution volume was standarized against molecular size with a hydrocarbon mixture of octadecane, hexadecane, and hexane in toluene as solvent, elutions occurring in that order.

The elution volumes of U_R, S_R, and the octadecane standard are nearly the same. This result means that the average molecular sizes of the jet fuel residues, U_R, and S_R, are similar and close to that of octadecane. If the residue is predominately hydrocarbon, the average molecular weight will also be about the same as octadecane, 254. Thus, this experiment also gives no evidence of deposit precursors of doubled molecular weight.

6.8. Deposits

Dr. R. N. Hazlett sent us the slightly discolored "aluminum heater tube from the JFTOT run." None of the solvents that we tried had any obvious effect on this deposit: methyl ethyl ketone, diacetone alcohol (as a proprietary carburetor cleaner), N-dimethylformamide (even in 15 min at 100°), or refluxing dibutyl phthalate (30 min at 320°C). One molar aqueous sodium hydroxide started to dissolve the aluminum and so this test was inconclusive. The discoloration disappeared rapidly when it was heated in a Bunsen flame but left light gray splotches of a residue, insoluble in water, that might be metal oxides.

Dr. Hazlett also supplied four outlet filters (I, II, 16, 17) for the Alcor JFTOT apparatus. Two were unused and two were plugged in tests with RAF 178-64. Filter 16 was plugged in a test where maximum temperature was 299°C (pressure drop = 25.4 cm Hg); filter 17 was plugged at maximum temperature of 288°C (pressure drop = 22.9 cm Hg). Each of these filters was washed with pure pentane, dried under high vacuum (10^{-6} torr), and tared. Filters I and 16 were heated in methyl ethyl ketone (MEK) at reflux for 3 hr. Filters II and 17 were heated in dimethylformamide (DMF) at reflux for 3 hr. There was no significant change in the weight of any filter, each of which could have contained <10 mg of deposit.

7. PRESENT STATUS OF DEPOSITION PROBLEM

This section augments Section 3 (Background), sets forth the authors' present opinion of the status of the gas turbine fuel deposit problem, indicates what we propose to do next, and (we hope) will initiate some useful discussion among various participants in the Program.

Deposits in thermally stressed fuels can originate homogeneously and become hard and insoluble when deposited on surfaces. Trace metals probably affect the homogeneous reactions and the hardening process is subject to the metal and irregularities in its surface.

Some oxygen is required for formation of deposits near 300°C. In the absence of oxygen, much higher temperatures are required to form smaller quantities of deposits.[15]

Deposit formation occurs even in pure hydrocarbons.[3,7] Our recycle experiment (Section 4.8) indicates that the ability of our fuel to yield deposit precessors is little affected by the first heating with oxygen. Thus deposit formation apparently does not depend on traces of reactive components that are readily depleted. While there is little doubt that some possible fuel components give more deposits than others and that addition of some very active components will increase deposits from a given fuel, we think that such experiments are likely to be unrewarding. For example, the work of Whisman et al.[16] with ^{14}C-labelled additives shows essentially that all additives were incorporated in deposits, but that in terms of averages the amounts incorporated depended more on the fuels than on the additives. Further, the recent results of Taylor[3] on deposits from mixtures of pure hydrocarbons (if reproducible) indicate that isopropylcyclohexane <u>dec</u>reases deposit formation from dodecane-2,2,5-trimethypentane mixtures but <u>inc</u>reases deposit formation from dodecane-2,2,5-trimethylpentane-sec-butylbenzene mixtures. This result suggests that useful answers will not be obtained easily from additions of pure compounds.

Williams[17] has used ^{14}C-labeled compounds to determine the origin of "lacquer" deposits from n-octadecane during brief oxidations on a spinning aluminum disk at 274°C. His principal conclusions are probably relevant to jet turbine fuels. Small proportions of octadecyl hydroperoxides added to octadecane form a disproportionately very large proportion of the lacquer but long chain alcohols, ketones, and acids (most reactive of the group) have only a little more tendency than the alkane to enter the lacquer. At the low effective oxygen concentrations employed, most of the primary alkyl radicals formed by cleavage of longer chains abstract hydrogen from the substrate to give new methyl groups and secondary alkyl radicals, which then oxidize. Of the oxygen consumed, only about 0.1% appears in the lacquer. Much of the lacquer probably comes from bifunctional oxidation products, formed by intramolecular propagation of alkylperoxy or alkoxyradicals, e.g., hydroxyacids and ketoacids resulting from more than one chain scission per octadecane molecule.

The basic questions in the fuel deposit problem seem to be: (1) What is the general chemistry, applicable to most hydrocarbons, of the homogeneous reactions that lead to higher molecular weight and less soluble condensation products, i.e., deposit precursors? (2) What is the general chemistry by which deposit precursors are converted to hard and insoluble deposits and how is it affected by surfaces and catalysts? (3) How closely are the laboratory deposits analogous to those formed in actual service? (4) How can this information be applied to obtain better predictive tests and more stable fuels?

We propose to address these questions as follows. Section 4 describes our latest efforts to maximize precursor formation. We need both the optimum conditions and enough material to answer questions (1) and (2) above. We propose to continue our experiments with a standard fuel, but similar work with pure hydrocarbons will have some advantages. The report of Hays[18] that deposits on Teflon surfaces are easily removed or suspended offers a means of investigating deposits before they have become intractable. Experiments should also be carried out by adding small proportions of our oxidation and condensation products to standard fuels in coker tests, to see if we are really dealing with precursors.

Finally, our own experiments in Section 6.1 suggest that much of the highest boiling residue (and possibly also the deposit) from a fuel subjected to the coker test came from added antioxidant or from reactions during storage. Unless data are already available, some coker tests should be run on some standard fuels that have, and have not, been distilled or chromatographed to remove materials not present in the virgin fuel.

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