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ALTERNATE FUELS NITROGEN CHEMISTRY.(U)

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ALTERNATE FUELS NITROGEN CHEMISTRY

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P. O. Box 8
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November, 1977

FINAL TECHNICAL REPORT

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PREFACE

This report was prepared by the Government Research Laboratory, Exxon Research and Engineering Company, Linden, New Jersey under Contract N00019-76-C-0675 for the Department of the Navy. The program was sponsored by the Naval Air Systems Command, Air 310C and was monitored by Dr. Hyman Rosenwasser.

This report covers the period from 19 October, 1976, to 20 October, 1977. The principal investigators were Dr. John W. Frankenfeld and Dr. William F. Taylor, assisted by Mr. Robert Bruncati and Mr. Edward Bucker.

SUMMARY

Present petroleum derived jet fuels experience few problems resulting from nitrogen compounds (as attested to by the lack of a total nitrogen level fuel specification), since they presently contain little if any nitrogen (e.g., less than 5 ppm total N). However, synthetic crude oils, particularly as derived from shale rock, contain drastically higher levels of nitrogen. In addition, research has indicated that such nitrogen compounds are much harder to remove than other trace impurities, and it is highly probable that future alternate jet fuels will contain much higher nitrogen levels than present petroleum derived fuels. Studies have shown that certain trace nitrogen containing impurities promote sediment formation in fuels of the JP-5 type. This formation occurs at ambient temperature and is of sufficient magnitude to cause storage stability problems in such fuel. As a result, a study of the fundamental chemistry of sediment formation caused by nitrogen compounds is being carried out to provide a greater insight into the probable causes of sedimentation and provide a sound basis for future work aimed at establishing acceptable nitrogen levels in synfuels which optimize properties such as storage stability vs cost and availability considerations.

The major objectives of the present program were to determine the magnitude of the sedimentation problem, especially with respect to the number of nitrogen compound types which promote it, to study the effects of light, storage conditions and the presence of other non-hydrocarbon impurities and investigate the structure and mechanism of formation of the sediment.

In carrying out the program, a simplified model system with purified normal decane as the diluent was employed. Various nitrogen compounds were added alone or together with organic acids and phenols to determine their individual effects on sedimentation. Duplicate samples were stored under UV light and in total darkness. The sediments formed were removed periodically, weighed and analyzed for C, H, N and by infrared and mass spectral methods. The results obtained and conclusions reached are as follows:

- Nitrogen compounds of the types found in synthetic derived crude oils such as obtained from shale rock can cause the formation of significant quantities of sediment in relatively short times and thus pose a potentially serious problem in the storage stability area.
- The type of nitrogen compounds present in the fuel is very important as not all classes of nitrogen compounds are deleterious. Pyrrolic types, in particular, and some amines have been shown to be deleterious; however, many other types of nitrogen compounds are not.
- Structural effects among pyrrolic types appear to be important also as the sediment formation rate is very high with 2,5-dimethylpyrrole compared to the rate of sediment formation with other pyrrole derivatives.
- Light has a very strong catalytic effect which markedly increases the rate of sediment formation.
- The interaction of nitrogen compounds with other trace impurities can exert a strong, but complex effect on the rate of sediment formation. The presence of carboxylic acids strongly accelerates the rate of sediment formation, with this effect being most pronounced in the dark.

In contrast, the presence of phenols reduces the rate of sediment formation. In addition, there are strong structural effects among phenolic types.

● The sediments have a definite structural character and with 2,5-dimethylpyrrole and indole appear to be a partially oxidized dimer, trimer and/or tetramer of the parent nitrogen compound containing about 1.5 units of oxygen per unit of parent compound. More than one species may be present but all appear closely related.

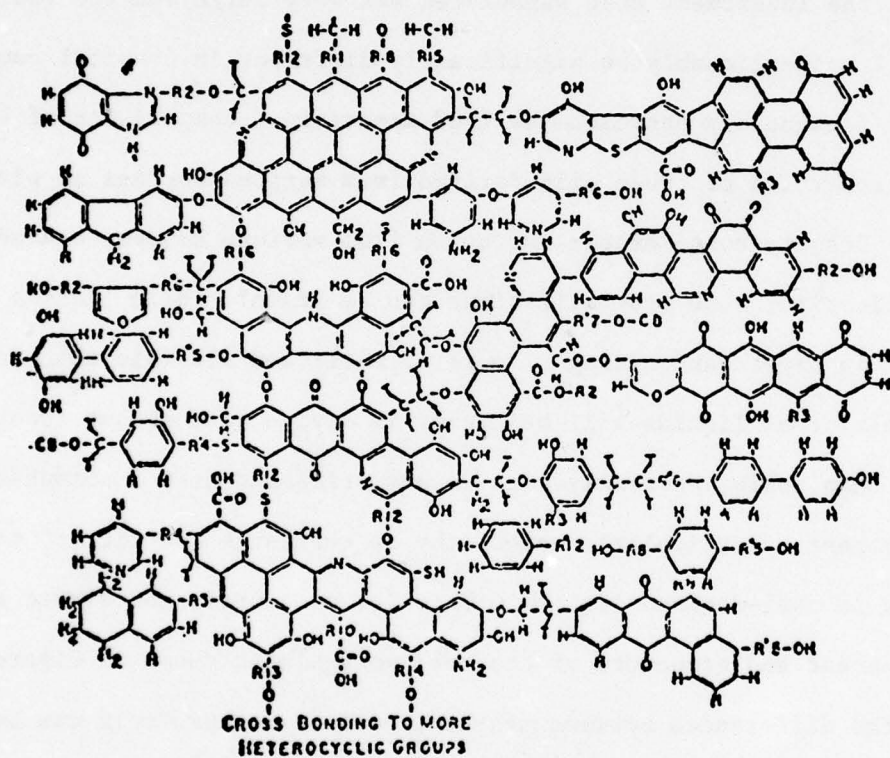
1. INTRODUCTION

Both the U. S. and world petroleum reserves are being depleted at a rate that can no longer be ignored. As a result, the development of alternate fuel sources is a virtual necessity within a few decades. Two of the most promising new sources are shale rock and coal (1). Although processes are available for the production of synthetic liquids from shale and coal, the investment cost associated are very large and the fuels produced will unquestionably be significantly different in chemical composition from present day petroleum-derived materials. Comparisons of some average properties of crude oils derived from various sources is given in Table 1. Despite considerable variation from various sources and methods of liquification, some generalizations can be drawn: shale liquids will be higher in oxygen and nitrogen, more aromatic and olefinic than petroleum-based fuels; coal liquids will be higher in oxygen content but lower in nitrogen than shale, extremely rich in aromatics and have a somewhat lower olefin content. Particularly noteworthy is the large quantity of polar compounds in coal-derived liquids. This is, of course, correlated with the oxygen content and structure of the coal molecule as shown in Figure 1 (1). Some of the differences between synthetic and petroleum fuels can be corrected by known processing techniques. However, these are expensive and can never be completely effective. It is important, therefore, to determine which types of variations from known fuels will be deleterious and which can be tolerated.

One of the substances most difficult to remove is nitrogen. A number of investigators have reported that catalytic removal of nitrogen compounds from both petroleum and shale oil fractions is much more difficult than sulfur removal (2, 3).

FIGURE 1

Molecular Structure of Coal(1)



- R*N = Alicyclic rings of N carbons.
- RN = Alkyl side chain of N carbons.
- R*N = Unsaturated alkyl side chain of N carbons.
- CB = Cross bonding by O or S to new heterocyclic groups with side chains.
- T = Tetrahedral 3 dimensional C-C bonds, C-O bonds and C-S bonds.

TABLE 1

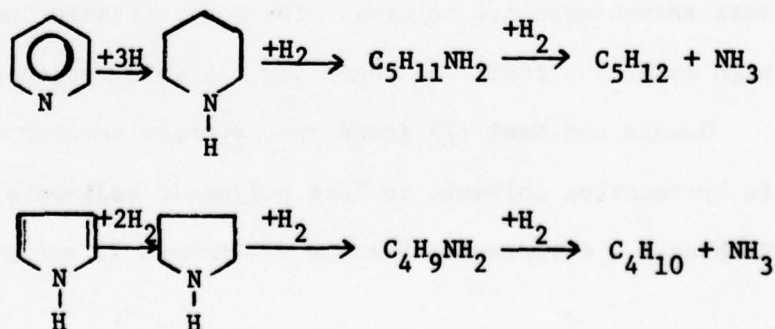
Average Properties of Crude Oils Derived from Various Sources(1)

	<u>Petroleum</u>	<u>Shale Liquid</u>	<u>Coal Liquid</u>
Carbon %	83-87	81	78-85
Hydrogen %	11-15	10	7.5-10
Oxygen %	0.5-5	5-6	7-15
Nitrogen %	0.1-0.5	1-3	0.6-1
Sulfur %	0.6-6	0.6-3	0.3-2
Saturates %	70-90	10-40	5-20
Aromatics %	10-20	25-50	10-50(a)
Polars %	<1	1-3	50-80(a)
Olefins %	1-2	25-50(b)	1-5

(a) Large numbers of aromatics in polar fraction.

(b) Content varies with method of liquification; retorting affords highly unsaturated oils while hydrofining produces many fewer olefins.

This difficulty in removing nitrogen compounds probably reflects the refractory nature of the ring compounds which contain the majority of the nitrogen. In contrast, much of the sulfur present is contained in compounds such as thiols, sulfides, disulfides, and polysulfides, where S-C bonds are much easier to cleave. Catalytic hydrodenitrogenation first involves the saturation of the nitrogen ring compound as illustrated below for pyridine and pyrrole.



Recently, Satterfield and his MIT co-workers have indicated that the initial hydrogenation step involved in hydrodenitrogenation of unsaturated

heterocyclic nitrogen compounds is equilibrium limited (4,5). This represents a serious impediment to improvements in nitrogen removal technology, since improved catalysts will not remove this thermodynamic limitation. In any event, nitrogen removal is difficult, and this, coupled with the much larger number of nitrogen compounds present in shale oils, indicates that synthetic jet fuels will have higher nitrogen levels than present petroleum derived jet fuels.

It is known that nitrogen content can adversely effect fuel stability. This is illustrated in Figure 2, where three jet fuels, prepared by catalytic hydrotreating shale liquids, were subjected to the standard JFTOT thermal stability test (6). Clearly, the higher the nitrogen content of a fuel, the poorer its thermal stability. Some of the samples shown in Figure 2 were severely hydrotreated yet still retained significant amounts of nitrogen and exhibited poor thermal stability (6).

Certain nitrogen compounds are also known to have adverse effects on color stability of various petroleum distillates (7-13). Nixon has discussed the effects of trace impurities on storage stability of jet fuels derived from petroleum (13). He states that pyrrolic compounds and some sulfur containing species are quite deleterious to fuel stability while most amines were not harmful. The most unstable fuels appear to be those high in both pyrrolic nitrogen and olefinic hydrocarbons (13).

Oswald and Noel (7) found that pyrrole reacted with O₂ or peroxides in hydrocarbon solvents to form polymeric sediments of a type called "pyrrole black". A tentative formula (Structure I) was proposed (3).

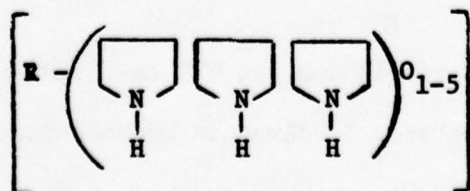
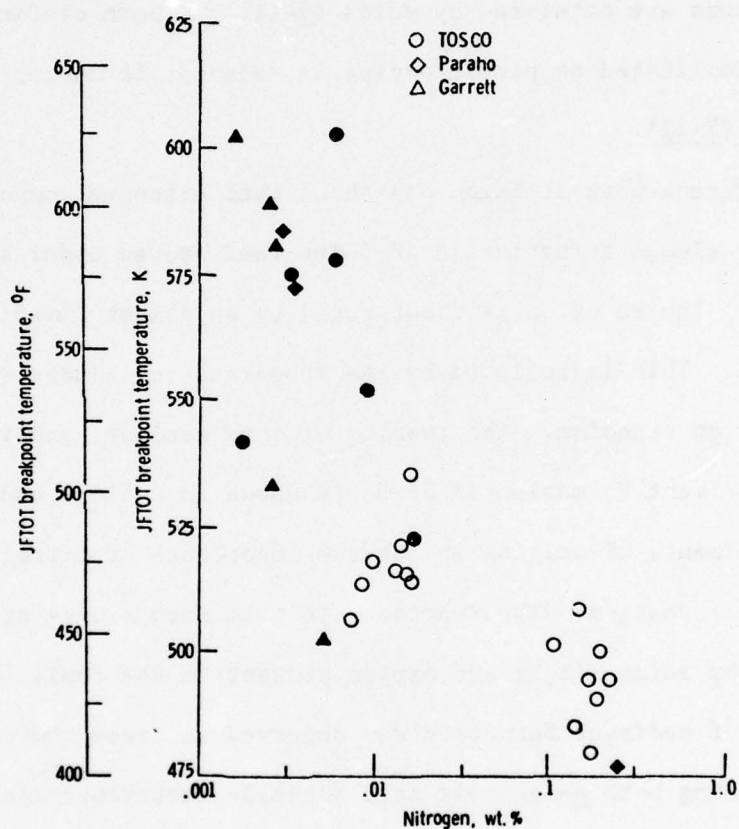


FIGURE 2
Variation of JFTOT Breakpoint Temperature
With Nitrogen Level After Hydrotreatment



The actual mechanism for sediment formation, however, is not well understood nor has its importance in fuel instability been fully appreciated. Mayo, et al. (8) found that oxygen and peroxides had a profound effect on deposit formation in pure hydrocarbons, although the importance of nitrogen compounds was not recognized. Other workers have observed that such reactions are catalyzed by acids (9-11) and both olefins and thiols have been implicated as participating in sediment formation under certain conditions (7-11).

Recent work at Exxon has shown that nitrogen compounds promote sediment or sludge formation in JP-5 jet fuel stored under ambient conditions (14). The reaction is first noted by an almost immediate darkening of the fuel. This is followed by the appearance of sludge which continues to increase on standing. The results of some earlier, preliminary experiments on sediment formation in JP-5 are shown in Table 2 and Figure 3. These experiments clearly establish the importance of nitrogen compounds in sediment formation. The reactions to form such sludge are strongly influenced by acids, light and oxygen present in the fuel. Thus, the most rapid rate of sediment formation was observed in cases where air saturated fuel containing both n-decanoic acid and 2,5-dimethylpyrrole were stored in the presence of light (top curve of Figure 3). Neither the base fuel nor the fuel with acid added alone produced any sediment. Particularly noteworthy was the amount of sediment formed. In the two experiments where both acid and pyrrole were present, this equalled or exceeded the amount of pyrrole added (top two curves of Figure 3).

These preliminary studies also suggest that different modes of sediment formation obtain under different storage conditions. This is particularly noteworthy in the case of light vs dark storage. The straight

FIGURE 3
SEDIMENT FORMATION IN JP-5 UNDER INFLUENCE OF DIMETHYLPYRROLE

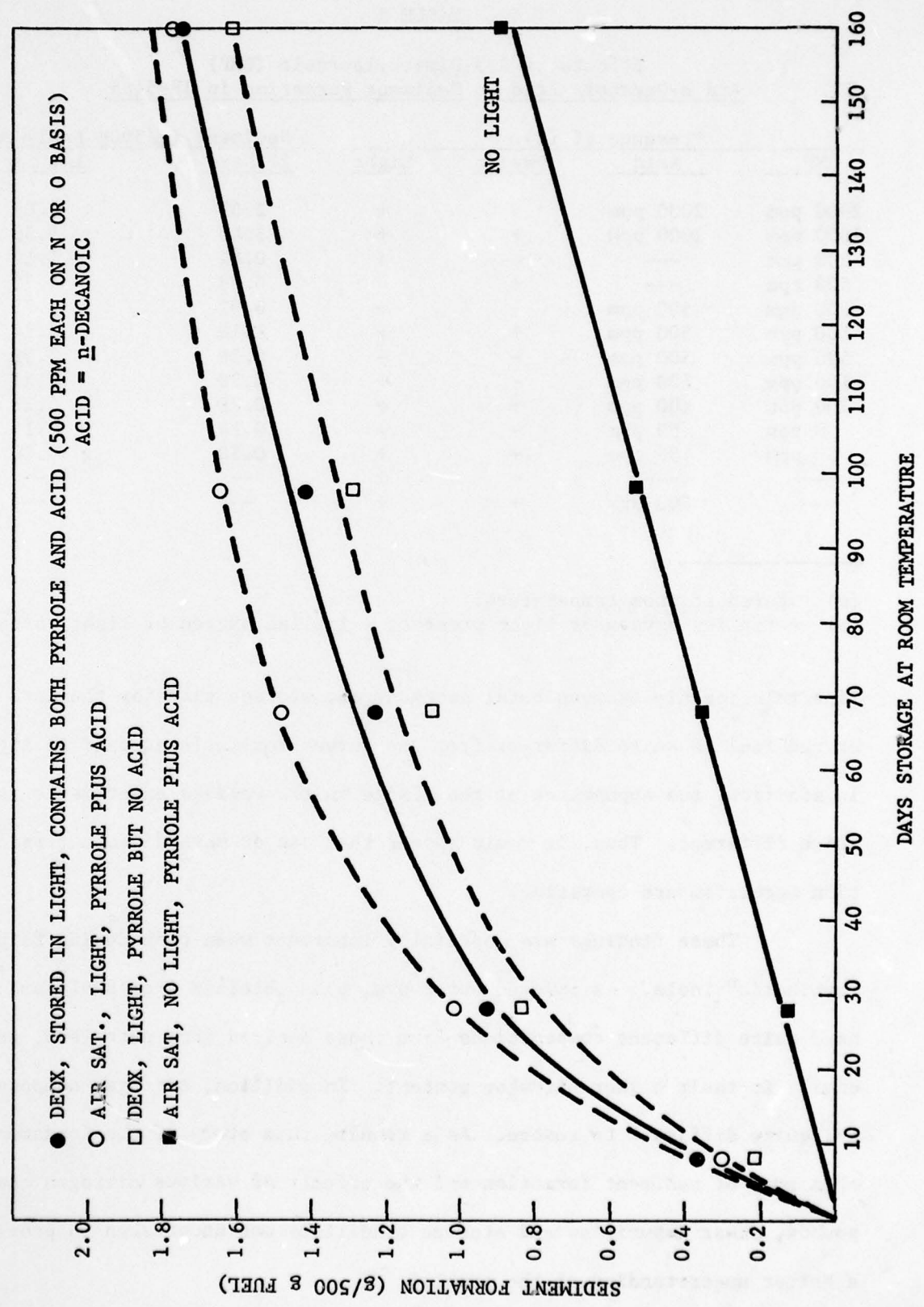


TABLE 2

Effects of 2,5-Dimethylpyrrole (DMP)
And n-Decanoic Acid on Sediment Formation in JP-5(a)

DMP	Presence of (b)			Sediment (g/500g Fuel) at	
	Acid	Oxygen	Light	28 Days	160 Days
2000 ppm	2000 ppm	-	+	2.61	4.07
2000 ppm	2000 ppm	+	+	3.43	5.39
500 ppm	---	-	+	0.81	1.62
500 ppm	---	+	-	0.98	1.73
500 ppm	500 ppm	-	+	0.92	1.75
500 ppm	500 ppm	+	+	1.10	1.74
500 ppm	500 ppm	-	-	0.38	0.92
100 ppm	100 ppm	-	+	0.30	0.31
100 ppm	100 ppm	+	+	0.28	0.28
50 ppm	50 ppm	-	+	0.14	0.15
50 ppm	50 ppm	+	+	0.18	0.20
---	---	+	+	--	--
---	500 ppm	+	+	--	--

(a) Stored at room temperature.

(b) + implies oxygen or light present; - implies oxygen or light absent.

line relationship between total sediment and storage time for the dark-stored fuel is quite different from the curves for fuels exposed to light. In addition, the appearance of the sludge in the various experiments is quite different. Thus, it would appear that one or more different reaction mechanism are operative.

These findings are especially important when considering future "synthetic" fuels. As pointed out above, oils obtained from shale and coal have quite different compositions from those derived from petroleum, especially in their higher nitrogen content. In addition, nitrogen compounds are quite difficult to remove. As a result, this study of the fundamental chemistry of sediment formation and the effects of various nitrogen compounds, other impurities and storage conditions was undertaken to provide a better understanding of the problem

2. TECHNICAL DISCUSSION

2.1 Objectives and Methods of Approach

The findings discussed in the previous section point up the need for a fundamental study to gain a better understanding of the factors which influence storage instability of synthetic fuels and to elucidate the mechanism of sediment formation caused by nitrogen compounds in such a fuel. The objectives of this program were:

- Study chemistry of sediment formation as caused by various nitrogen compounds present in synfuel; determine whether phenomena is unique for pyrrole-type compounds.
- Determine the effects of hydrocarbon types and certain trace impurities on nitrogen-containing sediments.
- Determine the effects of certain storage conditions on fuel stability.
- Characterize the deposits.

Model fuel compositions were used in order to simplify the system for mechanism studies. The base "fuel" was n-decane with other fuel components added singly or in simple combinations. Thus, the sediment formed had a limited number of possible molecular compositions and was more amenable to structural determinations. The following method of approach was followed.

- A. Conduct a literature survey to determine state of prior knowledge with respect to the influence of nitrogen compounds on fuel instability.

B. Study rate of sediment formation caused by nitrogen compounds in model systems at room temperature.

- Effects of nitrogen compound type
 - + Amines
 - + Heterocycles other than pyrrole
- Effects of light
- Interaction effects between pyrroles and acidic trace impurities
 - + Carboxylic acids
 - + Phenols

C. Study mechanism of sediment formation

- Elucidate structure of sediments
 - + Molecular weight determination
 - + C, H, N, O analysis
 - + Infrared spectrometry
- Determine reaction kinetics (if possible)
 - + Reaction order
 - + Effects of catalysts
 - + Effects of temperature

Progress toward achieving the above objectives is discussed in the ensuing sections of this report.

2.2 Literature Review

As a preliminary to the experimental program, a search of pertinent literature was conducted. This was carried out first in Chemical Abstracts searching such terms as "synthetic fuels", "jet fuel storage stability", "deposit formation", and the like. A large number of citations were found and it was decided that a more fruitful approach would be to use

Exxon's computer search facilities. This was done using the major heading and key words in Table 3. The number of citations found are also shown in Table 3. In addition to the computer search, certain secondary sources were checked by hand. No attempt at an exhaustive search was made. Of the citations uncovered, the majority proved to be irrelevant to this program. A listing of useful references on nitrogen fuel chemistry is given in the Appendix to this report.

TABLE 3
Results of Computer Literature Search

<u>Major Headings</u>	<u>Jet Fuel Stability</u>	<u>Shale Oil</u>	<u>Jet Fuel</u>
Key Words	Decomposition Oxidizable Oxidation Shelf Life Deposit Form. Sediment Aging Stability	Decomposition Deterioration Aging Stability Shelf Life Deposit Form. Sediment Oxidizable Oxidation	Decomposition Oxidize Oxidation Storage Stability Sediment Deposit Degradation Aging
No. of Citations	348	123	77

2.2.1 Effects of Nitrogen on Stability of Jet Fuels

It has been known for some time that certain nitrogen compounds can adversely affect the storage stability of petroleum-derived jet fuels. For example, Thompson, et al. (12) have pointed out that precipitates obtained from various fuels are much higher in nitrogen (and sulfur) than the parent oil (Table 4). This implies that sediment formation is due in large measure to polymerization of nitrogen containing species.

The literature prior to 1960 has been reviewed by Nixon (13) who states that while certain nitrogen bases are deleterious, others are not.

TABLE 4

Fuel Oil Sediments are Enriched in Nitrogen and Sulfur (12)

<u>Fuel Oil</u>	<u>Oil</u>		<u>Sediment</u>	
	<u>Sulfur %</u>	<u>Nitrogen %</u>	<u>Sulfur %</u>	<u>Nitrogen %</u>
1	1.28	0.01	3.38	3.58
2	0.96	0.02	1.72	0.80

Anilines may exert a beneficial effect while pyrroles are markedly unstable (13). Apparently, other components of the fuel, especially unsaturated hydrocarbons, may interact with nitrogen containing impurities to produce deposits. Thus, according to Nixon and co-workers (13,21,22), the most unstable fuels are those containing thermally and/or catalytically cracked base stocks (high in unsaturates) in combination with a high nitrogen content. This observation is supported by Dinneen and Bickel (39) and also by Taylor and Frankenfeld (14,15) who report interactions between 2,5-dimethylpyrrole and olefins both under high temperature conditions (15) and on room temperature storage (14). The deleterious combination of olefins and nitrogen impurities also may inhibit the action of antioxidants in fuels (22). The data given in Table 4 also implicate sulfur containing species in sediment formation (12) as do Oswald's reports (7).

Various Russian workers have demonstrated the beneficial effects of removing nitrogen bases from jet fuels (16,17). A three-fold reduction in oxidation residue and nearly a 10-fold reduction in gum was observed in removing the nitrogen from test materials in one experiment (16). Similar results were reported by Reynolds (6) who subjected fuels containing various amounts of nitrogen to the JFTOT, thermal stability test (see Figure 2, previous section of this report). Aliphatic amines (17,18) have recently been implicated in gum formation in jet fuels as have various pyrroles (25).

Thompson et al. (12) and Dinneen and Bickel (39) implicate both pyrroles and pyridines as promoters of sludge in fuel oils. On the other hand, other workers (13,19,20) have found that some nitrogen bases have little or no effect on fuel stability. In fact, enhanced stability has been claimed for fuels containing pyridines (19) and Mannich bases (20) under certain circumstances.

In general, however, it appears that nitrogen compounds contribute to instability in petroleum-derived fuels.

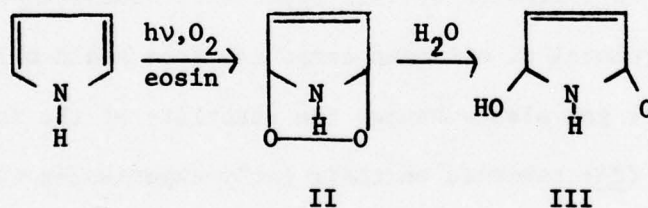
Jet fuels derived from coal and shale have been studied to a lesser extent. However, the deleterious effect of nitrogen compounds has been recognized (1,6,8,23). Smith et al., for example, found that oxidation reduced the nitrogen content of shale-oil naphtha and thereby enhanced its stability to further degradation (23). Both pyrrolic and pyridinic nitrogen compounds were removed by this treatment. These same workers report that partial removal of nitrogen compounds from shale oil naphtha by absorption on silica gel also enhanced the stability of the fuel (23). McBrien and Martin (24) reported on their early experiences with shale liquids as fuels and found them quite unstable, partially due to nitrogen content. The nitrogen content of deleterious deposits was quite high (24). Repeated attempts under mild conditions to remove nitrogen from the fuel were only partially successful. Finally, a severe acid treatment was resorted to. The resulting fuel, with reduced nitrogen levels, was more stable (24).

It appears, therefore, that the deleterious influence of nitrogenous species is well established. What is not yet clear is the magnitude and breadth of this effect and the mechanism of sediment formation in shale liquids. It is one of the goals of this program to shed more light on these questions.

2.2.2 Oxidation of Pyrroles and Related Compounds

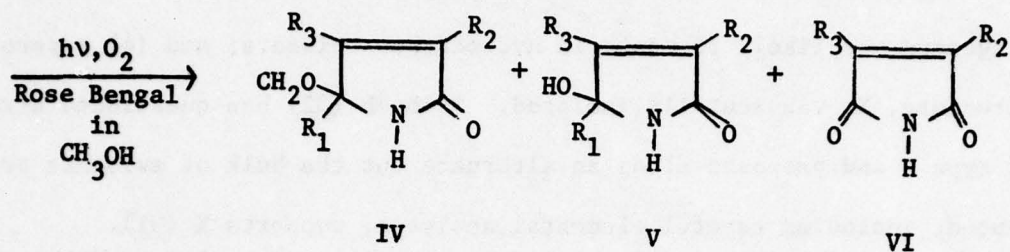
Since pyrroles and related compounds have been implicated as a major source of sediment, a brief review of the photo- and autoxidative chemistry of pyrroles is in order. The majority of studies have involved pyrrole and aryl pyrroles rather than alkyl substituted pyrroles and have employed conditions different from those which obtain under fuel storage. Nevertheless, these findings are of value in helping to identify sediment found in jet fuels.

In an early paper, de Mayo and Reid (26) identified the major product of the eosin-sensitized photooxidation of pyrrole as 5-hydroxy-3-pyrrolin-2-one (Structure III). The proposed intermediate was II by analogy with the well established photooxidation of furans (27):

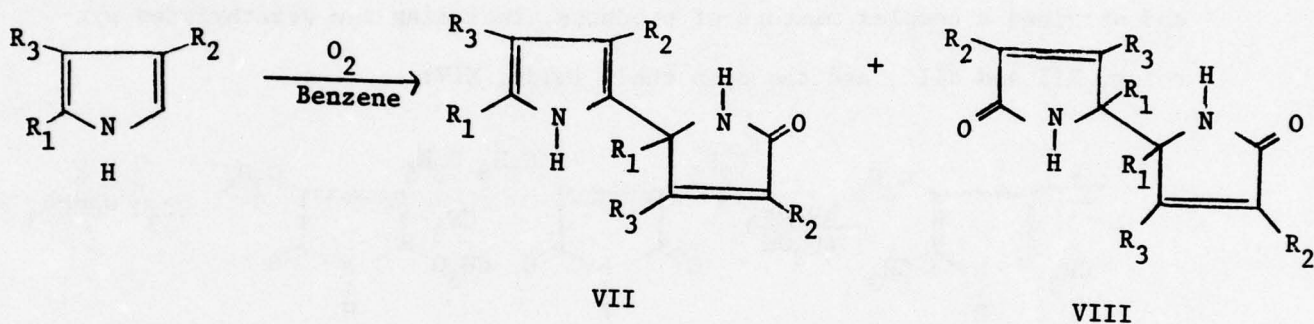


Following this, most studies of pyrrole oxidations concentrated on phenyl-substituted derivatives (28). Recently, however, a few pertinent reports of the oxidations of alkyl substituted pyrroles have appeared. When either the 2- or 5- position of the alkyl pyrrole is unsubstituted, the products of either photooxidation or autoxidation have been formulated as structures IV-XI, depending on conditions, Scheme I (28-31). Several noteworthy observations may be made of this work: (1) in no case was the N-H band ruptured, implicating intermediates analogous to II in most cases;

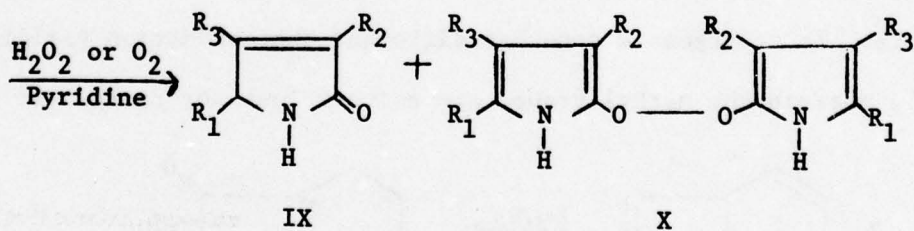
SCHEME I



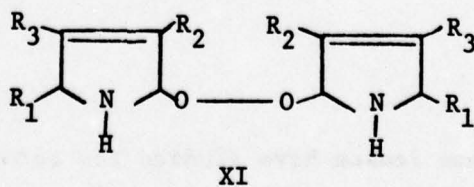
Ref. 29, $R_1 = \text{CH}_3$; $R_2 = R_3 = \text{C}_2\text{H}_5$



Ref. 30, $R_1 = R_2 = R_3 = \text{CH}_3$



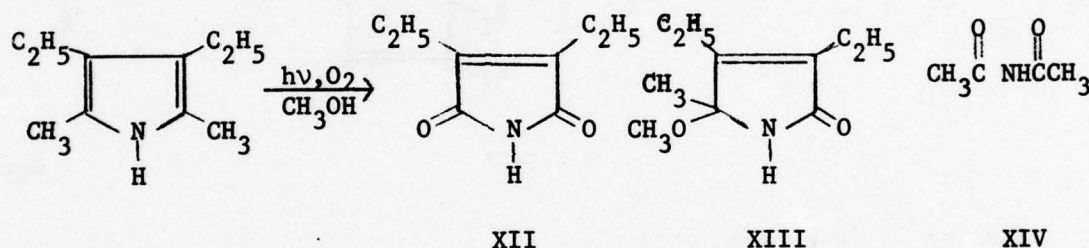
Ref. 31, $R_1 = R_2 = R_3 = \text{CH}_3$



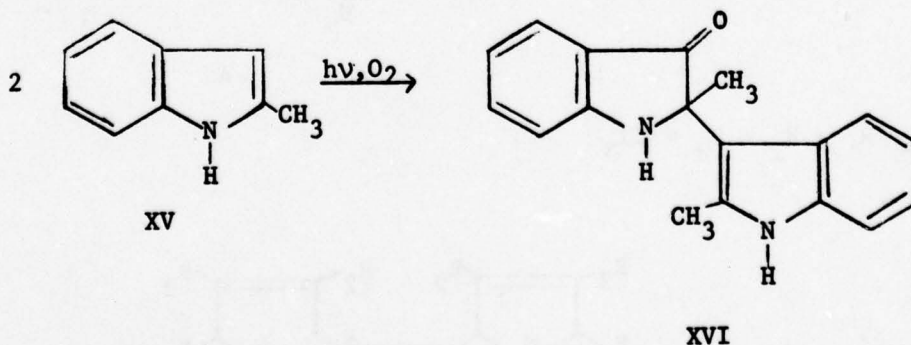
Ref. 32, $R_1 = R_2 = R_3 = \text{CH}_3$

(2) a novel dealkylation has occurred to give VI; (3) dimers or higher oligomers are likely to occur in hydrocarbon solvents; and (4) a peroxide structure, X, was actually isolated. Seebach (32) has questioned structures of type X and proposed XI as an alternate but the bulk of evidence presented, including careful elemental analysis, supports X (31).

Few reports of the oxidation of 2,5-dialkylpyrroles have appeared. Lightner and Quistad (33) photooxidized 3,4-diethyl-2,5-dimethylpyrrole and obtained a complex mixture of products, including the demethylated pyrroles, XII and XIII, and the open chain imide, XIV:

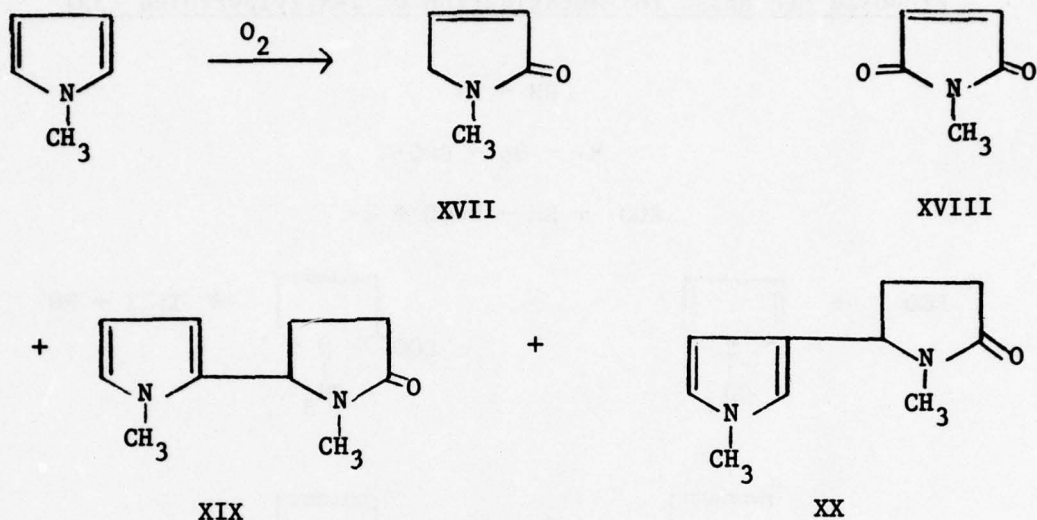


The compound 2-methylindole (XV) may be looked upon as a 2,5-disubstituted pyrrole. It undergoes a somewhat different photooxidation yielding a dimer (XVI), wherein the methyl groups are neither lost nor rearranged (34):



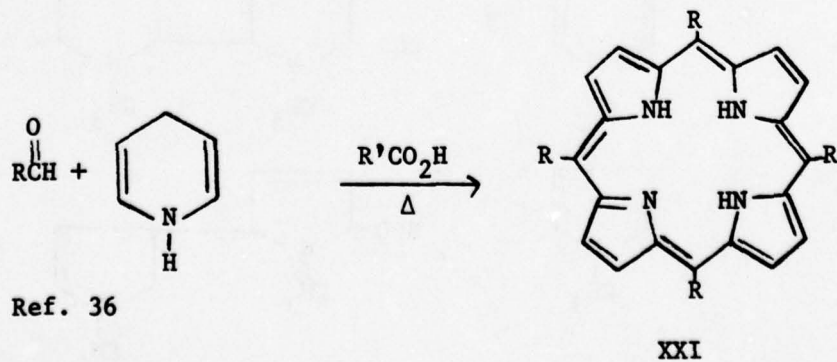
Smith and Jensen have studied the autoxidation of 1-alkylpyrroles (35). They found that these derivatives reacted more slowly than *c*-alkylpyrroles. Four reaction products, structures XVII-XX, were identified (Scheme II).

SCHEME II



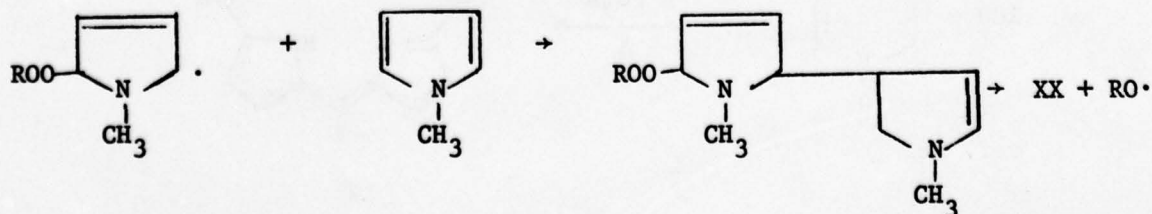
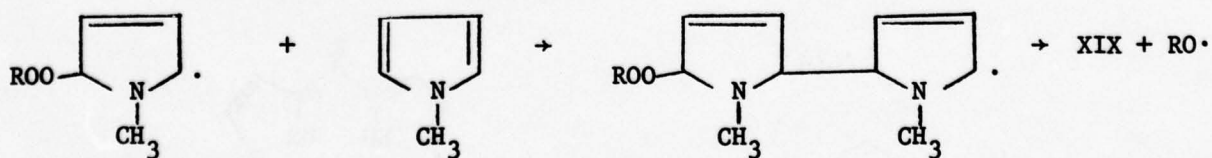
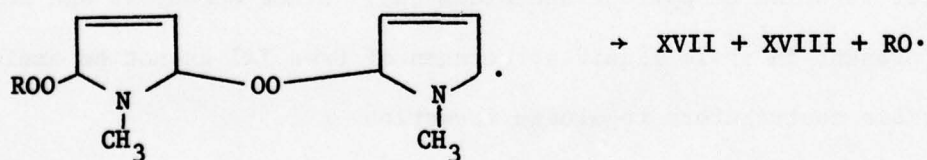
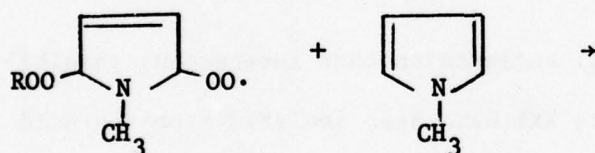
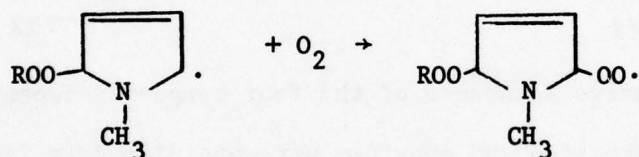
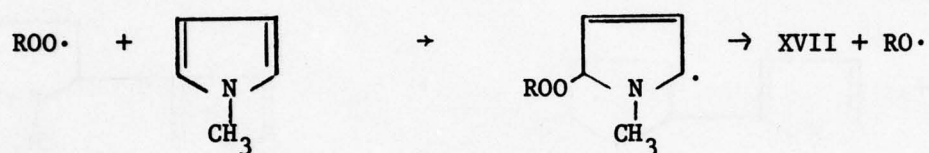
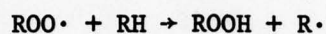
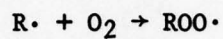
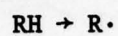
The relative abundance of the four compounds depended on the reaction time. Peroxides and epoxides were postulated as intermediates and shown in Scheme III.

A recent report (36) suggests another interesting possibility. Macrocyclic rings of structure XXI have been isolated from the acid catalyzed reaction of pyrrole and aldehydes. Since aldehydes and acids may be present in shale liquid structures of type XXI cannot be excluded as possible contributors to sludge formation.

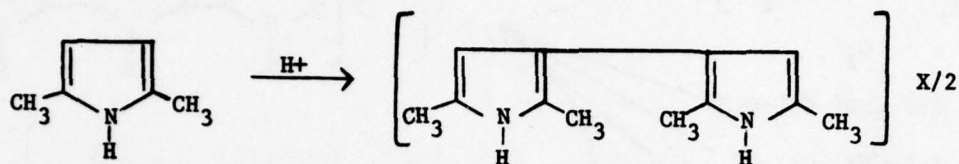


SCHEME III

Proposed Mechanism for Autoxidation of 1-Alkylpyrroles (35)

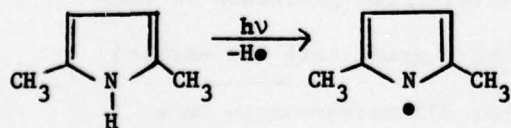
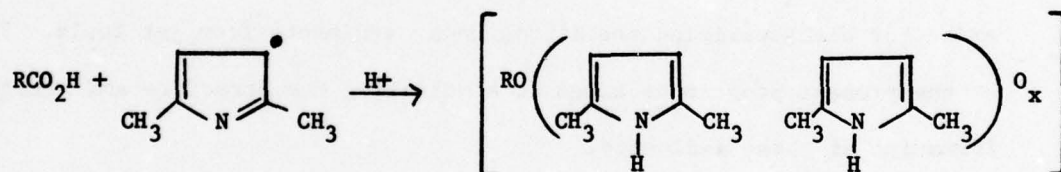
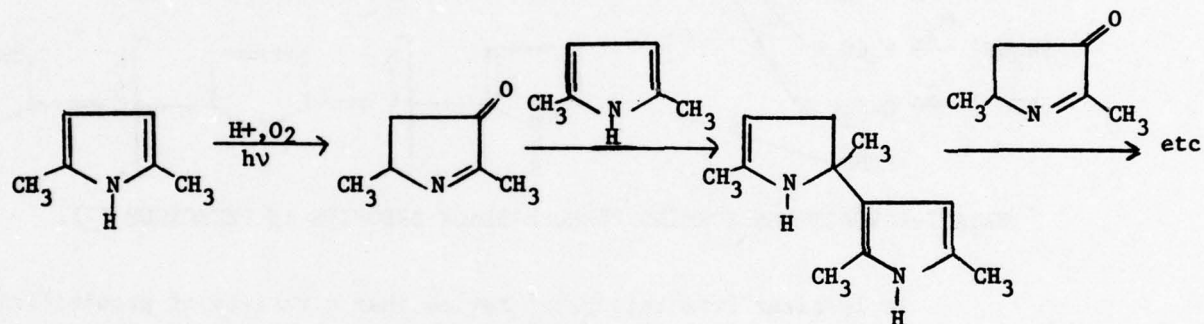


It was pointed out in Section 1 that sediment formation from JP-5 is strongly influenced by acids. Although the acid may be functioning simply as a catalyst:

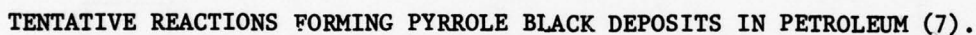


See Oswald and Noel, (Ref. 1).

it is also possible that complicated mechanisms are operative with the acid functioning both as a catalyst and as an active participant:



In addition, other components of the fuel, such as thiols, sulfides, olefins and carbonyl compounds of various types may enter into sludge formation. Oswald and Noel (7) have proposed some tentative reactions leading to pyrrole deposits under the influence of various other fuel components (Scheme IV).



2.3 Experimental Methods

The test compounds were the highest quality commercially available. They were purified by distillation when necessary. High quality n-decane was employed as the diluent. This was further purified by percolation through columns of activated aluminum oxide to remove traces of reactive.

polar materials as well as water. The nitrogen compounds were tested at the 2,000 ppm level (nitrogen basis) which is within the limits expected from fuels derived from shale or coal (1). The oxygenated compounds were added in amounts equivalent to 500 ppm O.

Duplicate sets of samples were set up using glass bottles. One set was stored in darkness at ambient temperatures (24°C). The second set was irradiated with long wave (366 nm) UV light with an intensity of 1100 $\mu\text{W}/\text{cm}^2$ (37). A separate sample of *n*-decane with 4,000 ppm N as 2,5-dimethylpyrrole was exposed to normal sunlight to serve as a control. The bottles were removed from storage at intervals, the precipitate filtered and dried under vacuum at 110°C for 1-1/2 hours before weighing and subsequent analysis.

2.4 Results and Discussion

2.4.1 Effects of Various Nitrogen Compounds on Sediment Formation

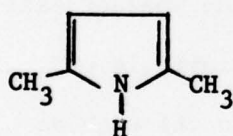
An important part of this program was to determine whether sediment formation is peculiar to fuels containing 2,5-dimethylpyrrole or whether other types of nitrogen compounds can contribute to the problem as well. A variety of representative nitrogen compounds were tested. Compound type analyses of various light distillates of shale liquids have been reported (38). These are summarized in Table 4. They show that pyrroles, quinolines, and pyridines are the dominant species present along with lesser amounts of amides, anilides and alkyl amines. Compounds of these types were, therefore, chosen for this study. The actual materials employed are shown in Table 5.

TABLE 4

Nitrogen Compounds Found in Shale Oil Light Distillate (38)

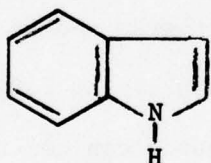
<u>Type</u>	<u>Wt. % of Total N</u>
Alkylpyridines	42
Alkylquinolines	21
Alkylpyrroles and Indoles	19
Cyclic Amides	3
Anilides	2
Weak and Non-Basic N	11

The sediment obtained from the various nitrogen compounds studied is given in Table 6. Plots of sediment vs time are shown in Figure 4. It is clear from this data that sediment formation is not unique to 2,5-dimethylpyrrole (DMP) although of those compounds tested DMP easily produced the greatest amount. It is interesting that the three compounds giving the most sediment were all of the pyrrole type, DMP, indole and carbazole (Structures XXII-XXIV).



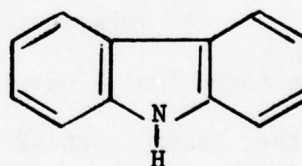
XXII

DMP



XXIII

INDOLE



XXIV

CARBAZOLE

Of the other compounds studied, only 2,6-dimethylaniline and 2-methylpiperidine afforded any measurable sediment. However, several of the primary amines produced colored solutions which intensified with time. Their effects on long term storage stability is unknown.

The data in purified n-decane closely paralleled those obtained earlier in JP-5 (compare Figures 3 and 4). The shapes of the curves in Figures 3 and 4 are similar to a plot of oxidative gum formation in high nitrogen shale liquid published by Dinneen and Bickel (39), but are quite

Table 5

Nitrogen Compounds Evaluated As Possible Sources of Sediment⁽¹⁾

Experiment	Additive	Mol. Wt.	Level Added (g/500g n-Decane) (2)	Stored In	
				Light (3)	Dark
1	None	---	---	X	
2	None	---	---		X
3	2,5-Dimethylpyrrole	95	6.79	X	
4	2,5-Dimethylpyrrole	95	6.79		X
5	Indole	117	8.35	X	
6	Indole	117	8.35		X
7	Carbazole	167	11.95	X	
8	Carbazole	167	11.95		X
9	2,4,6-Trimethylpyridine	121	8.65	X	
10	2,4,6-Trimethylpyridine	121	8.65		X
11	Quinoline	129	9.21	X	
12	Quinoline	129	9.21		X
13	2,6-Dimethylaniline	121	8.65	X	
14	2,6-Dimethylaniline	121	8.65		X
15	n-Hexylamine	101	7.21	X	
16	n-Hexylamine	101	7.21		X
17	Methylcyclohexylamine	114	8.14	X	
18	Methylcyclohexylamine	114	8.14		X
19	2-Methylpiperidine	99	7.07	X	
20	2-Methylpiperidine	99	7.07		X
21	n-Caproamide	115	8.21	X	
22	n-Caproamide	115	8.21		X

- 23 -

⁽¹⁾ Purified n-decane used as model fuel; all samples air saturated stored at ambient temp. (21-25°C).⁽²⁾ All at 2,000 ppm N level.⁽³⁾ Irradiated constantly with UV lamp, 366 nm at 1100 $\mu\text{W}/\text{cm}^2$.

TABLE 6

Effects of Nitrogen Compounds on Sediment Formation in Purified n-Decane

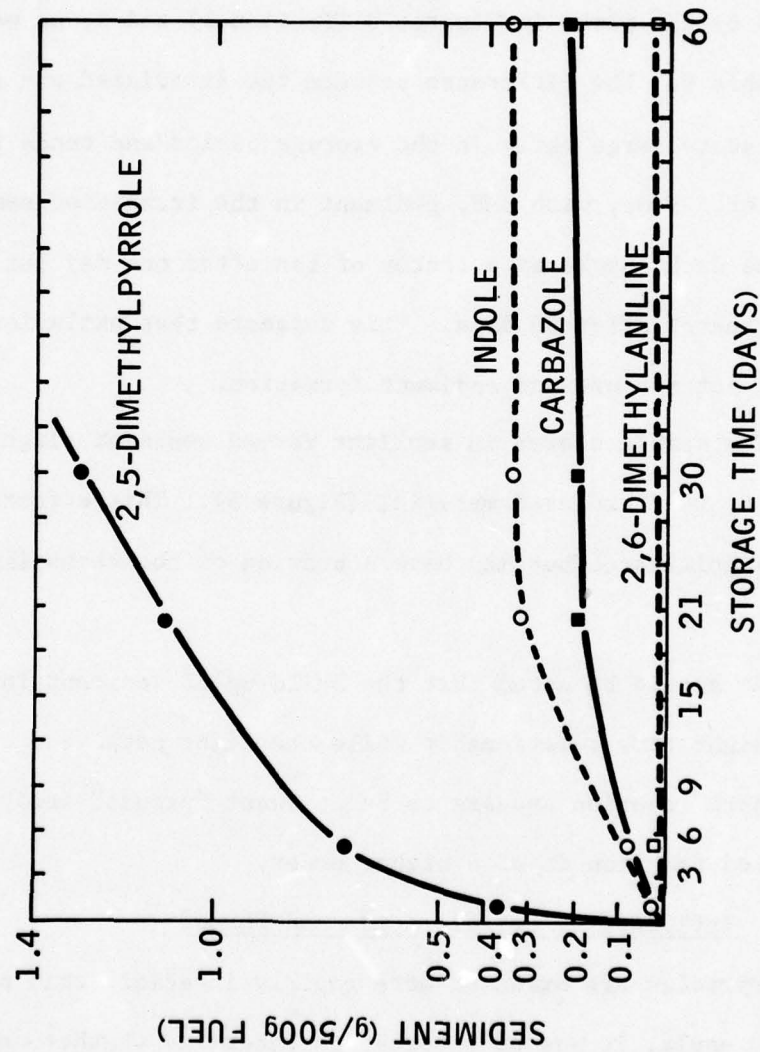
Compound Added (1)	Storage (2) Conditions	Cumulative Sediment (g/500g Decane)					Comments
		1 Day	5 Days	20 Days	30 Days	60 Days	
None	Light	-	-	-	-	-	Clear, Colorless
None	Dark	-	-	-	-	-	Throughout
2,5-Dimethylpyrrole	Light	.362	.718	1.13	1.30	1.69	Dark Brown Solution
2,5-Dimethylpyrrole	Dark	.036	0.100	.353	.524	1.05	Dark Brown Solution
Indole	Light	.012	.021	.022	.036	.043	Pink Solution
Indole	Dark	-	-	-	-	-	Colorless
Carbazole	Light	Trace	Trace	.019	.020	.051	Yellow Solution
Carbazole	Dark	-	-	-	-	-	Yellow Solution
2,4,6-Trimethylpyridine	Light	-	-	-	-	-	Clear, Colorless
2,4,6-Trimethylpyridine	Dark	-	-	-	-	-	Clear, Colorless
Quinoline	Light	-	-	Trace	Trace	Trace	Light Yellow Solution
Quinoline	Dark	-	-	-	-	-	Clear, Colorless
2,6-Dimethylaniline	Light	-	.004	.004	.005	.005	Purple Solution
2,6-Dimethylaniline	Dark	-	.001	.001	.002	.002	Purple Solution
n-Hexylamine	Light	-	-	-	-	-	Clear, Colorless
n-Hexylamine	Dark	-	-	-	-	-	Clear, Colorless
Methylcyclohexylamine	Light	-	-	-	-	Trace	Yellow Solution
Methylcyclohexylamine	Dark	-	-	-	-	Trace	Light Yellow Solution
2-Methylpiperidine	Light	Trace	Trace	.001	.001	.001	Light Yellow Solution
2-Methylpiperidine	Dark	-	-	Trace	.001	.001	Light Yellow Solution
n-Caproamide	-	-	-	-	Trace (3)	Trace (3)	Light Yellow Solution
n-Caproamide	-	-	-	-	Trace (3)	Trace (3)	Light Yellow Solution

(1) Each compound added to purified n-decane at 2000 ppm N level.

(2) Light = (UV) irradiation (366 nm, 1100 $\mu\text{W}/\text{cm}^2$); Dark = stored in darkness.

(3) Trace of liquid appeared after 30 days.

FIGURE 4
EFFECTS OF VARIOUS NITROGEN COMPOUNDS
ON SEDIMENT FORMATION
(STORED AT RT UNDER UV LIGHT)



different from plots of gum formation in fuels derived from petroleum (40). This suggests different mechanisms of sediment formation may be operative in the presence of active nitrogen compounds.

2.4.2 Importance of Light as a Promoter

The importance of light as a catalyst for sediment formation is illustrated by the plots in Figures 3 (Section 1) and 5, as well as data given in Table 6. The difference between the irradiated and dark-stored samples is quite large early in the storage period and tends to get much smaller later. Thus, with DMP, sediment in the irradiated sample exceeded that for the dark sample by a factor of ten after one day but was only about 38% greater after 60 days. This suggests that exclusion of light will retard but not prevent sediment formation.

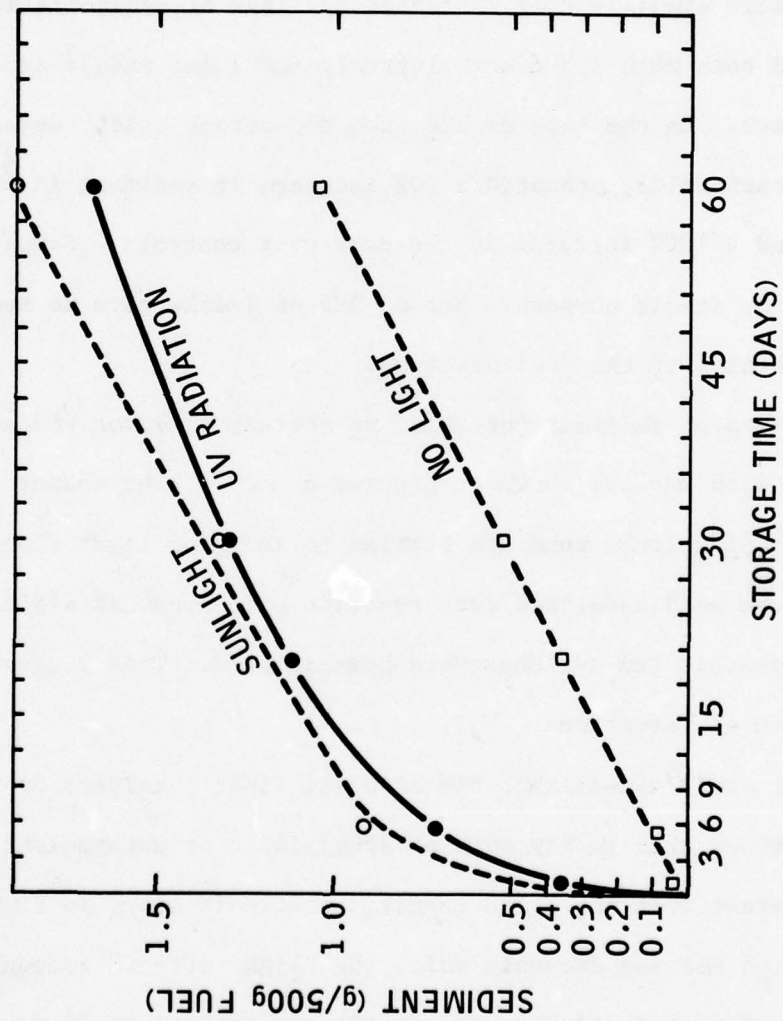
The sample stored in sunlight formed sediment slightly more rapidly than the UV irradiated material (Figure 5). This effect is not of practical significance but may have a bearing on the mechanism of sediment formation.

It should be noted that the build up of sediment in the dark follows a straight time relationship while the light catalyzed reaction does not. The dark reaction appears to be at least "pseudo" zero order while the catalyzed reaction is of a higher order.

2.4.3 Influence of Organic Acids and Phenols

Pyrroles are oxidized more rapidly in acidic than neutral media (7). As a result, it was of interest to determine whether organic acids, likely to be present in synfuels, would catalyze the formation of sediments in hydrocarbon media. Preliminary experiments in JP-5 indicated a significant effect (Figure 3, Section 1). This result was confirmed using n-decane as the diluent. The effects of acidic compounds on sediment formation with

FIGURE 5
EFFECTS OF UV RADIATION
ON SEDIMENT FORMATION BY
2,5-DMP IN N-DECANE



both DMP and indole were studied. Two types of organic "acids", carboxylic acids and phenols, were employed. The representative compounds are shown in Table 7.

2.4.4 Effects of Carboxylic Acids

The data shown in Table 8 clearly illustrate the effects of carboxylic acids on sediment formation. Both n-decanoic acid and cyclohexanecarboxylic acid significantly increased the rate of sedimentation. This was observed both with 2,5-dimethylpyrrole (DMP) and indole and in both light and dark. In the case of DMP, the two strong acids, decanoic and cyclohexanecarboxylic, promoted a 20% increase in sediment in 60 days in the light and a 100% increase in the dark over controls. Samples containing the acidic compounds but no DMP or indole gave no sediment nor was any darkening of the fuel observed.

Plots of sediment formation vs storage time for the strong acid experiments with DMP are shown in Figures 6 and 7. The shapes of the curves for the acid plus light runs are similar to those of light alone while the curves for the acid catalyzed dark reaction have somewhat different shapes, both with decanoic and cyclohexanecarboxylic acid. This suggests a different mechanism of formation.

It would appear that the acid and light catalysts operate independently rather than in any sort of synergistic or antagonistic fashion. This is apparent from the 3 x 3 factorial analysis shown in Figures 8-11. In the case of DMP and decanoic acid, the "light effect" accounted for 0.674 g of sediment in 15 days (Figure 8) and 0.683 g in 60 days (Figure 9). The corresponding values for the "acid effect" are .303 g and .663 g. The sums of the two acting independently would be .977 g for 15 days and 1.34 g for 60 days. These values are fairly close to the 1.06 g and 1.00 g obtained in the same time periods from the experiment when both light and acid were

TABLE 7
Experimental Design for Interaction Study
Between Organic Acids and Phenols and Nitrogen Compounds in n-Decane (1)

Experiment	Nitrogen Compound (2)	g/500g n-Decane	Acid (2)	g/500g n-Decane	Storage (3) Conditions
1	2,5-Dimethylpyrrole	6.80	None	--	Light
2	2,5-Dimethylpyrrole	6.80	None	--	Dark
3	2,5-Dimethylpyrrole	6.80	n-Decanoic	1.35	Light
4	2,5-Dimethylpyrrole	6.80	n-Decanoic	1.35	Dark
5	2,5-Dimethylpyrrole	6.80	Cyclohexanecarboxylic	1.00	Light
6	2,5-Dimethylpyrrole	6.80	Cyclohexanecarboxylic	1.00	Dark
7	None	--	Cyclohexanecarboxylic	1.00	Light
8	None	--	Cyclohexanecarboxylic	1.00	Dark
9	2,5-Dimethylpyrrole	6.80	2,4,6-Trimethylphenol	2.13	Light
10	2,5-Dimethylpyrrole	6.80	2,4,6-Trimethylphenol	2.13	Dark
11	None	--	2,4,6-Trimethylphenol	2.15	Light
12	None	--	2,4,6-Trimethylphenol	2.15	Dark
13	2,5-Dimethylpyrrole	6.80	2,6-di-t-Butylphenol	3.20	Light
14	2,5-Dimethylpyrrole	6.80	2,6-di-t-Butylphenol	3.20	Dark
15	None	--	2,6-di-t-Butylphenol	3.20	Light
16	None	--	2,6-di-t-Butylphenol	3.20	Dark
17	Indole	8.4	n-Decanoic	1.35	Light
18	Indole	8.4	n-Decanoic	1.35	Dark
19	Indole	8.4	2,6-di-t-Butylphenol	3.20	Light
20	Indole	8.4	2,6-di-t-Butylphenol	3.20	Dark

(1) n-Decane purified by silica gel percolation; ambient temperature used during storage; sediment weighed at 1, 5, 15, 30, and 60 days.

(2) Nitrogen compounds at 2,000 ppm N level; acids at 500 ppm O level.

(3) Light = stored under UV light (366 nm); Dark = dark storage.

TABLE 8

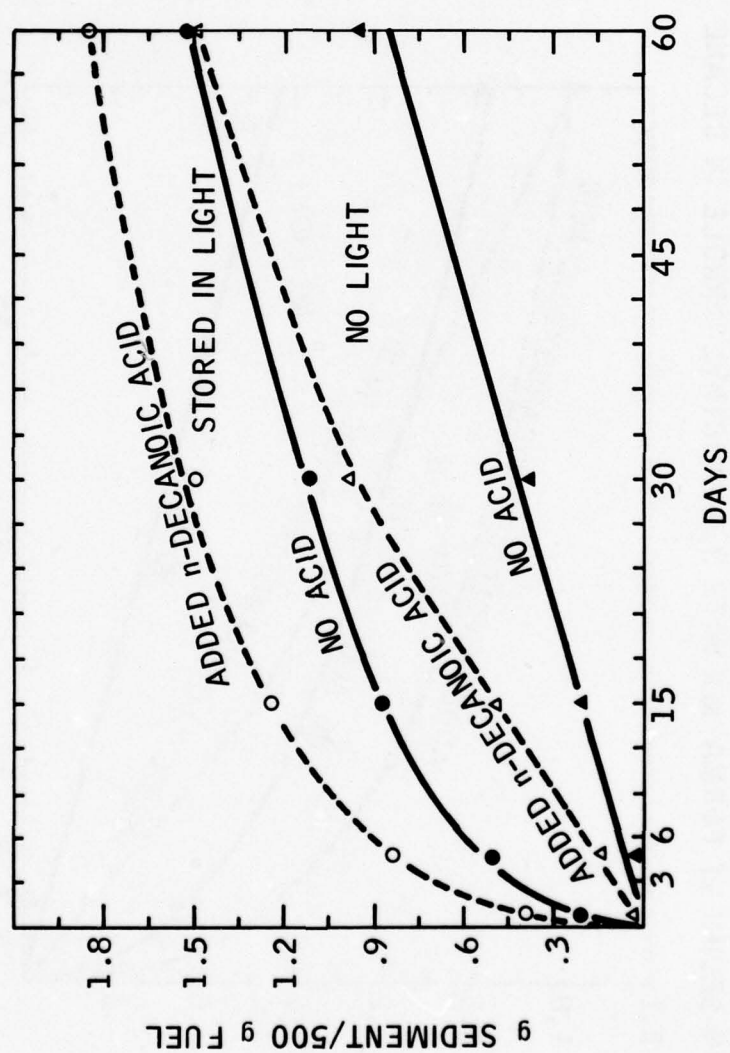
Sediment Formation Under the Influence of Organic Acids

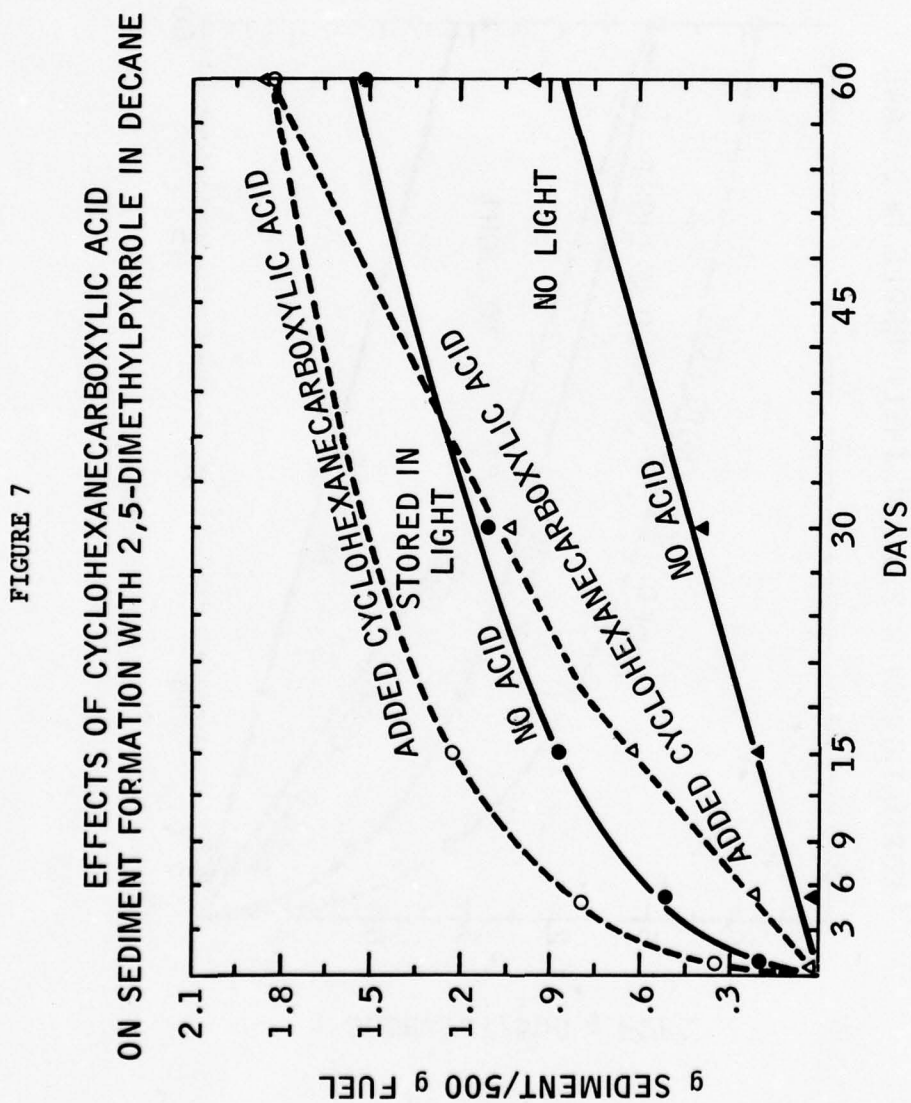
Compounds Added (1)	Storage (2) Conditions	Cumulative Sediment (g/500 g Decane)					Comments
		1 Day	5 Days	15 Days	30 Days	60 Days	
2,5-Dimethylpyrrole (DMP)	Light	.213	.524	.869	1.12	1.52	Dark Red
2,5-Dimethylpyrrole (DMP)	Dark	--	.060	.197	.394	.840	Dark Red
2,5-DMP plus Decanoic Acid	Light	.390	.821	1.25	1.49	1.84	Dark Red
2,5-DMP plus Decanoic Acid	Dark	.057	1.47	.497	.990	1.50	Dark Red
2,5-DMP plus Cyclohexane Carboxylic Acid	Light	.391	.821	1.26	1.56	1.83	Dark Red
2,5-DMP plus Cyclohexane Carboxylic Acid	Dark	.083	.216	.621	1.08	1.84	Dark Red
Cyclohexane Carboxylic Acid	Light	--	--	--	--	--	Clear,
Cyclohexane Carboxylic Acid	Dark	--	--	--	--	--	Colorless
2,5-DMP plus 2,4,6-Trimethylphenol	Light	.275	.459	.682	.910	1.33	Colorless
2,5-DMP plus 2,4,6-Trimethylphenol	Dark	--	.010	.126	.336	1.00	Colorless
2,4,6-Trimethylphenol	Light	--	--	--	--	--	Clear,
2,4,6-Trimethylphenol	Dark	--	--	--	--	--	Colorless
2,5-DMP plus di-t-Butylphenol	Light	--	.022	.173	.376	.639	
2,5-DMP plus di-t-Butylphenol	Dark	--	--	.035	.131	.496	
Di-t-Butylphenol	Light	--	--	--	--	--	Clear,
Di-t-Butylphenol	Dark	--	--	--	--	--	Colorless
Indole plus Decanoic Acid	Light	--	Trace	.131	.236	.347	Dark Red
Indole plus Decanoic Acid	Dark	--	--	--	--	--	Colorless
Indole plus di-t-Butylphenol	Light	--	--	.023	.036	.039	Dark Red
Indole plus di-t-Butylphenol	Dark	--	--	--	--	--	Colorless
Indole	Light	.012	.013	ND	.045	.046	
Indole	Dark	--	--	--	--	--	

(1) Nitrogen compounds added at 2,000 ppm N level; acids and phenols at 500 ppm O level.

(2) Light = UV radiation (366 nm; 1100 $\mu\text{W}/\text{cm}^2$).

FIGURE 6
EFFECT OF n-DECANOIC ACID ON SEDIMENT
FORMATION WITH 2,5-DIMETHYLPYRROLE IN DECANE





g Sediment/500 g Fuel

Presence of Nitrogen Compound	NO		YES	
Presence of Acid →	NO	YES	NO	YES
Light Storage ↓				
NO	0	0	.194	.497
YES	0	0	.868	1.25

FIGURE 8

3x3 Factorial Design for
Dimethylpyrrole Plus n-Decanoic Acid
 (15 Day Data)

g Sediment/500 g Fuel

Presence of Nitrogen Compound	NO		YES	
Presence of Acid →	NO	YES	NO	YES
Light Storage ↓				
NO	0	0	.837	1.50
YES	0	0	1.52	1.84

FIGURE 9

3x3 Factorial Design for
DMP and n-Decanoic Acid

(60 Day Data)

g Sediment/500 g Fuel

Presence of Nitrogen Compound	NO		YES	
Presence of Acid →	NO	YES	NO	YES
Light Storage ↓				
NO	0	0	.194	.621
YES	0	0	.868	1.26

FIGURE 10

3x3 Factorial Design for
DMP + Cyclohexanecarboxylic Acid
 (15 Day Data)

g Sediment/500 g Fuel

Presence of Nitrogen Compound	NO		YES	
Presence of Acid →	NO	YES	NO	YES
Light Storage ↓				
NO	0	0	.837	1.85
YES	0	0	1.52	1.83

FIGURE 11

3x3 Factorial Design for
DMP + Cyclohexanecarboxylic Acid
 (60 Day Data)

present. It would appear that the two catalysts do not interact. A similar analysis was made for cyclohexanecarboxylic acid (Figures 10 and 11), with comparable results. The phenols, however, behaved quite differently as discussed below.

Decanoic acid significantly increased sediment formation in the case of indole (Table 8, Figure 12). A 6-fold increase in sediment was observed in the sample stored under UV light. Insufficient data is available for a factorial design analysis but, in this case, light and acids may interact in some way to promote especially heavy sediment formation.

It is clear that carboxylic acids are deleterious to storage stability of fuels containing nitrogen compounds of the pyrrole type. This may have an impact on future synfuel processing technology.

2.4.5 Effects of Phenols on Sediment Formation

The two phenols, 2,4,6-trimethylphenol and di-t-butylphenol, reacted quite differently with respect to promoting sediment formation. Both had an inhibitory effect although that of di-t-butylphenol was much more pronounced (Table 8). Plots of sediment formation with DMP both with and without 2,4,6-trimethylphenol are shown in Figure 13. A significant reduction in sediment formation is observed, especially near the beginning of the storage period.

A much greater effect was observed with 2,6-di-t-butylphenol (Table 8, Figure 14). A 58% reduction in sediment formation was obtained under light storage at 60 days and 80% reduction after 15 days as compared to controls. Under dark storage conditions, the corresponding reductions were 45% and 82%. The 3 x 3 factorial analysis for these experiments is shown in Figure 15. The "light effect" in this case is .683 g (1.52 g -

FIGURE 12
EFFECTS OF n-DECANOIC ACID AND
2,6-DI-t-BUTYLPHENOL ON SEDIMENT
FORMATION WITH INDOLE IN n-DECANE -
STORAGE IN PRESENCE OF UV LIGHT

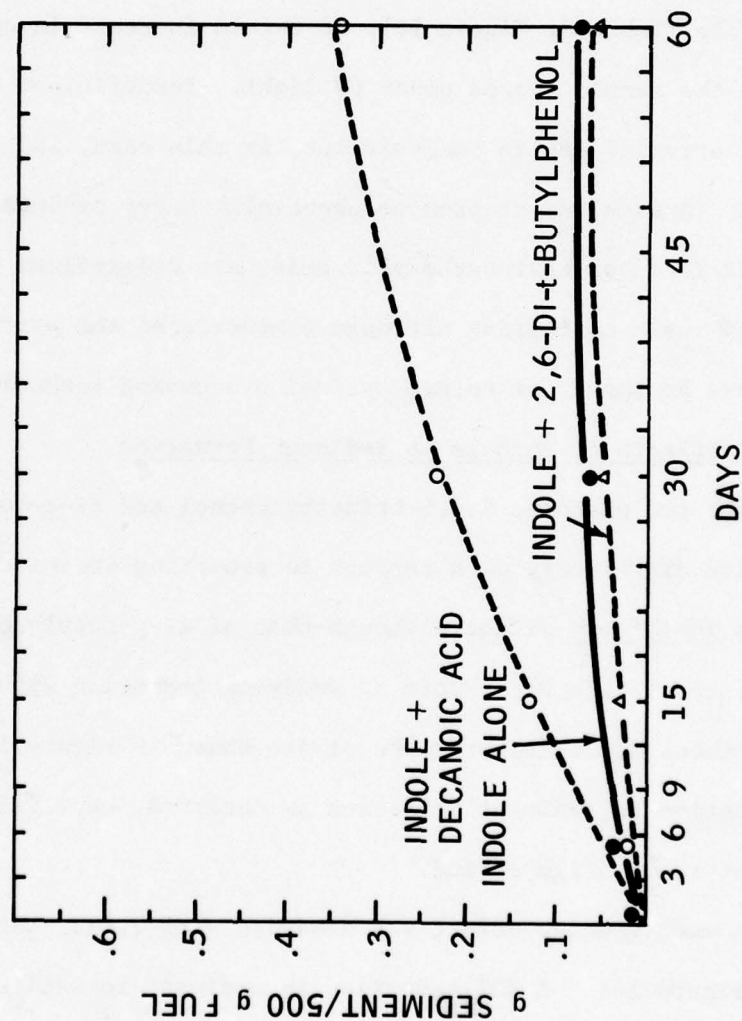


FIGURE 13
EFFECT OF 2,4,6-TRIMETHYLPHENOL ON
SEDIMENT FORMATION WITH 2,5-
DIMETHYLPYRROLE IN DECANE

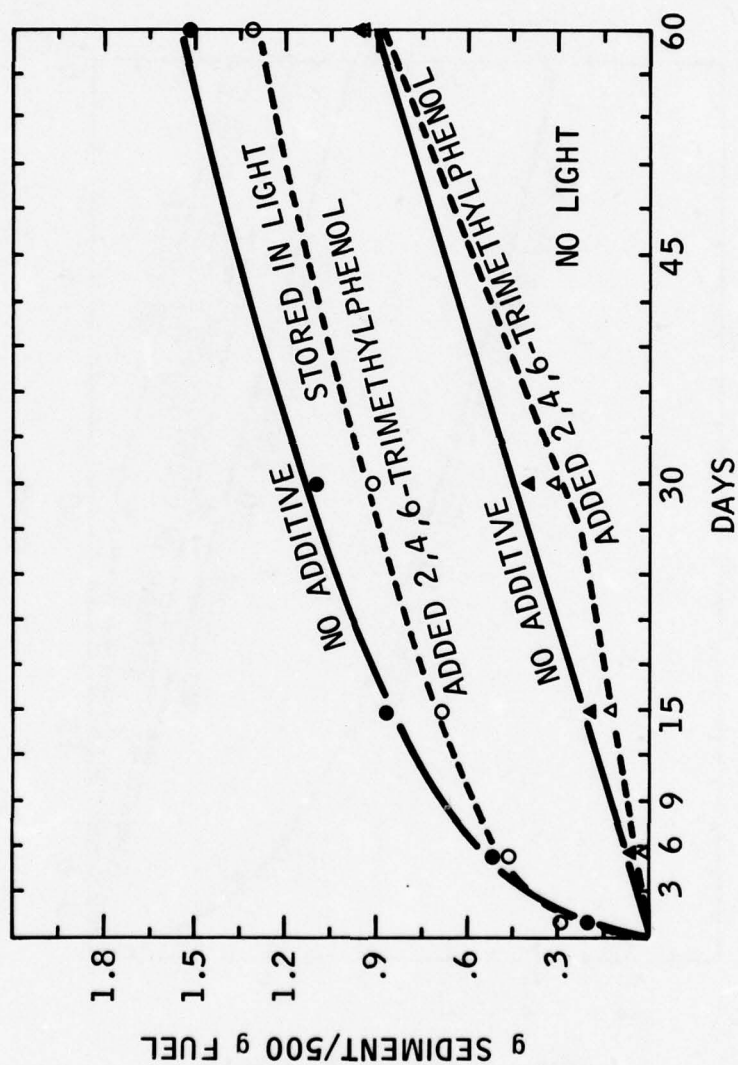
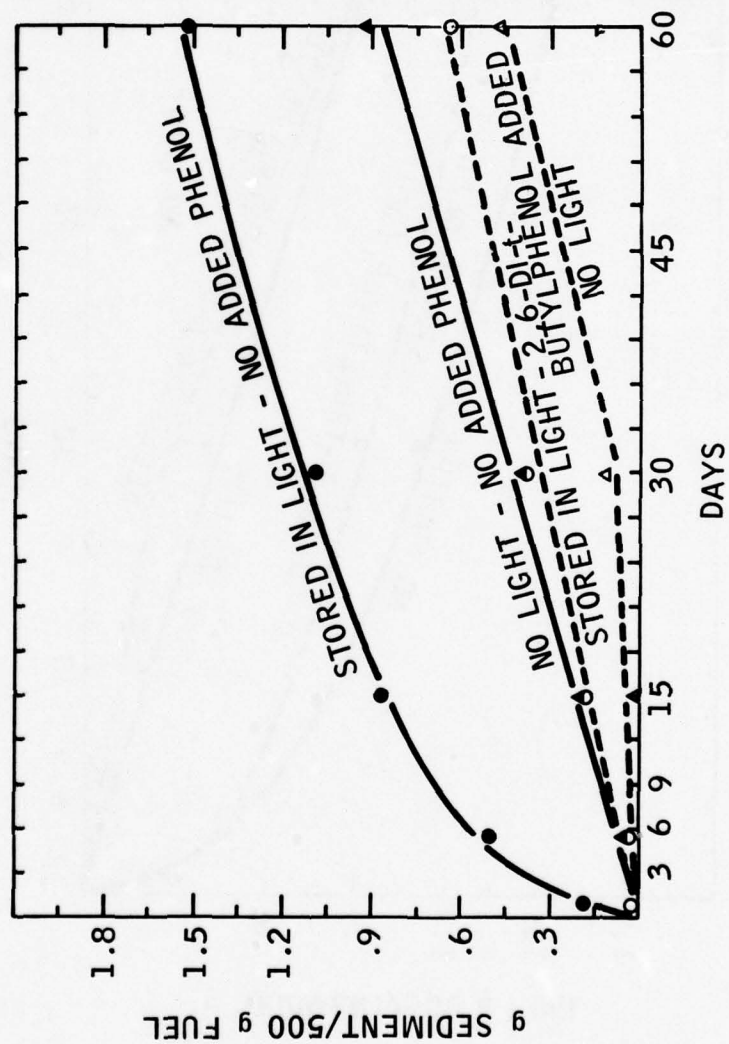


FIGURE 14
EFFECT OF DI-*t*-BUTYLPHENOL ON SEDIMENT
FORMATION WITH 2,5-DIMETHYLPYRROLE IN DECANE



g Sediment/500 g Fuel

Presence of Nitrogen Compound	NO		YES	
Presence of Acid →	NO	YES	NO	YES
Light Storage ↓				
NO	0	0	.837	.493
YES	0	0	1.52	.640

FIGURE 15

3x3 Factorial Design for
DMP + 2,6-Di-t-butylphenol
 (60 Day Data)

.837 g) and the "phenol effect" is -.344 g. The net additive effect would be .339 g (.683 g - .344 g). However, the actual sediment obtained in the presence of both the phenol and light is .640 g, .197 g less than that observed under dark storage alone. Apparently, this phenol is effective in combatting the effects of the light catalyzed reaction as well as sedimentation under dark storage conditions.

Di-t-butylphenol also appears to have a slight inhibitory effect on sediment formation with indole (Figure 12). These findings suggest that certain phenols may prove useful as sludge-preventing additives for future synfuels of the JP-5 type.

2.4.6 Characteristics and Chemical Structure of the Sediments

Determining the structure of the nitrogenous sediment is useful for elucidating the mechanism of formation and thereby finding methods of preventing it. Elemental analyses for selected sediment samples are given in Table 9. Although storage conditions and the presence of acid may affect the rate of formation and quantity of sediment, they do not seem to alter the characteristics of the sediment. This is apparent from the results in Table 9 which show that the sediments obtained from a variety of storage conditions have very similar conditions.*

The data suggest that the deposits are made up largely of repeating units of oxidized dimethylpyrrole. This is clear since the average C/N ratio in the sediments (6.3/1) is very close to the C/N ratio of dimethylpyrrole (6/1). Thus, no other carbon-containing species have been introduced into the polymer. On the other hand, considerable oxygen (about 1.5 atoms per N) has been incorporated, mostly at the expense of hydrogen

*It should be noted that one important parameter, oxygen level of the solvent, has not been varied in these experiments.

TABLE 9

Analysis of Sediments from Various Nitrogen Containing Additives in Hydrocarbon Fuels (1)

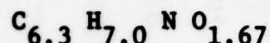
Additive(s)	Storage Conditions	Fuel (2)	Storage Time	% C	% H	% N	% O	% S
DMP	Light	n-Decane	5 days	62.28	5.33	11.86	20.53	--
DMP	Light	n-Decane	60 days	63.89	5.09	12.31	18.71	--
DMP	Light	JP-5	80 days	59.71	5.54	11.29	23.28	.18
DMP & Decanoic Acid	Light	JP-5	80 days	62.30	5.88	10.95	20.07	.80
DMP & Decanoic Acid	Dark	JP-5	80 days	61.09	5.88	10.84	22.04	.15
Average of 11 Samples			---	61.30	5.67	11.29	21.51	--

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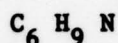
(1) All samples air saturated, stored under ambient conditions; n-Decane samples irradiated with UV light (366 nm); JP-5 sample irradiated by sunlight; O₂ level = saturation at beginning of experiment.

(2) n-Decane was purified by silica gel percolation; JP-5 was ordinary jet fuel.

(Table 9). The approximate average molecular composition of 11 sediment samples is:



while that of dimethylpyrrole is:



This indicates 1.5 atoms of oxygen have been incorporated into the molecule at the expense of two hydrogen atoms under the conditions studied.

The major infrared bands from the sediments are shown in Table 10. The spectra were obtained as smears or mulls between salt plates since the extreme insolubility of the sediment precludes the measurement of solution spectra. The analysis confirms that the pyrrole ring is intact and suggests that oxygen has been introduced in the form of a carbonyl group. The strong $-\text{CH}_3$ absorption relative to $-\text{CH}_2$ indicates the methyl groups remain intact and that no long chain $-\text{CH}_2-$ units (from other components of the media) have been introduced. These analyses do not support the reported structure I (Section 1) for pyrrole black since no "R" group is present and a carbonyl group clearly is.

TABLE 10

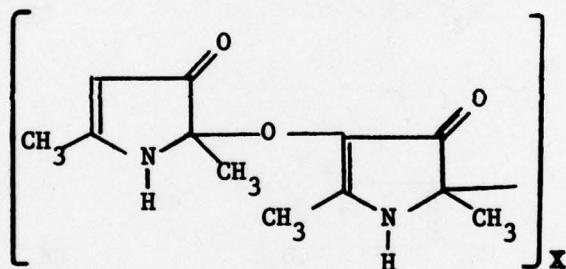
Major IR Bands in Sediment from 2,5-Dimethylpyrrole⁽¹⁾

<u>Cm⁻¹</u>	<u>Significance</u>
3300-3500 (s)	-NH or -OH
2970 (s) 1375 (s)	-CH ₃
2925 (w) 1450 (w)	Lack of -CH ₂
1640 - 1670 (vs)	Conj C ^O or Amide

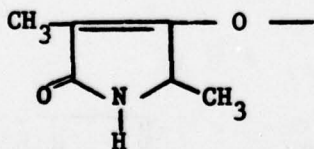
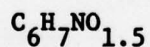
(1) Smear or mull between salt plates.

(2) s = strong; vs = very strong; w = weak.

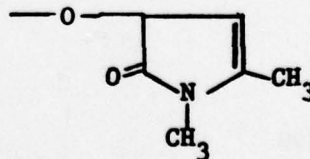
The more important mass spectral peaks and their possible fragment assignments are given in Table 11. From the elemental analysis, IR and mass spectral data one can clearly rule out structures such as I for the sediment obtained in the current program. If a single structure is present, the representation best fitting all data is XXV, although partial structures XXVI and XXVII cannot be ruled out. In addition, the mass spectra of several samples suggests the sediment may consist of several compound types of which four (XXVIII - XXXI) are prevalent. The average properties of the sediment, as analyzed by elemental and infrared methods, therefore could readily be accounted for by such a mixture.



XXV



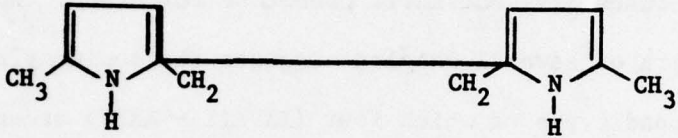
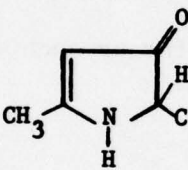
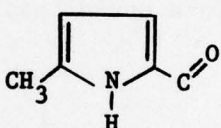
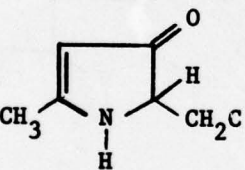
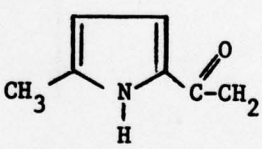
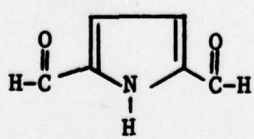
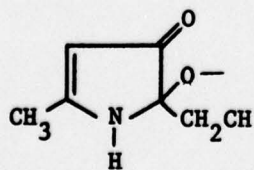
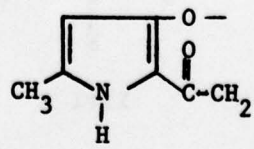
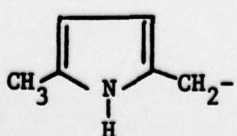
XXVI

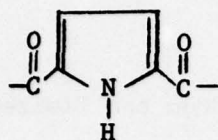


XXVII

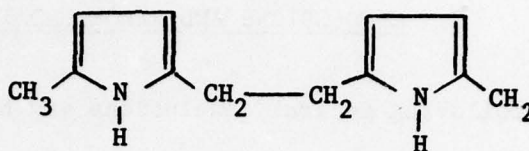
TABLE 11

Principal Mass Spectral Peaks For
Sediment from 2,5-Dimethylpyrrole in n-Decane

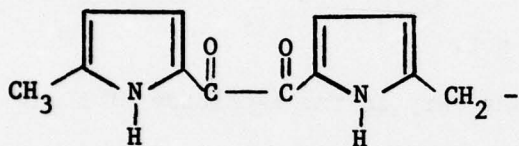
<u>m/e</u>	<u>Possible Fragment</u>
250-400	Parent peak - molecular weight
188	
108	 or 
122	 or 
123	
138	 or 
94	



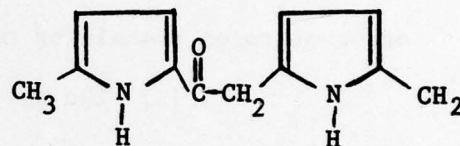
XXVIII



XXIX



XXX



XXXI

Surprisingly, the highest parent peaks observed (~400 mass units) correspond to no more than 3-4 pyrrolic units. This is consistent with Smith and Jensen's work on the autoxidation of 1-methylpyrrole (35). They found no more than five repeating pyrrole units in a short chain of structures XXIX or XX (Section 2.2.2). Additional work is needed in this area to determine the character and mechanism of sediment formation.

3. CONCLUSIONS AND RECOMMENDATIONS

The following general conclusions may be drawn from the limited results obtained so far:

- Nitrogen compounds can be seriously deleterious to the storage stability of synfuels.

- (a) Pyrrolic types and some amines are deleterious; many other nitrogen containing compounds are not.

- (b) The pyrrolic compounds vary in the magnitude of their influence on sediment formation. The rate is very high with 2,5-dimethylpyrrole.

- Storage conditions may play an important role; the effect of light is particularly noteworthy.

- Certain trace impurities are also important in their effects on promoting sediment formation.

- (a) Carboxylic acids accelerate the formation rate; the effect is most pronounced in the dark.

- (b) Some phenols inhibit sediment formation; structural effects are important.

- The sediments appear to have a definitive structure which may be amenable to analysis. With DMP this appears to be low to medium molecular weight oligomers consisting of partially oxidized repeating units of the nitrogen compound.

In order to confirm and extend these findings, the following additional research is recommended:

1. Further definition of the scope and magnitude of the problem:
 - (a) Effects of nitrogen compound classes not yet studied.
 - (b) Structural effects with pyrrolic compounds.
 - (c) Effect of other trace impurity compounds found in syn-fuels:
 - sulfur containing
 - oxygen containing
 - hydrocarbon types such as olefins
2. Theoretical studies to promote better understanding of the problem:
 - (a) Kinetic studies.
 - (b) Additional sediment structure studies.
3. Further investigation of leads to reduce sediment formation:
 - (a) Additional studies with phenols.
 - (b) Deoxygenation.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) An investigation of the effects of nitrogen compounds on sediment formation was initiated. Several different nitrogen compounds were studied including 2,5-dimethylpyrrole, indole, carbazole and a number of aromatic and aliphatic amines. The diluent employed was purified n-decane. All of the compounds caused darkening of the fuel although appreciable amounts of sediment were formed only with the pyrrole derivatives. The sediment		

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formation was found to be strongly catalyzed by light and by organic acids. Some phenols retarded the sedimentation. A start was made toward characterizing the sediment obtained from 2,5-dimethylpyrrole. It appeared to be a low molecular weight oligomer of partially oxidized pyrrole units.

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