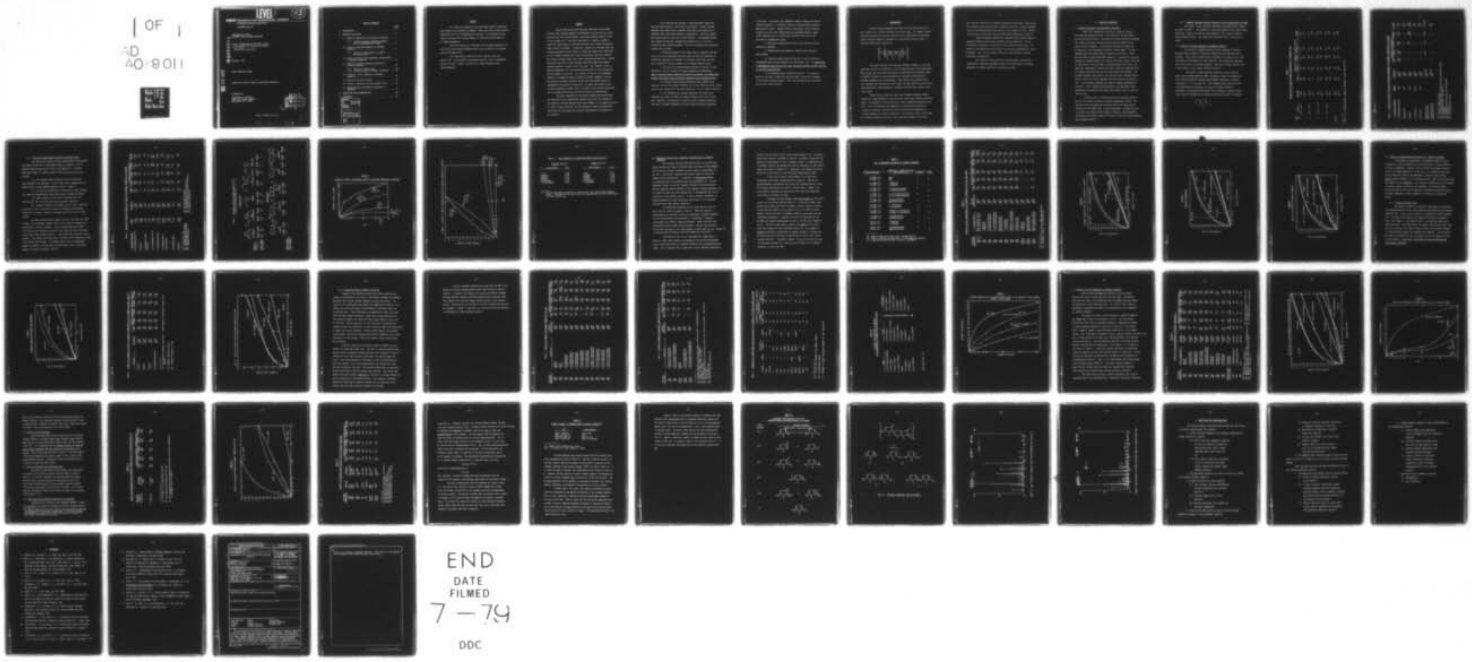
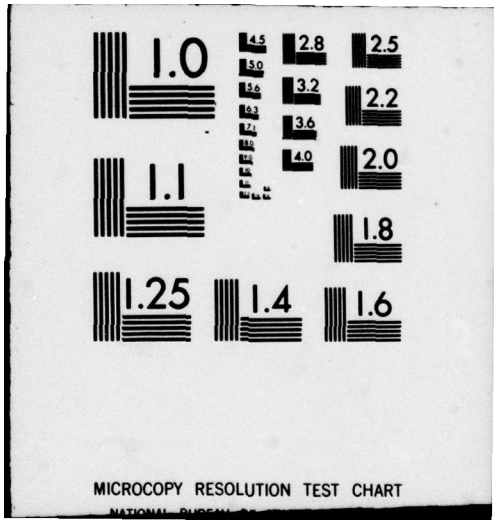
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CONTINUATION STUDY OF ALTERNATE FUELS NITROGEN CHEMISTRY

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FINAL TECHNICAL REPORT

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TABLE OF CONTENTS

		Page
1.	INTRODUCTION	1
2.	TECHNICAL DISCUSSION	3
	2.1 Method of Approach and Experimental Technique	3
	2.1.1 Standard (Average) Sediment Formation with 2,5-Dimethylpyrrole (DMP)	4
	2.2 Effects of Nitrogen Compounds on Sediment Formation	4
	2.2.1 Effects of Substituents on Pyrrole and Indole Rings	7
	2.3 Effects of Various Fuel Components (Hydrocarbons) on Sediment Formation	13
	2.4 Effects of Oxygen-Containing Impurities on Sediment Formation	20
	2.4.1 Effects of Benzoic Acid	20
	2.4.2 Continuing Study of Effects of Phenols	24
	2.5 Effects of Sulfur Compounds on Sediment Formation	31
	2.6 Effects of Dissolved Oxygen	35
	2.7 Effects of Moisture and Trace Mineral Acids	35
	2.8 Characteristics and Chemical Structure of Sediments	35
3.	CONCLUSIONS AND RECOMMENDATIONS	46
4.	REFERENCES	49

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PREFACE

This report was prepared by the Government Research Laboratory, Exxon Research and Engineering Company, Linden, New Jersey, under Contract N00019-78-C-0177 for the Department of the Navy. The program was sponsored by the Haval Air Systems Command, Air 310C and was monitored by Dr. Hyman Rosenwasser.

The initial program on "Alternate Fuels Nitrogen Chemistry" was carried out under Contract N00019-76-0675 over the period of 19 October 1976 to 20 October 1977.

This report covers the period from 1 February 1978 to 31 January 1979. The principal investigators were Dr. John W. Frankenfeld and Dr. William F. Taylor, assisted by Mr. Robert Bruncati and Mr. Joseph Rehburger.

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 other trace impurities 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. Weak to non-basic types, especially pyrroles and indoles, are deleterious; however, many other types of nitrogen compounds such as amines are not.

- Structural effects among deleterious types appear to be important also as the sediment formation rate is very high with ALKYL indoles and pyrroles; especially if the alkyl groups are in the 2 and/or 5 position.

- 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. Aromatic thiols also markedly inhibit sediment formation but lose their effectiveness on prolonged storage. Other sulfur compounds such as sulfides and mercaptans have very little influence on sedimentation rates.

- The type of hydrocarbons present in the fuel have little influence on sediment.

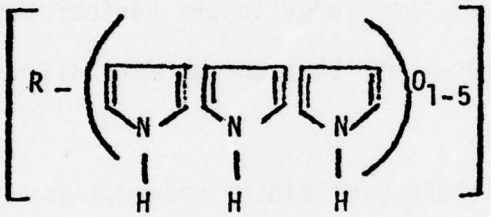
- Moisture and trace amounts of mineral acids have only minor effects.

- Dissolved oxygen content of the fuel is quite important; deoxygenated fuels produce sediment of a much slower rate. The combination of deoxygenation and exclusion of light can reduce sediment by more than 80% in a 60 day storage period.

- The sediments have a definite structure. This consists mostly of mixtures of partially oxidized dimers, trimers and tetramers of the parent nitrogen compound. More than one species may be present but all are closely related.

I. INTRODUCTION

Certain nitrogen compounds are known to have adverse effects on color stability of various petroleum distillates (1-6). For example, Oswald and Noel (1) found that pyrrole reacted with O_2 or peroxides to form hydrocarbon insoluble polymeric compounds of a type called "pyrrole black". A tentative formula was proposed (1):



The actual mechanism for sediment formation, however, is not well understood nor has its importance in fuel instability been fully appreciated. Mayo, et al. (2) also 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 (3-5), and both olefins and thiols have been implicated as participating in sediment formation under certain conditions (1,6).

Recent work at Exxon has shown that nitrogen compounds promote sediment or sludge formation in JP-5 jet fuel stored under ambient conditions (7,8). 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 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 a nitrogen compound such as 2,5-dimethylpyrrole were stored in the presence of light. Neither the base fuel nor the fuel with acid added alone produced any sediment.

These preliminary studies also suggested that different modes of sediment formation obtain under different storage conditions. This is particularly noteworthy in the case of light vs dark storage (7,8). In addition, the appearance of the sludge in the various experiments is quite different. Thus, it would appear that one or more different reaction mechanisms are operative.

As a result of these preliminary observations, a program was undertaken to study the fundamental chemistry of the effects of nitrogen compounds on storage stability of simulated jet fuels.

2. TECHNICAL DISCUSSION

2.1 Method of Approach and Experimental Technique

Model fuel compositions were used in order to simplify the system for mechanism studies. The "base fuel" was the highest quality n-decane available. The decane was further purified by passage over a bed of activated aluminum oxide in order to remove the last traces of polar compounds. This material was used as diluent for the majority of the experiments described in this report. The test compounds were the highest quality commercially available. These were purified by distillation when necessary. In particular, the base compound, 2,5-dimethylpyrrole was freshly distilled to give a colorless oil and stored in the dark under a nitrogen blanket until used. The additives, hydrocarbons, phenols and sulfur containing compounds, were the highest grade available and were used without purification. The nitrogen compounds were tested at the 2000 ppm level (nitrogen basis) which is within the limits expected from fuels derived from shale or coal. The oxygenated compounds were added in amounts equivalent to 500 ppm O. Sulfur compounds were employed at the 3000 ppm S level. Hydrocarbons were added at the levels they normally occur in fuels of the JP-5 type.

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 $\mu W/cm^2$ (8). In some experiments, sunlight was used. 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.

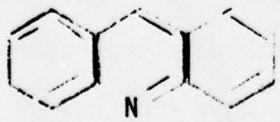
2.1.1 Standard (Average) Sediment Formation with 2,5-Dimethylpyrrole (DMP)

The results of four replicate experiments using DMP alone in decane are given in Table 1. The agreement is quite good especially for light storage conditions. Hence, this data has been employed as the "control" standard unless otherwise noted. The average (now "standard") run is also given in Table 1.

2.2 Effects of Nitrogen Compounds on Sediment Formation

The survey of nitrogen-containing species designed to identify nitrogen species capable of producing sediment was continued under this contract. These results confirm earlier findings (8-11) that not all nitrogen species are deleterious to fuel stability. Most deleterious compounds fall into the weak to non-basic category. Many basic nitrogen species, such as most amines, do not promote sediment formation.

The results of some screening studies are given in Table 2. Apart from 2,5-dimethylpyrrole (DMP, included as a basis for comparison) only acridine showed any tendency toward deposit formation. Acridine (structure I) is a very weak base. The strongest bases, pyrrolidine and trioctylamine had no noticeable influence on sediment formation. Quinoline, in the presence of decanoic acid, produced a colored solution and a trace of sediment but the amount obtained was too small to measure.



I

TABLE 1

COMPARISON OF SEVERAL DMP* RUNS-DEVELOPMENT OF "STANDARD" DATA

Exp No	Date	Storage	Cumulative Sediment (g/500 g Decane) 1 Day	5 Day	15 Day	30 Day	60 Day
1	2/77 - 4/77	Light	.362	.718	1.13	1.30	1.69
		Dark	.036	.100	.353	.524	1.05
2	6/77 - 7/77	Light	.213	.524	.869	1.12	1.52
		Dark	----	.060	.197	.394	.840
3	10/77 - 12/77	Light	.221	.621	.869	1.21	1.54
		Dark	.019	.060	.140	.389	.793
4	3/78 - 5/78	Light	.229	.500	.888	1.14	1.42
		Dark	.002	.030	.125	.278	.530
Average		Light	.256	.591	.939	1.19	1.54
		Dark	.014	.063	.204	.396	.803

*DMP = 2.5 - Dimethylpyrrole, added at 2000 ppm N level (See ref. 8).

TABLE 2. SURVEY OF EFFECTS OF VARIOUS NITROGEN COMPOUNDS ON SEDIMENT FORMATION IN n-DECANE

Nitrogen Compound	Amount	Storage(2)	Cumulative Sediment(1) 1 Day	5 Days	15 Days	30 Days	60 Days
2,5-Dimethylpyrrole(3)	6.8g	Light	.256	.591	.939	1.19	1.54
"	"	Dark	.018	.086	.136	.377	.710
Isoquinoline	9.2g	Light	--	--	--	--	(5)
"	"	Dark	--	--	--	--	(5)
Acridine	12.0g	Light	--	--	.086	.008	.147
"	"	Dark	--	--	--	trace	trace
Trioctylamine	25.3g	Light	--	--	--	--	(5)
	"	Dark	--	--	--	--	(5)
Pyrrolidine	5.1g	Light	--	--	--	--	(5)
	"	Dark	--	--	--	--	(5)
Quinoline plus decanoic acid(6)		Light(4) Dark	--	trace	trace	trace	trace(7)
Isoquinoline plus decanoic acid (6)		Light(4) Dark	--	--	--	--	(5)
			--	--	--	--	(5)

(1) Given as g/500 g decane.
(2) UV light at 366 nm and 1100 $\mu W/cm^2$ unless otherwise noted.
(3) Average of 4 runs - See Table 1.
(4) Sunlight.
(5) Solution colorless and clear throughout.
(6) 500 ppm 0.
(7) Yellow colored, cloudy.

2.2.1 Effects of Substituents on Pyrrole and Indole Rings

The type and positioning of alkyl substituents on the pyrrole and indole nucleus have a considerable effect on sediment. This is apparent from the data given in Table 3 and Figures 1-3. Although additional research is needed, some preliminary generalizations can be drawn:

(1) The sediment forming tendencies do not follow the base strength of the compounds. This is clear from a comparison of pK values (Table 4) with sediment formation (Table 3, Figure 1).

(2) At least one double bond in the pyrrolic ring is needed for oxidative polymerization; pyrrolidine gives no sediment whatever.

(3) Methyl groups in the 2- and 5- position, and, to a lesser extent the 1-(N-) position enhance sediment formation.

(4) Sediment formation is retarded if the 3- and 4- positions of pyrrole or the 3- position of indole are blocked by bulky groups. Carbazole, for example, affords no sediment under either dark or light storage.

The above generalizations appear to hold in both dark and light storage. The differences between "active" and "inactive" compounds are accelerated in the dark, however. Thus, 2,5-dimethylpyrrole affords five times as much sediment as pyrrole in the light but nearly 100 times as much under dark storage (Figure 1). With indole the variation is even greater. The 2-methyl derivative gives >15 times as much sediment as indole itself under light storage. In the dark indole gives an unmeasurable amount of sediment in 60 days while 2-methylindole gives a significant amount (1.4 g/500 g of decane, Table 3).

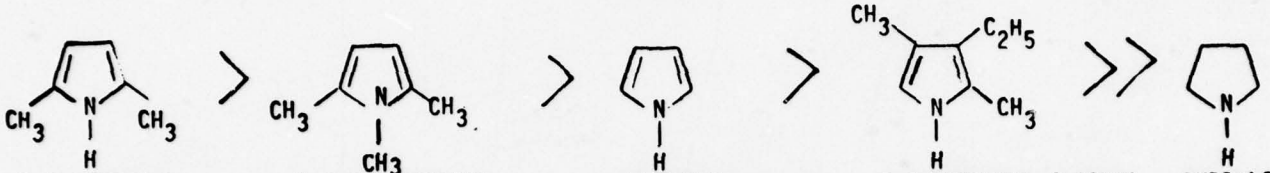
TABLE 3. EFFECTS OF VARIOUS PYRROLES AND INDOLES ON SEDIMENT FORMATION IN n-DECANE

Nitrogen Compound	Amount	Storage(2)	Cumulative Sediment(1) 1 Day	5 Days	15 Days	30 Days	60 Days
2,5-Dimethylpyrrole(3)	6.8g	Light	.(5)	.654	.782	1.07	1.40
"	6.8g	Dark	.(5)	.060	.204	.396	.803
Pyrrole(4)	4.8g	Light	---	.062	.207	.309	.400
"	4.8g	Dark	---	---			
2,4-Dimethyl-3-ethyl-pyrrole	8.8g	Light	(5)	.117	.143	.145	.194
"	8.8g	Dark	(5)	.110	.112	.149	.171
1,2,5-Trimethylpyrrole	7.8g	Light	(5)	.087	.331	.695	.935
"	7.8g	Dark	(5)	---	---	.040	.089
2,6-Dimethylquinoline	11.2g	Light	(5)	---	trace	trace	trace
"	11.2g	Dark	---	---	---	---	---
1,2-Dimethylindole	10.4g	Light	(5)	.079	.079	.192	.384
"	10.4g	Dark	(5)	---	---	---	---
2-Methylindole	9.4g	Light	(5)	.413	.649	2.09	2.27
"	9.4g	Dark	(5)	.010	.600	1.15	1.40
2,5-Dimethyindole	10.4g	Light	(5)	.078	.270	1.48	2.27
Indole(7)	8.4g	Light	(5)	.005	.040	0.90	.180
"	8.4g	Dark	(5)	---	---	---	---

(1) In grams per 500 g decane.
(2) Light Storage was sunlight.
(3) Average of two runs.
(4) Stored under UV light.
(5) Not measured at this time period.
(6) Solution colorless and clear throughout.
(7) Average of three runs.

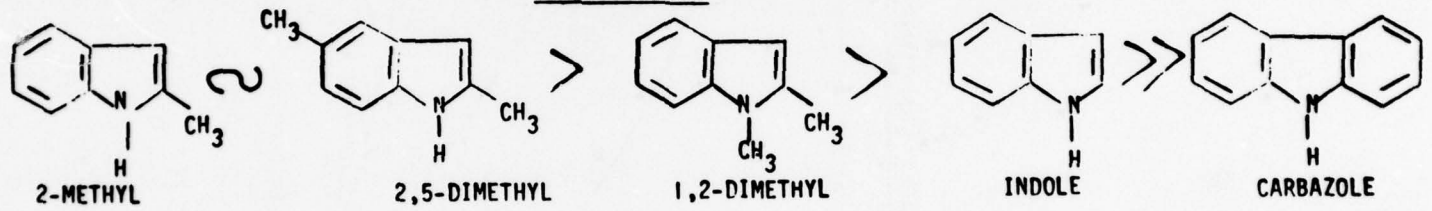
FIGURE 1. STRUCTURAL EFFECTS ON SEDIMENT FORMATION WITH PYRROLE AND INDOLE DERIVATIVES

PYRROLE SERIES



Deposits Relative to Pyrrole=1	2,5-DIMETHYL		1,2,5-TRIMETHYL		PYRROLE		2,4-DIMETHYL-3-ETHYL		PYRROLIDINE	
	15 Day	60 Day	15 Day	60 Day	15 Day	60 Day	15 Day	60 Day	15 Day	60 Day
LIGHT STORAGE	4.7	4.3	2.5	1.6	1.0	1.0	.67	.70	0	0
DARK STORAGE	>80	80	1.0	11	1.0	1.0	1.0	1.7	0	0

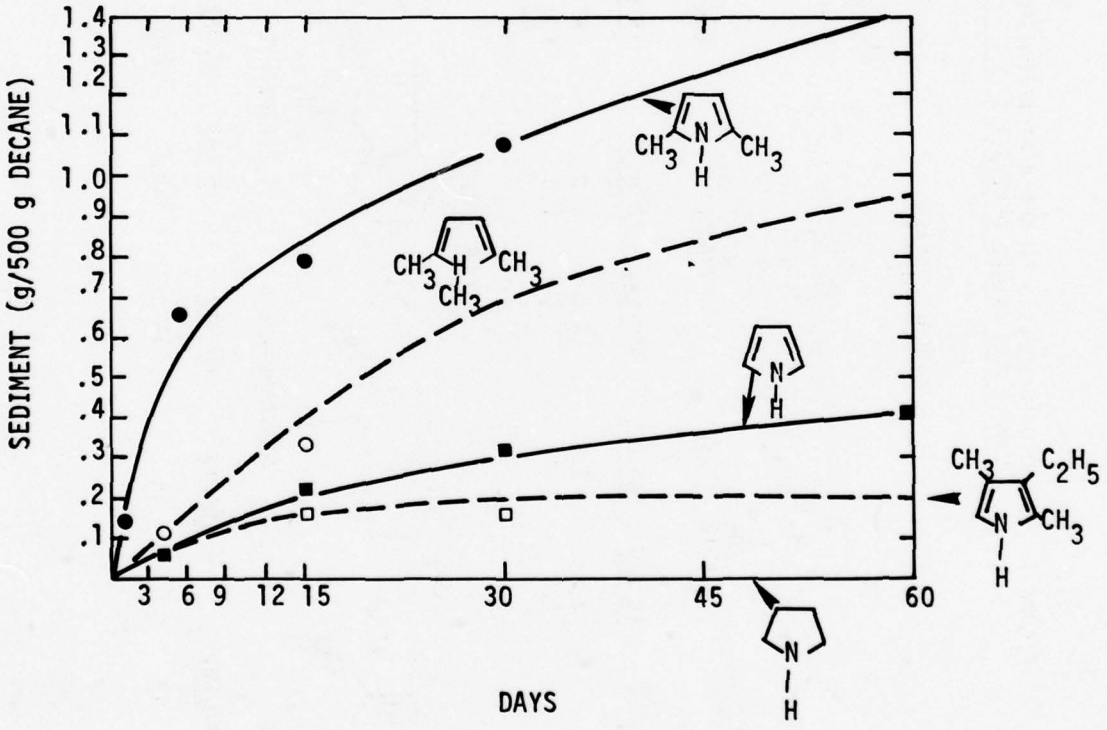
INDOLE SERIES



Deposits Relative to Indole=1 (LIGHT STORAGE)	2-METHYL		2,5-DIMETHYL		1,2-DIMETHYL		INDOLE		CARBAZOLE	
	15 Day	60 Day	15 Day	60 Day	15 Day	60 Day	15 Day	60 Day	15 Day	60 Day
	32	15	15	15	2.0	2.0	1.0	1.0	0	0

FIGURE 2

EFFECTS OF PYRROLE STRUCTURES ON RATE OF SEDIMENT FORMATION IN SUNLIGHT



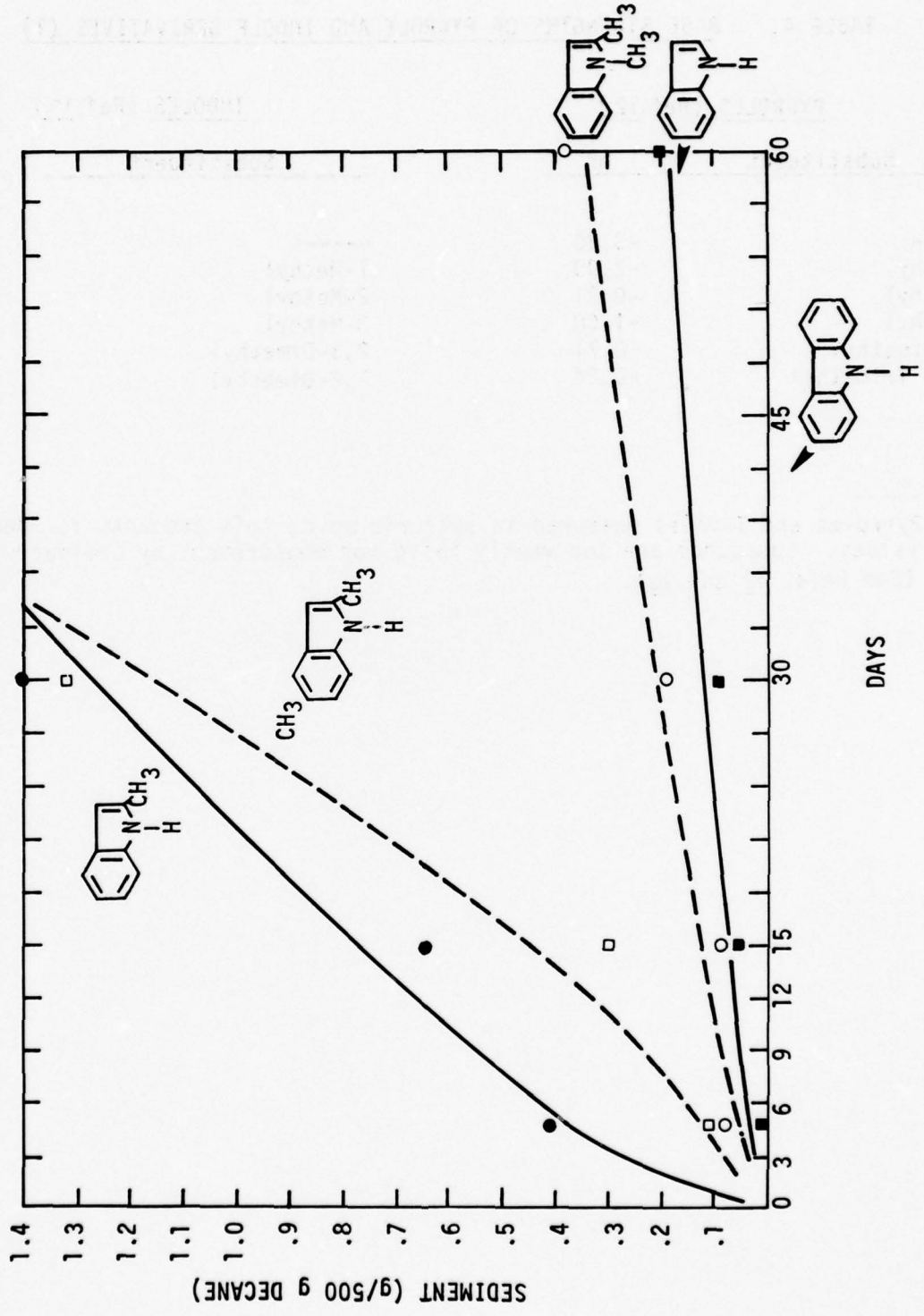


FIGURE 3. EFFECTS OF INDOLE STRUCTURE ON RATE OF SEDIMENT FORMATION IN SUNLIGHT

TABLE 4. BASE STRENGTHS OF PYRROLE AND INDOLE DERIVATIVES (1)

PYRROLES (Ref.12)		INDOLES (Ref.13)	
Substituent	pK	Substituent	pK
------	-3.80	------	-3.5
1-Methyl	-2.90	1-Methyl	-2.32
2-Methyl	-0.21	2-Methyl	-0.28
3-Methyl	-1.00	3-Methyl	-4.55
2,5-Dimethyl	-0.71	2,3-Dimethyl	-1.49
1.2.5-Trimethyl	-0.24	1,2-Dimethyl	+0.30

(1) Pyrroles and Indoles measured in sulfuric acid; this accounts for negative values. Compounds are too weakly basic for measurement by ordinary techniques (See Refs. 12 and 13).

2.3 Effects of Various Fuel Components (Hydrocarbons) on Sediment Formation

Prior studies with petroleum derived fuels of the JP-5 type (7,9) indicated that deposit formation under conditions of high temperature stress was strongly affected by certain types of hydrocarbons in the fuel. Particularly important were certain types of olefins and aromatic-olefin combinations. In addition, an interaction between 2,5-dimethylpyrrole and 2-methylstyrene was encountered (7). The two compounds, present in the fuel together afforded 41% greater deposits than the expected additive effects of the compounds studied separately (7). (It should be noted that these effects were in deoxygenated fuel and in conditions of high thermal stress.) It was of interest, therefore, to determine whether the same interactions could occur in air saturated n-decane stored under ambient conditions.

The hydrocarbons employed in this study and the levels at which they are tested are shown in Table 5. These were chosen as representative of the major classes of hydrocarbons, branched paraffins (2,2,4-trimethylhexane) cycloparaffins or "naphthenes" (isopropyl cyclohexane) and aromatics (sec-butylbenzene). Normal paraffins were represented by the standard diluent n-decane. Various representative olefins were included in this study because of their known (7, 14). tendencies to promote deposit formation under high temperature conditions.

The results of this set of experiments are summarized in Table 6. Under light storage, the presence of the various hydrocarbons had no significant effects on sediment formation with 2,5-dimethylpyrrole (DMP). This is apparent from a comparison of total sediment accumulation

(Table 6) and the rate at which it was formed (Figures 4-7). The values range from a high of 1.58 g/500 g liquid to 1.28 g/500 g liquid with the majority falling between 1.4 and 1.5 g/500 g liquid. In addition, plots of sediment formation vs storage time under UV radiation all have similar shapes (top curves in Figures 4-7). Apparently, the composition of the medium has little effect on light catalyzed sedimentation of DMP.

In the case of indole, there appears to be significant differences under light storage conditions (Table 6). Addition of sec-butylbenzene afforded more than twice and 1-dodecene nearly 3 times the sediment encountered with indole in decane alone. However, the total deposits obtained were quite small with indole and unequivocal conclusions are difficult to draw.

The total (60 day) sediment under dark storage was also quite similar for the various samples (Table 6). In the case of DMP, these ranged from slightly more than 0.5 g/500 g liquid to about 0.8 g/500 g liquid with most samples in the range of 0.6 to 0.75 g/500 g liquid. However, some of the plots of sediment formation vs storage time show significant differences. Straight line plots are obtained with the paraffin and aromatic hydrocarbons as well as the DMP alone (Figures 4 and 5). With two of the olefins, however, the shapes of the curves under dark storage are quite different (Figure 6). This suggests a possible difference in mechanisms of sediment formation in these runs. We have noted before (8) that the mechanisms can differ under various storage conditions. In general, however, it may be said that the type of hydrocarbon diluent has a relatively minor effect on the sediment formation, at least with DMP.

TABLE 5

FUEL HYDROCARBONS EVALUATED AS SEDIMENT PROMOTERS

Additives - g/500 g Diluent			
Nitrogen Compound	Hydrocarbon (2)	Light(3)	Dark
2,5-DMP, 6.8	None	X	
2,5-DMP, 6.8	None		X
2,5-DMP, 6.8	1-Dodecene	X	
2,5-DMP, 6.8	1-Dodecene		X
2,5-DMP, 6.8	i-Propylcyclohexane	X	
2,5-DMP, 6.8	i-Propylcyclohexane		X
2,5-DMP, 6.8	2,2,4-Trimethylpentane	X	
2,5-DMP, 6.8	2,2,4-Trimethylpentane		X
2,5-DMP, 6.8	sec-Butylbenzene	X	
2,5-DMP, 6.8	sec-Butylbenzene		X
2,5-DMP, 6.8	1,7-Octadiene	X	
2,5-DMP, 6.8	1,7-Octadiene		X
2,5-DMP, 6.8	4-Methyl-1-cyclohexene	X	
2,5-DMP, 6.8	4-Methyl-1-cyclohexene		X
2,5-DMP, 6.8	2-Methylstyrene	X	
2,5-DMP, 6.8	2-Methylstyrene		X
Indole, 8.4	1-Dodecene	X	
Indole, 8.4	1-Dodecene		X
Indole, 8.4	sec-Butylbenzene	X	
Indole, 8.4	sec-Butylbenzene		X

(1) Added at 2000 ppm N level, DMP - dimethylpyrrole.
(2) Added in amounts characteristics of that class of compound.
(3) Irradiated constantly with UV lamp at 1100 $\mu W/cm^2$.

TABLE 6

EFFECTS OF FUEL HYDROCARBONS ON SEDIMENT FORMATION WITH DMP AND INDOLE

Nitrogen Compound(1)	Hydrocarbon(1)	Storage Conditions(1)	Cumulative Sediment (g/500 g Liqiud) 1 Day	5 Days	15 Days	30 Days	60 Days
DMP (2)	None (n-decane only)	Light	.221	.621	.869	1.21	1.58(2)
DMP (2)	None (n-decane only)	Dark	.019	.060	.140	.389	.793(2)
DMP	1-Dodecene	Light	.213	.378	.750	.999	1.28
DMP	1-Dodecene	Dark	.037	.065	.163	.317	.599
DMP	i-Propylcyclohexane	Light	.231	.392	.841	1.14	1.45
DMP	i-Propylcyclohexane	Dark	.023	.061	.158	.292	.514
DMP	2,2,4-Trimethylhexane	Light	.257	.502	.839	1.08	1.36
DMP	2,2,4-Trimethylhexane	Dark	.015	.056	.151	.356	.797
DMP	sec-Butylbenzene	Light	.195	.515	.856	1.17	1.45
DMP	sec-Butylbenzene	Dark	.009	.044	.145	2.80	.566
DMP	1,7-Octadiene	Light	.348	.642	.962	1.19	1.44
DMP	1,7-Octadiene	Dark	.023	.124	.288	.466	.693
DMP	4-Methyl-1-Cyclohexene	Light	.210	.482	.933	1.10	1.49
DMP	4-Methyl-1-Cyclohexene	Dark	.067	.166	.314	.505	.734
DMP	α-Methylstyrene	Light	.253	.536	.802	1.11	1.41
DMP	α-Methylstyrene	Dark	.008	.033	.122	2.73	.602
Indole	1-Dodecene	Light	--	--	.053	.076	.127
Indole	1-Dodecene	Dark	--	--	--	--	--
Indole	sec-Butylbenzene	Light	--	--	.057	.075	.101
Indole	sec-Butylbenzene	Dark	--	--	--	--	--
Indole	None (n-Decane alone)	Light	.012	.021	.022	.036	.043
Indole	None (n-Decane alone)	Dark	--	--	--	--	--

(1) See Table 5 for levels added and conditions.
(2) Average of several runs (See Table 1).

FIGURE 4

SEDIMENT FORMATION WITH DMP IN PRESENCE OF PARAFFINS

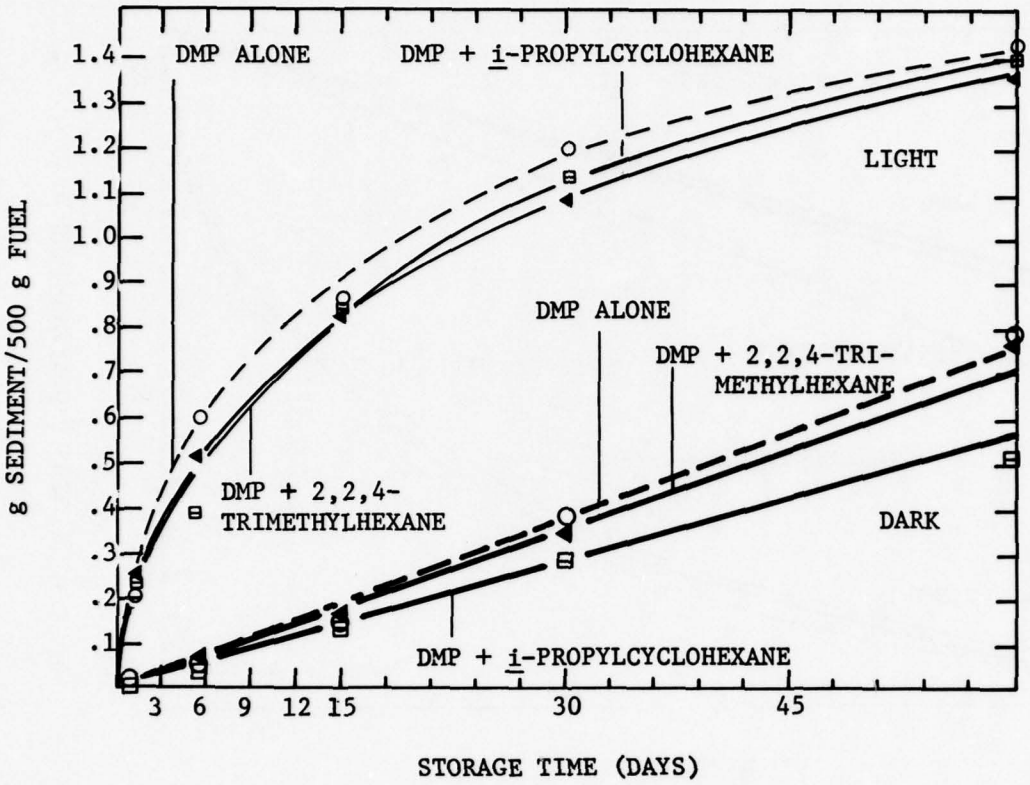


FIGURE 5

EFFECTS OF AROMATICS

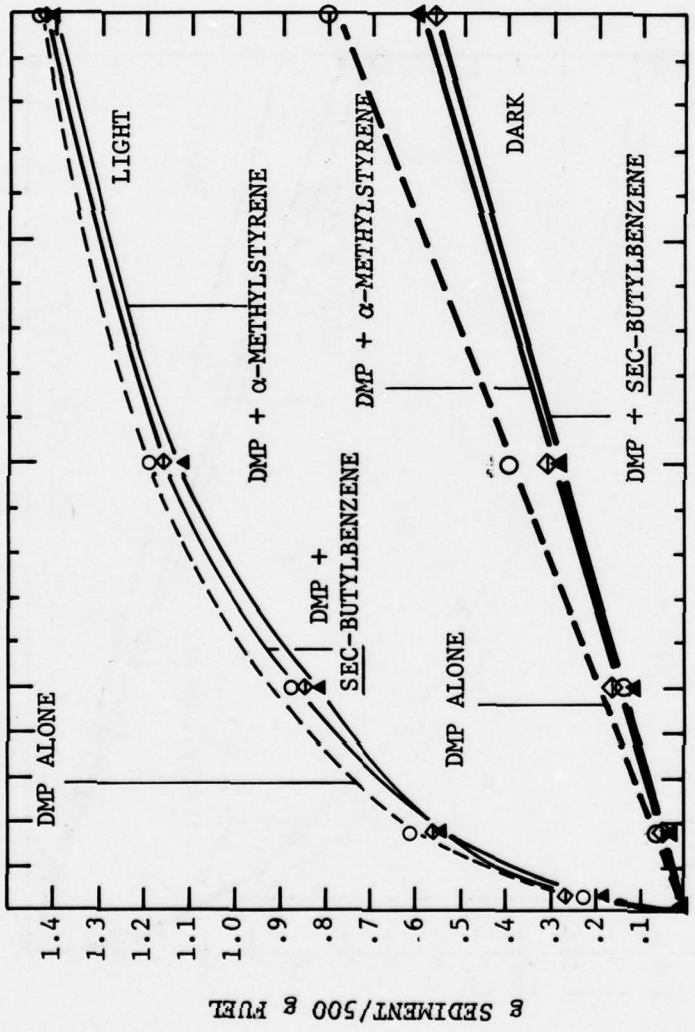
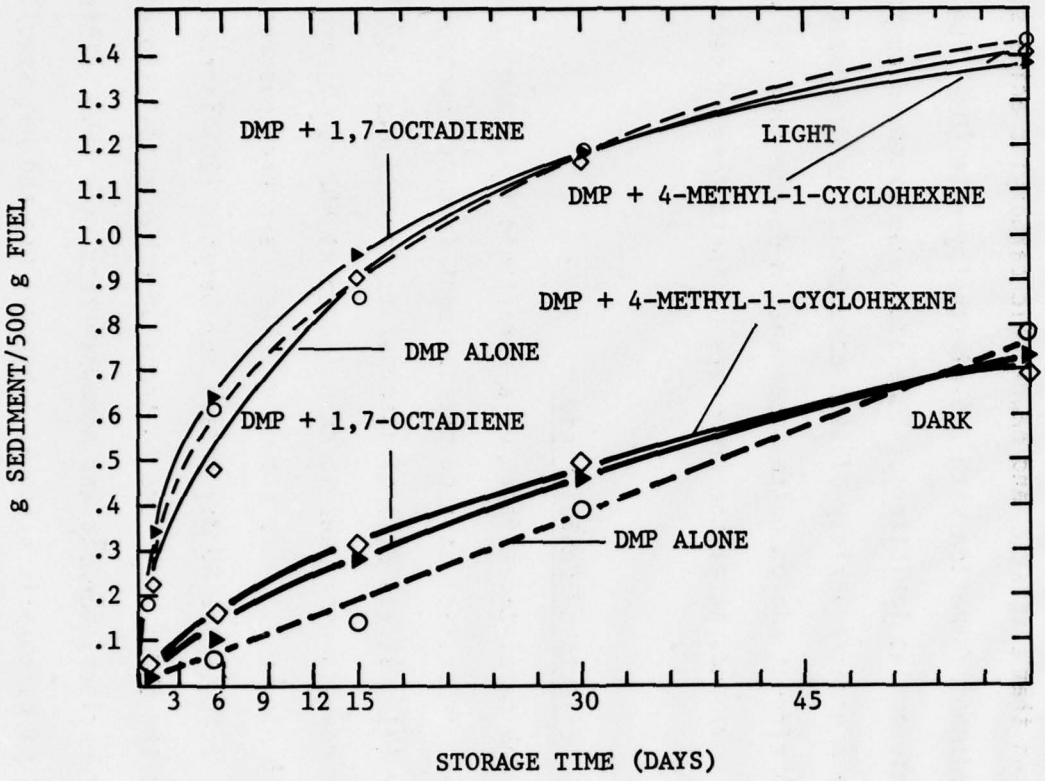


FIGURE 6

EFFECTS OF OLEFINS ON SEDIMENT FORMATION



2.4 Effects of Oxygen-Containing Impurities on Sediment Formation

As pointed out previously (8, 9), oxygenated impurities such as carboxylic acids and phenols, are not deleterious to storage stability of fuels in themselves. However, they can affect the sediment formation caused by nitrogen compounds in various ways. In a previous report (8), it was shown that aliphatic and naphthenic carboxylic acids strongly promote sediment formation with 2,5-dimethylpyrrole (DMP). On the other hand, most phenols act as inhibitors. This study was extended during this program to include a greater variety of such compounds. As discussed below, structural effects can be quite important in determining the effectiveness of oxygen compounds as either promoters or inhibitors of sediment formation.

2.4.1 Effects of Benzoic Acid

The catalytic effects of a paraffinic (n-decanoic) and napthenic (cyclohexanecarboxylic) acid on the sediment forming reaction were reported previously (8). It was also of interest to investigate a typical aromatic acid. The results with benzoic acid (added at 500 ppm O) are given in Table 7 and Figure 7. Also shown in Table 7 are previous results with some other acids. The 60 day totals for benzoic (25% increase under light and 60% in the dark) are close to those of other acids studied, although at shorter periods, benzoic was somewhat less effective. This indicates the effect of carboxylic acids is a general one and not specific to one or two examples. In all cases, the effects are most pronounced under dark storage conditions.

FIGURE 7

SEDIMENT FORMATION WITH DMP AND 1-DODECENE

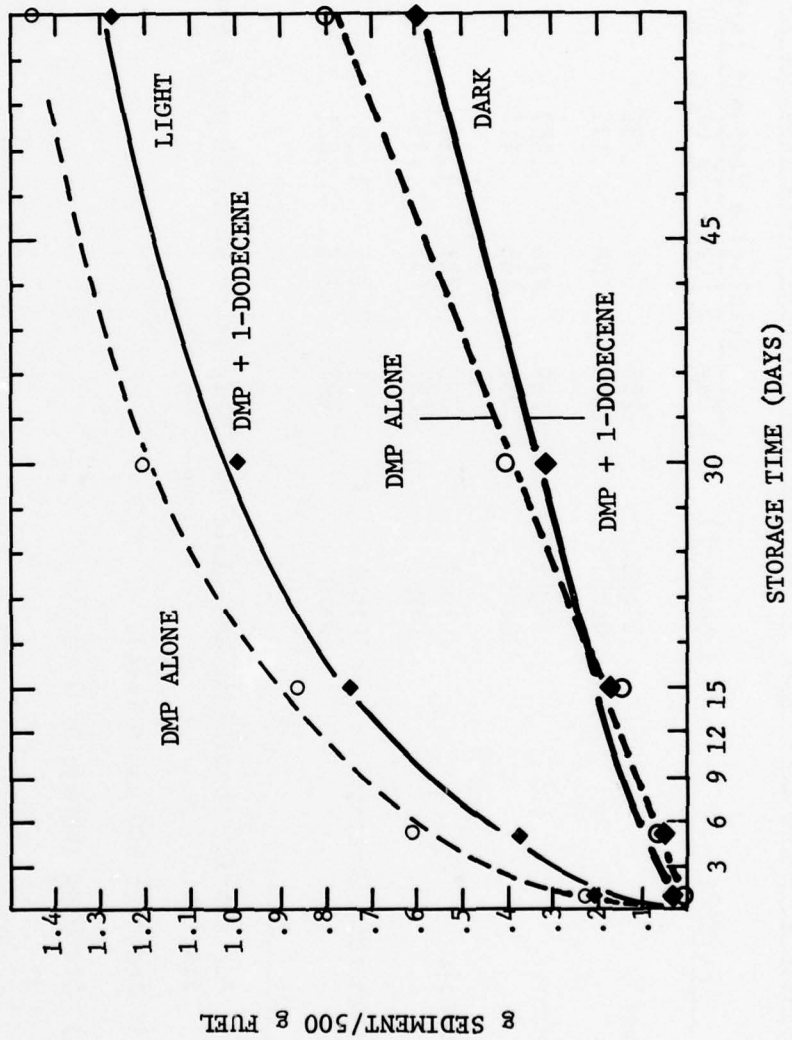


TABLE 7. EFFECTS OF CARBOXYLIC ACIDS ON SEDIMENT FORMATION WITH 2,5-DIMETHYLPYRROLE (DMP)(1)

Acid(2)	Storage(1)	Cumulative Sediment (g/500 g Decane)				
		1 Day	5 Days	15 Days	30 Days	60 Days
None(3)	Light	.256	.591	.939	1.19	1.54
"	Dark	.018	.086	.136	.377	.710
Benzoic	Light	.259	.475	.857	1.06	1.96
"	Dark	.057	.165	.414	.585	1.12
Decanoic	Light	.390	.821	1.25	1.49	1.84
"	Dark	.057	.147	.497	.990	1.50
Cyclohexane Carboxylic	Light	.391	.821	1.26	1.56	1.83
"	Dark	.083	.216	.621	1.08	1.84

(1) For storage conditions see Table 1. DMP present at 2,000 ppm N level in all samples.

(2) Added at 500 ppm 0 level.

(3) Standard average of 3 runs.

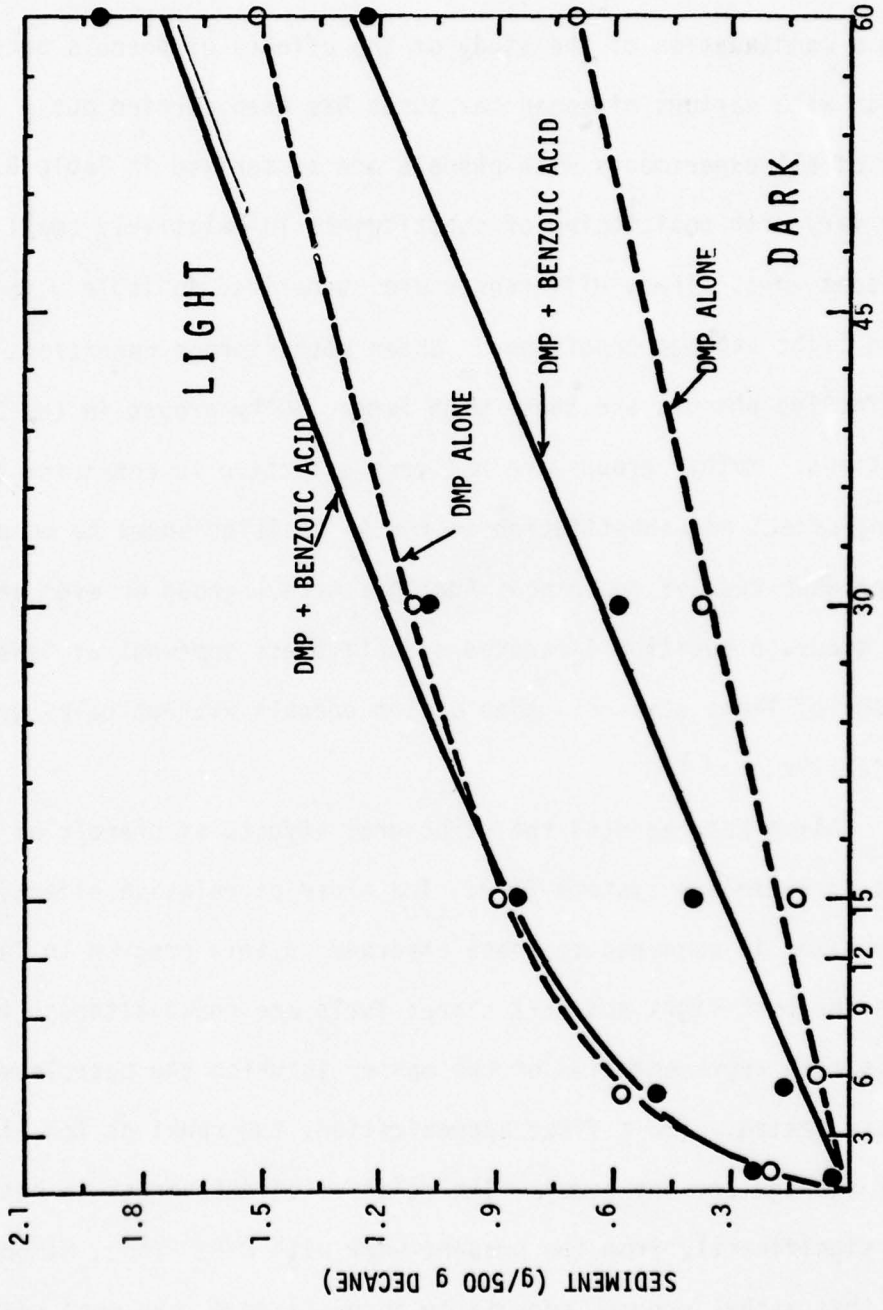


FIG. 8 EFFECTS OF BENZOIC ACID ON SEDIMENT FORMATION WITH DMP

2.4.2 Continuing Study of Effects of Phenols

Because of the interesting structural effects observed previously a continuation of the study of the effects of phenols on sediment formation with various nitrogen compounds has been carried out. The results of all experiments with phenols are summarized in Table 8. The effects vary with positioning of substituents in relatively small but significant ways. These differences are summarized in Table 9 for both dark and light storage conditions. Under both storage conditions the most effective phenols are those with large, bulky groups in the 2- and 6- positions. Methyl groups are not very effective in enhancing the retarding effect and substitution in the 4- position seems to be undesirable no matter what type of grouping. Adding a methyl group or even another t-butyl group to position 4 reduced effectiveness somewhat at least under conditions of light storage. None of the phenols without bulky groups were effective.

Nixon has reported the structural effects of phenols as antioxidants in petroleum systems (15). The order of relative effectiveness given by Nixon is compared to those observed in this program in Table 10. Rankings for both light and dark stored fuels are shown although the latter is more representative of the manner in which the petroleum products were tested. (To a first approximation, the rankings for light and dark storage are the same). The relative effectiveness in petroleum differs significantly from the present work with DMP. Thus, Nixon (15) reports that methyl groups, especially in position 4, are most effective, while we observe just the opposite effect. This suggests a different mechanism of autoxidative sediment formation may be operative in the present case over that previously observed in petroleum.

A plot of sediment formation vs storage time for DMP in the presence of various hindered phenols under light storage is given in Figure 9. In general, the shapes of the curves are similar although the more effective sediment retarding compounds show flattened curves. This reflects the relatively larger inhibition early in the storage period. Similar curves are obtained in the dark although they are much less dramatic. Phenols, in general, are relatively much more effective in inhibiting the light catalyzed reaction.

TABLE 8. EFFECTS OF PHENOLS ON SEDIMENT FORMATION WITH DMP

Nitrogen Compound(1)	Additive(1)	Storage Conditions(2)	Cumulative Sediment(g/500g Decane) 1 Day	5 Days	15 Days	30 Days	60 Days
DMP	None(3)	Light	.256	.591	.939	1.19	1.54
DMP	None(3)	Dark	.014	.063	.204	.369	.803
DMP	Phenol	Light	(4)	(4)	.015(5)	.092(5)	1.34
DMP	Phenol	Dark	(4)	(4)	.011(5)	.090(5)	.659
DMP	4-t-Butylphenol	Light	(4)	.414	(4)	.815	1.26
DMP	4-t-Butylphenol	Dark	(4)	.043	.045(4)	.314	.890
DMP	2,4-Dimethylphenol	Light	.081	.271	.569	.658	1.15
DMP	2,4-Dimethylphenol	Dark	--	.018	.213	.573	1.15
DMP	2,3-Dimethylphenol	Light	.148	2.66	.266(4)	.482	.930
DMP	2,3-Dimethylphenol	Dark	--	.059	.269	.448	1.08
DMP	2,6-di-t-Butylphenol	Light	--	.022	.173	.376	.639
DMP	2,6-di-t-Butylphenol	Dark	--	--	.035	.131	.496
DMP	2,4-di-t-Butylphenol	Light	.042	.275	.540	.843	1.20
DMP	2,4-di-t-Butylphenol	Dark	--	.010	.178	.532	.981
DMP	2-t-Butyl-4-methylphenol	Light	.033	2.62	.512	.810	1.11
DMP	2-t-Butyl-4-methylphenol	Dark	--	.069	.196	.544	1.19
DMP	2,5-di-Isopropylphenol	Light	--	.146	.356	.587	.879
DMP	2,5-di-Isopropylphenol	Dark	--	--	.093	.335	.864
DMP	2,4,6-Trimethylphenol	Light	.275	.459	.682	.910	1.33
DMP	2,4,6-Trimethylphenol	Dark	--	.010	.126	.336	1.00
DMP	2,4,6-tri-t-Butylphenol	Light	.006	.202	.405	.634	.927
DMP	2,4,6-tri-t-Butylphenol	Dark	--	.001	.057	.187	.637

TABLE 8. EFFECTS OF PHENOLS ON SEDIMENT FORMATION WITH DMP (cont.)

Nitrogen Compound(1)	Additive(1)	Storage Conditions(2)	Cumulative Sediment(g/500g Decane) 1 Day	5 Days	15 Days	30 Days	60 Days
DMP	2-Hydroxy-3-isopropyl(6)	Light	--	.092	.270	.473	.770
DMP	2-Hydroxy-3-isopropyl(6)	Dark	--	--	.020	.099	.283
DMP	2,6-di-t-Butyl-4-methylphenol	Light	.003	.040	.153	.272	.823
DMP	2,6-di-t-Butyl-4-methylphenol	Dark	--	.010	.058	.108	.603
Indole	None(7)	Light	.012	.021	.022	.036	.043
Indole	None(7)	Dark	--	--	--	--	--
Indole	2,5-di-t-Butylphenol(7)	Light	--	--	.023	.036	.039
Indole	2,5-di-t-Butylphenol(7)	Dark	--	--	--	--	--
Indole	2,6-di-t-Butyl-4-methylphenol(7)	Light	--	.006	.065	.065	.067
Indole	2,6-di-t-Butyl-4-methylphenol(7)	Dark	--	--	--	--	--

(1) Nitrogen compound at 2,000 ppm N; oxygen at 500 ppm O; DMP = 2,5-Dimethylpyrrole.
(2) Light = UV light, 366nm at 1100μW/cm^2.
(3) Average for several runs; see Table 1.
(4) Too tacky to filter.
(5) Glassy sediment could not be measured accurately until end of test period. These values are too low.
(6) 3-i-Propylcatechol.
(7) Previous data; see reference (8).

TABLE 9. IMPORTANCE OF SUBSTITUENT POSITION ON ABILITY OF PHENOLS TO RETARD SEDIMENT WITH DMP

Substituent				% Reduction in Sediment (as compared to DMP alone)			
				Light		Dark	
2 pos.	3 pos.	4 pos.	6 pos.	15 Day	60 Day	15 Day	60 Day
t-Bu	---	---	t-Bu	80	65	80	40
i-Propyl	---	---	i-Propyl	62	43	55	0
---	---	t-Bu	---	(c)	18	(c)	0
t-Bu	---	t-Bu	---	42	22	13	0
t-Bu	---	t-Bu	t-Bu	57	40	58	25
t-Bu	---	Methyl	---	45	28	4	(a)
t-Bu	---	Methyl	t-Bu	69	50	84	50
Methyl	Ethyl	Methyl	---	21	14	7	0
Methyl	---	Methyl	Methyl	35	(a)	(a)	(a)
Methyl	Methyl	---	---	(c)	40	(c)	(a)
Methyl	---	Methyl	---	39	25	(c)	(a)
---(b)	---	---	---	(c)	13	(c)	7

(a) Slightly more sediment with phenol present.

(b) Unsubstituted phenol.

(c) Sediment to tacky to measure properly at this time period.

TABLE 10

RELATIVE EFFECTIVENESS OF PHENOLS
AS ANXIOXIDANTS IN SYNFUEL AND PETROLEUM SYSTEMS

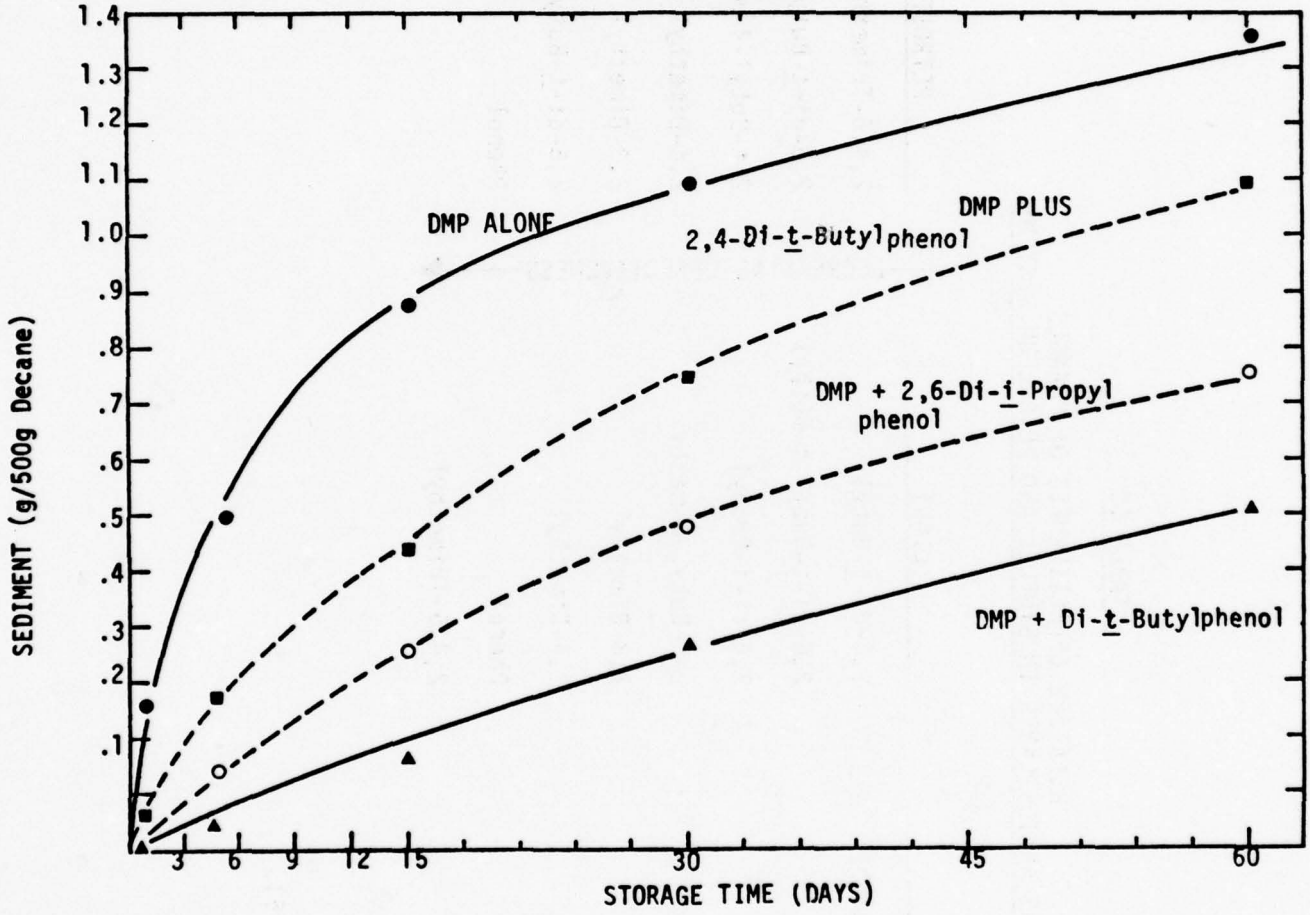
DARK	LIGHT	PETROLEUM*
2,6-di-t-Butyl-4-methyl	2,6-di-t-Butyl	2,4,6-Trimethyl
2,6-di-t-Butyl	2,6-di-t-Butyl-4-methyl	2,6-di-t-Butyl-4-methyl
2,6-di-i-Propyl	2,6-di-i-Propyl	2-t-Butyl-4-methyl
2-t-Butyl-4-methyl	2-t-Butyl-4-methyl	2,4-Dimethyl
Phenol	2,3-Dimethyl	2,3-Dimethyl
2,3-Dimethyl	2,4-Dimethyl	2,6-di-t-Butyl
2,4-Dimetyl	Phenol	Phenol
2,4,6-Trimethyl	2,4,6-Trimethyl	

DECREASING EFFECTIVENESS

*See Nixon (ref. 15).

FIGURE 9

SEDIMENT FORMATION WITH 2,5-DIMETHYPYRROLE (DMP) IN THE PRESENCE OF SOME HINDERED PHENOLS - LIGHT STORAGE



2.5 Effects of Sulfur Compounds on Sediment Formation

Sulfur containing compounds are found in both petroleum derived fuels and in liquids from shale and coal (16). In addition, they have been found to be deleterious both to thermal (14) and storage (1) stability in fuels where they occur. As a result, this study was undertaken to determine the effects of representative sulfur compounds on sediment formation.

The effects of various sulfur compounds on sediment formation are summarized in Table 11 and Figures 10 and 11. The two sulfides studied had little effect on sediment formation. Dodecanethiol tended to reduce sediment formation to some extent (Figure 10). The aromatic thiols, however, showed a large inhibitory effect early in the storage period. Thus, 3,000 ppm of thiophenol (S basis) reduced sediment with DMP by 93% over a 30 day period in the light while 500 ppm effected a 75% reduction over the same period. The corresponding reductions for 60 days storage, however, were 62% and 27% respectively. This tendency is illustrated by the curves in Figure 11. Under dark storage conditions, the inhibitory effect was observed for the entire 60 days (Table 11, Figure 10). Similar results were obtained with p-thiocresol and DMP and with thiophenol and 2-methylindole (Table 11). Both 1- and 2-naphthalene thiols were studied under sunlight storage (Table 11). The former reduced sediment by about 60% over 60 days while the latter was somewhat more effective (70% reduction over controls after 60 days storage in sunlight).

The thiols may be acting as radical scavengers until they are exhausted later in the storage period. Alternately, the thiols themselves

TABLE 11

EFFECTS OF SULFUR COMPOUNDS ON SEDIMENT FORMATION(1)

Nitrogen Compound(2)	Sulfur Compound(3)	Storage	Cumulative Sediment (g/500g Decane) 1 Day	5 Days	15 Days	30 Days	60 Days
DMP	None(4)	UV Light	.256	.275	.939	1.19	1.54
DMP	None(4)	Dark	.014	.063	.204	.396	.803
DMP	n-Octylsulfide	UV Light	.209	.577	.867	1.13	1.41
DMP	n-Octylsulfide	Dark	--	--	.039	.174	.681
DMP	n-Dodecanethiol	UV Light	.161	.296	.551	.802	1.15
DMP	n-Dodecanethiol	Dark	--	--	.047	.202	.468
DMP	Benzyldisulfide	Sunlight	(5)	.317	.656	.968	1.26
DMP	Benzyldisulfide	Dark	(5)	.049	.153	.426	.704
DMP	Benzylphenylsulfide	Sunlight	(5)	.301	.632	.966	1.59
DMP	Benzylphenylsulfide	Dark	(5)	.049	.152	.356	.628
DMP	Thiophenol	UV Light	.080	.081	.081	.081	.587
DMP	Thiophenol	Dark	--	--	--	.013	.014
DMP	Thiophenol(6)	UV Light	.001	.021	.226	.301	1.12
DMP	Thiophenol(6)	Dark	--	--	--	trace	.064
DMP	p-Thiocresol	UV Light	(5)	.024	.032	.069	.233
DMP	p-Thiocresol	Dark	(5)	--	--	.013	.014
2-Methylindole	Thiophenol	UV Light	.002	.032	.124	.125	.361
2-Methylindole	Thiophenol	Dark	trace	trace	trace	trace	.005
DMP	1-Naphthalenethiol	Sunlight	.028	.204	(7)	.423	.756
DMP	2-Naphthalenethiol	Sunlight	.063	.108	(7)	.158	.572
DMP	None	Sunlight	.134	.671	(7)	1.32	1.94

(1) For conditions, see Table 2.
(2) Added at 2,000 ppm N level, DMP = 2.5-Dimethylpyrrole.
(3) Added at 3,000 ppm S unless otherwise noted.
(4) Standard - See Table 1.
(5) Too tacky to measure at this oint.
(6) 500 ppm S level.
(7) Not measured at this time period

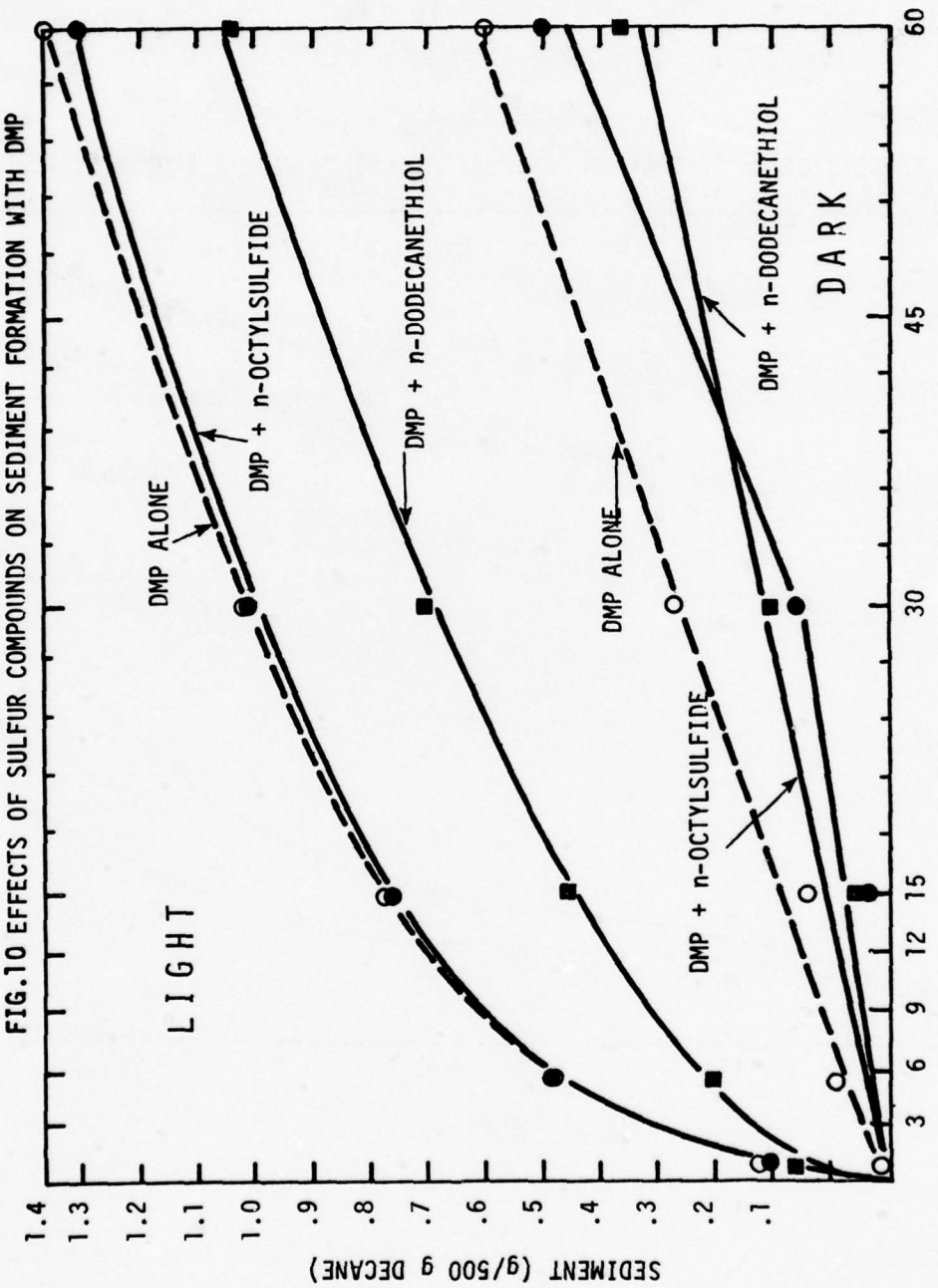
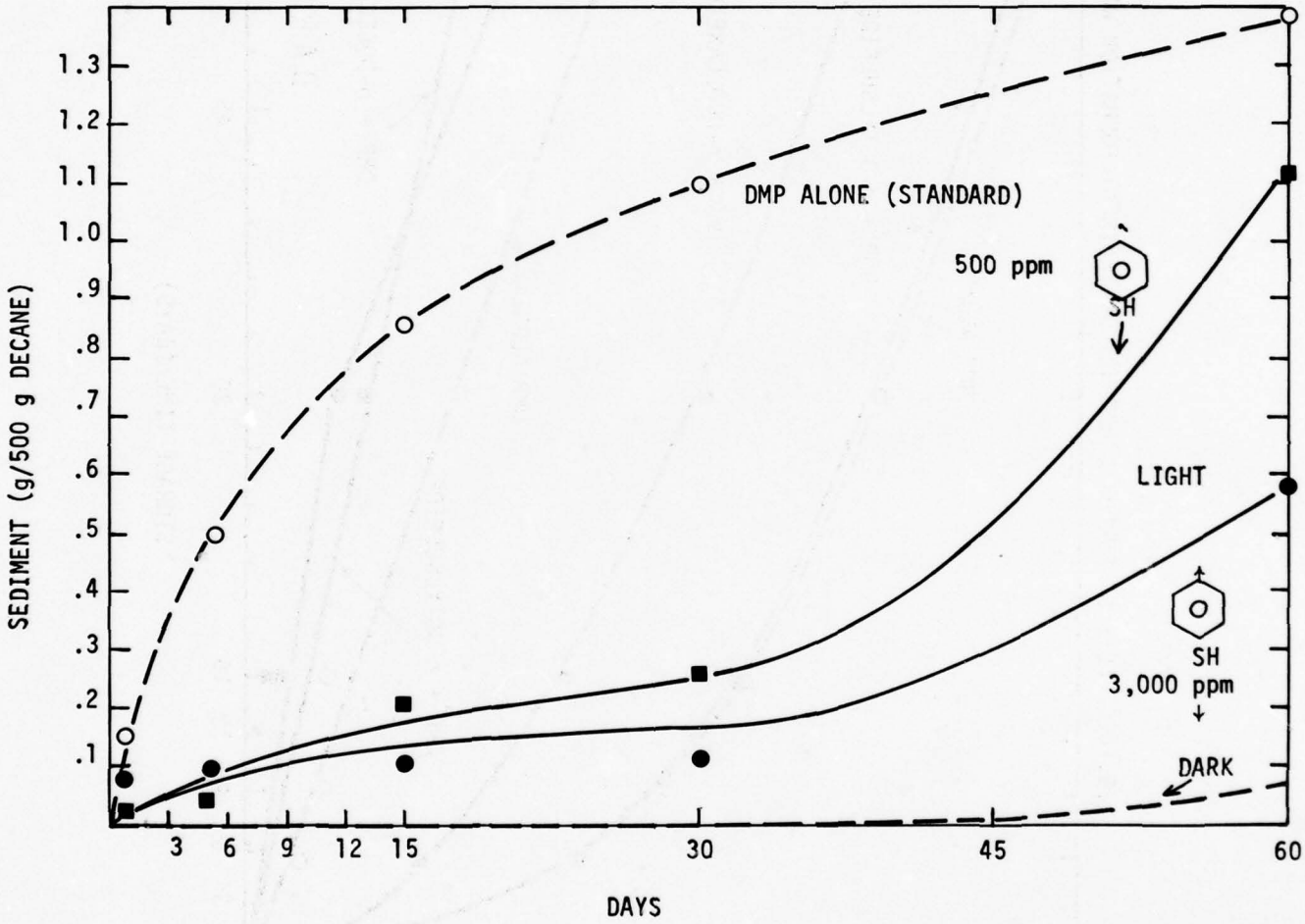


FIG.10 EFFECTS OF SULFUR COMPOUNDS ON SEDIMENT FORMATION WITH DMP

FIGURE 11

EFFECTS OF THIOPHENOL ON SEDIMENT FORMATION WITH 2,5-DIMETHYLPYRROLE



may be slowly oxidized to sulfonic acids which then became catalysts for sediment formation. Such "induction" periods have been observed in petroleum autoxidations "catalyzed" by aromatic thiols (17). Additional research is needed to clarify the mechanism of this "thiol effect".

2.6 Effects of Dissolved Oxygen

Dissolved oxygen clearly plays an important role in promoting sediment formation. Excluding oxygen reduces sediment caused by DMP by about 50% over the 60 day period when stored in light and 75% in darkness (Table 12)*. It is noteworthy that the combined exclusion of light and oxygen reduces sediment by 87% over 60 days and by over 95% in 15 or 30 days. Plots of these data are shown in Figure 12. The plots suggest that dissolved oxygen may play nearly as great a role as light in promoting sediment formation. Deoxygenation should be explored further as a method for stabilizing shale liquids.

2.7 Effects of Moisture and Trace Mineral Acids

The results of some preliminary experiments with adding water and sulfuric acid to decane solutions of DMP and indole are given in Table 13. All previous "standard" runs have been made with n-decane which was dried by passing through activated alumina or silica gel. Surprisingly, moisture appears to retard sediment formation somewhat while sulfuric acid appears to have little or no effect. This finding requires confirmation in light of the effects of organic acids discussed above (Section 2.4.1).

2.8 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

*It should be noted that the runs in Table 12 were maintained O_2 saturated by sparging with air after each storage period. They differ slightly from standard runs (see Table 1) where samples were not sparged, but were simply air saturated at the start.

TABLE 12

EFFECTS OF DEOXYGENATION ON SEDIMENT FORMATION WITH 2,5-DIMETHYLPYRROLE (1)

Dissolved Oxygen	Storage	Cumulative Sediment (g/500g Decane) 1 Day	5 Days	15 Days	30 Days	60 Days
<1 ppm (2)	UV Light	.032	.154	.298	.645	.918
	Dark	---	.032	.024	.025	.230
70 ppm (3)	UV Light	.204	.363	1.06	1.41	1.72
	Dark	.022	.092	.219	.483	.890

(1) See TAble 1 for experimental details.

(2) O_2 removed by sparging fuel with N_2.

(3) Air sparged after each weighing period; data not strictly comparable to "standard" runs in Table 1.

FIGURE 12

EFFECTS OF DISSOLVED OXYGEN ON SEDIMENT FORMATION WITH DMP

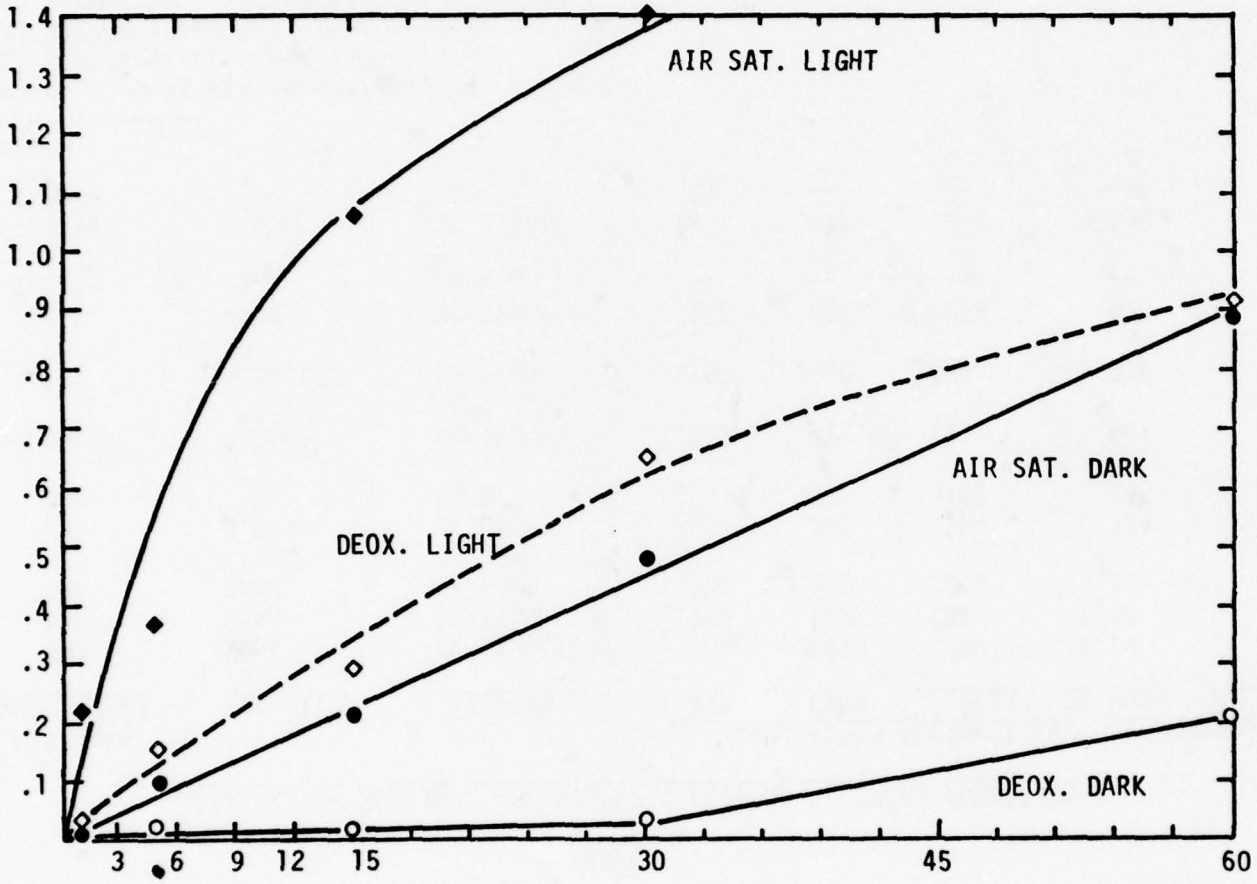


TABLE 13

EFFECTS OF MOISTURE AND SULFURIC ACID ON SEDIMENT FORMATION

Nitrogen Compound(1)	Additive	Storage	Cumulative Sediment (g/500g Decane) 1 Day	5 Days	15 Days	30 Days	60 Days
DMP	None	UV Light(2)	.256	.591	.939	1.19	1.54
DMP	None	Sunlight	.134	.672	(3)	1.34	1.94
DMP	None	Dark(2)	.014	.063	.204	.396	.803
DMP	H_2O(4)	UV Light	(3)	.358	.584	.714	1.06
DMP	"	Dark	(3)	.042	.122	.249	.594
DMP	H_2O(4)	Sunlight	.142	.418	(3)	.661	1.16
DMP	H_2SO_4(5)	Sunlight	.198	.660	(3)	.937	1.89
Indole	None	UV Light	.012	.021	.022	.036	.043
Indole	None	Dark	--	--	--	--	--
Indole	H_2O(4)	UV Light	(3)	.017	.032	.032	.069
Indole	"	Dark	(3)	--	--	--	--

(1) For levels and conditions, see Table 2.
(2) Standard run - see Table 1.
(3) Not measured this time period.
(4) Saturated solution of H_2O in decane.
(5) Saturated solution of H_2SO_4 in decane.

preventing it. Elemental analyses for selected sediment samples from DMP have been reported previously (8). Although storage conditions may affect the rate of formation and quantity of sediment, they do not seem to alter the characteristics of the sediment. 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. The approximate average molecular composition of 11 sediment samples normalized to 1 N atom was shown to be (8):

$$C_{6.3}H_{7.0}NO_{1.67}$$

while that of dimethylpyrrole is:

$$C_6H_9N$$

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 14. 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 $-CH_3$ absorption relative to $-CH_2$ indicates the methyl groups remain intact and that no long chain $-CH_2-$ units (from other components of the media) have been introduced.

TABLE 14

MAJOR IR BANDS IN SEDIMENT FROM 2,5-DIMETHYLPYRROLE(1)

cm^{-1}	Significance
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.

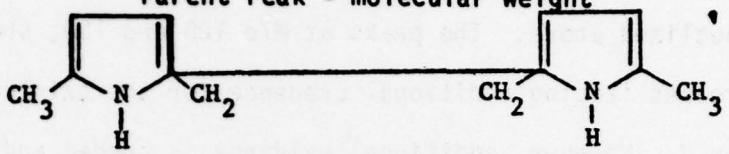
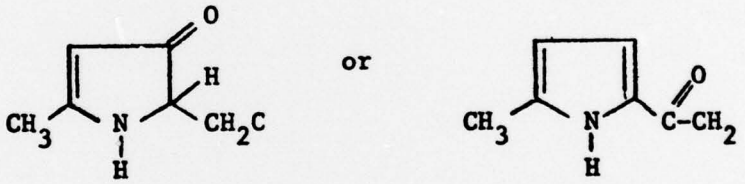
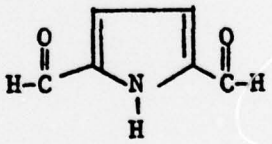
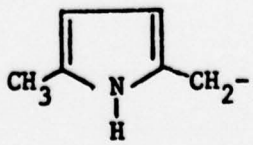
The more important mass spectral peaks and their possible fragment assignments are given in Table 15. From the elemental analysis, IR and mass spectral data one can begin to draw partial structures for the sediment obtained in the current program. These are shown in Table 16. If a single structure is present, the representation best fitting all data is I. However, the mass spectra of several samples suggests the sediment may consist of several compound types of which four (II-V) 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.

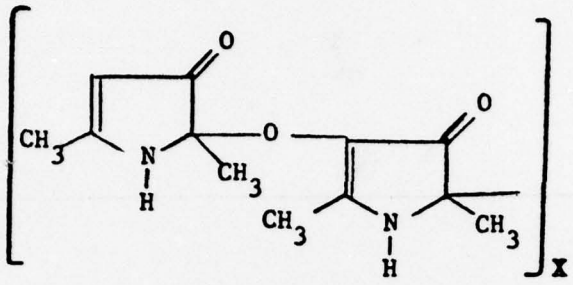
If forms such as II-V exist, the relative contribution of each should be influenced by the degree of oxidation of the nitrogen compound. This, in turn, should be a function of the dissolved oxygen content of the fuel at m/e 108,. That is, peaks 122 and 123, due to oxygenated structuresII, IV and V, might be expected to increase in intensity in samples run in the presence of oxygen relative to the peak at M/e 94 which arises from Structure III which contains no oxygen. From deoxygenated samples, the opposite would be true.

Figures 13 and 14 give the mass spectra of sediments from DMP obtained under deoxygenated and air saturated conditions respectively. The ratios of the 94 peak to the 122 peak are 11.3 for the deoxygenated sample and 3.7 for the air saturated case. This is the expected trend as outlined above. The peaks at M/e 108 and 109, show corresponding increases lending additional credence for the existence of structures IV or V. However, additional evidence is needed and work should be continued in this area. It appears, however, that structures such as I - V are the most reasonable representations of the sediments obtained from DMP.

TABLE 15

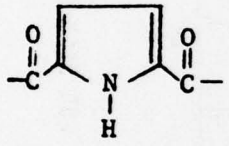
PRINCIPAL MASS SPECTRAL PEAKS FOR SEDIMENT FROM 2,5-DIMETHYLPYRROLE IN n-DECANE

m/e	Possible Fragment
250-400	Parent Peak - molecular weight
188	
108	
122	
123	
138	
94	

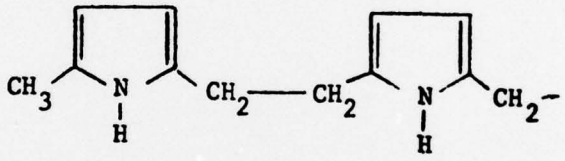


I

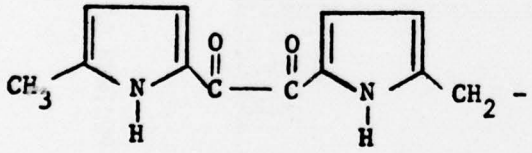
$C_6H_7NO_{1.5}$



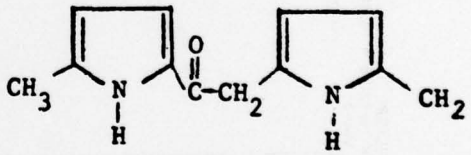
II



III



IV



V

TABLE 16. POSSIBLE STRUCTURES FOR DMP SEDIMENT

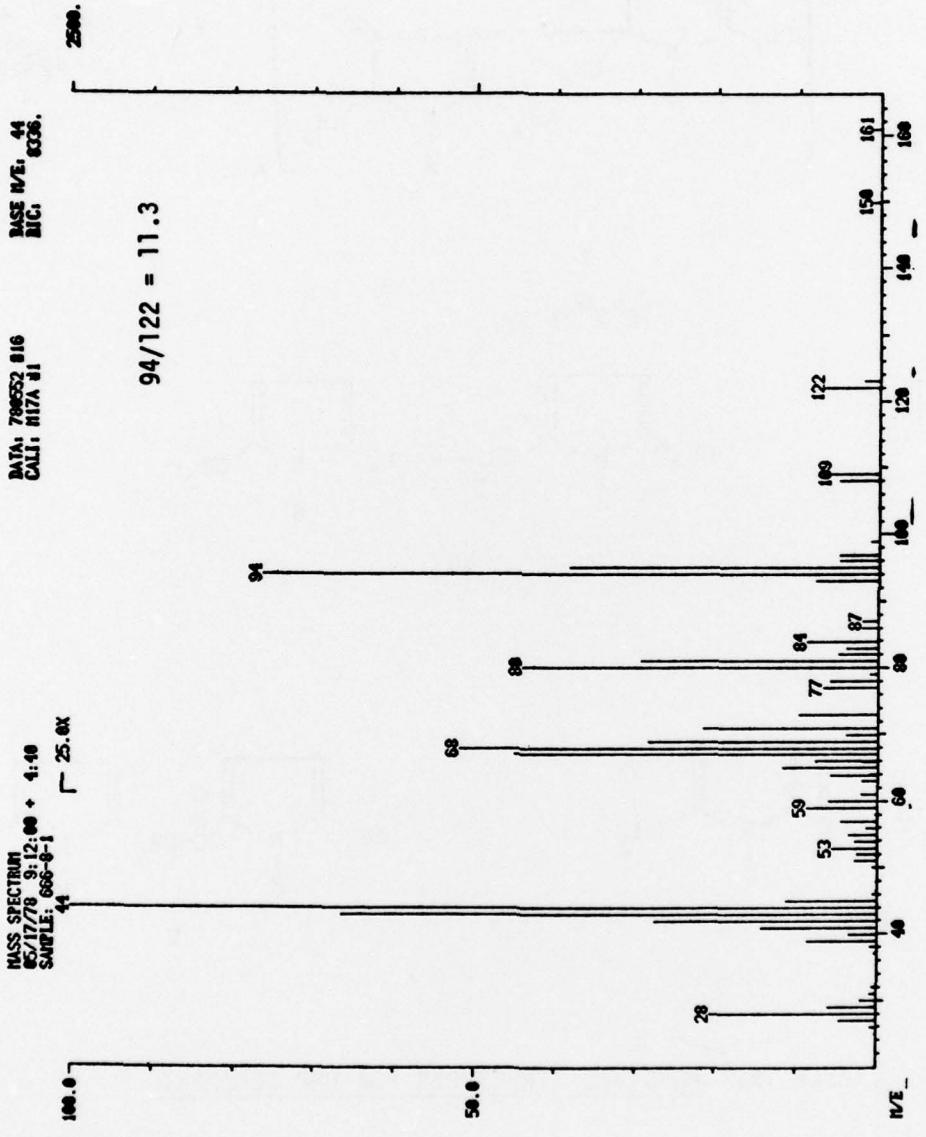


FIGURE 13. MASS SPECTRUM OF SEDIMENT PERIOD FOR DEOXYGENATED DMP SOLUTION.

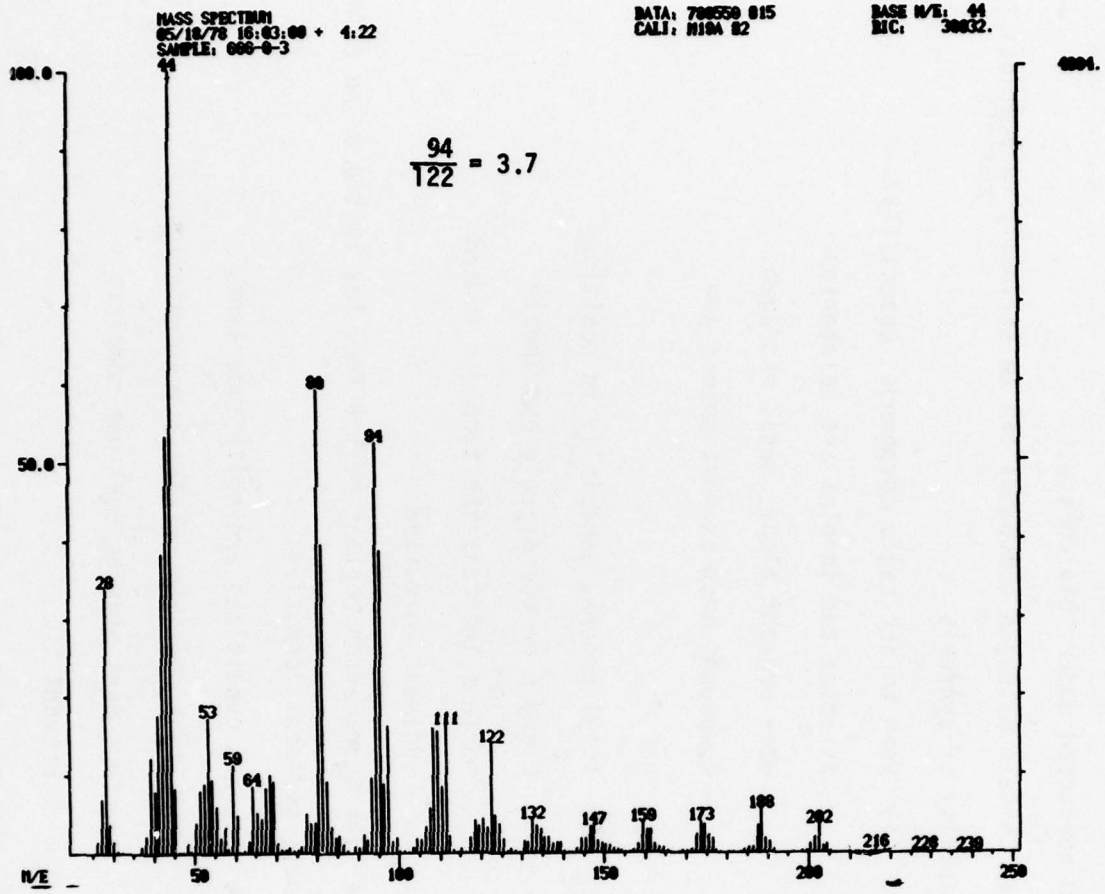


FIGURE 14 MASS SPECTRUM OF SEDIMENT FROM DMP UNDER AIR SATURATED CONDITIONS.

3. CONCLUSIONS AND RECOMMENDATIONS

The following general conclusions may be drawn from the results of research conducted under this contract.

- Certain nitrogen compounds can be seriously deleterious to storage stability of synfuels.
  - (1) Weak to non-basic compounds, especially pyrroles and indoles are deleterious when present alone; basic nitrogen compounds such as most amines are not.
  - (2) Alkyl groups, especially in positions 2 and 5 on the pyrrole and indole nucleus increase the tendency toward sediment formation.
- The hydrocarbon content of the fuel has little or no effect on nitrogenous sediment formation.
- Storage conditions are quite important.
  - (1) Light strongly catalyzes sedimentation, but dark storage does not completely prevent it.
  - (2) Dissolved oxygen level is quite important.
  - (3) Moisture and mineral acid contents are relatively unimportant.
- Certain trace impurities may interact with the nitrogen compounds to promote or retard sediment formation.

(1) Carboxylic acids are catalysts; the effect is especially noteworthy in the dark.

(2) Many phenols are inhibitors; structural effects are important.

(3) Sulfides and aliphatic thiols have little effect on sediment.

(4) Aromatic thiols are strong inhibitors early in the storage period but become much less effective later.

- The sediments have a definable chemical structure which appears to consist of repeating units of partially oxidized nitrogen compound.

These findings should be confirmed and extended by means of the following additional research:

1. The magnitude of the problem should be defined further:
   a). Survey of possible deleterious species should continue.
   b). A study of possible interactions between nitrogen compounds should be conducted to determine whether certain compounds, innocuous when tested alone, may become deleterious in the presence of active species.
   c). Study of effective levels of various deleterious species; determination of degree of denitrogenation needed for stability.

2. Studies aimed at promoting a better understanding of the sedimentation reaction.

   a). Kinetic studies using temperature, level of nitrogen species and catalyst as variables.

   b). Continued studies of sediment structure using IR, Mass spectra and NMR.

   c). Studies of deposit morphology using scanning electron microscopy.

   d). Studies of effects of known free radical initiators in darkness; comparison of radical initiated sedimentation with light catalyzed reaction.

3. Additional work on sediment prevention.

   a). Deoxygenation.

   b). Use of additives.

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Indoles	Storage Stability	Deoxygenation
Amines	Sediment Formation	

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

An investigation of the effects of nitrogen compounds on sediment formation during fuel storage was carried out using model fuel systems. Various weak to non-basic nitrogen compounds, especially alkyl pyrroles and indoles were found to promote sediment formation; basic nitrogen compounds such as most amines did not. The sediment formation was strongly catalyzed by light and carboxylic acids. Phenols and aromatic thiols retard sedimentation. Sulfides and aliphatic thiols had little effect. Moisture and traces of mineral acid also had

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little or no influence on sediment formation. The structure of the sediment was investigated using infrared and mass spectroscopy.