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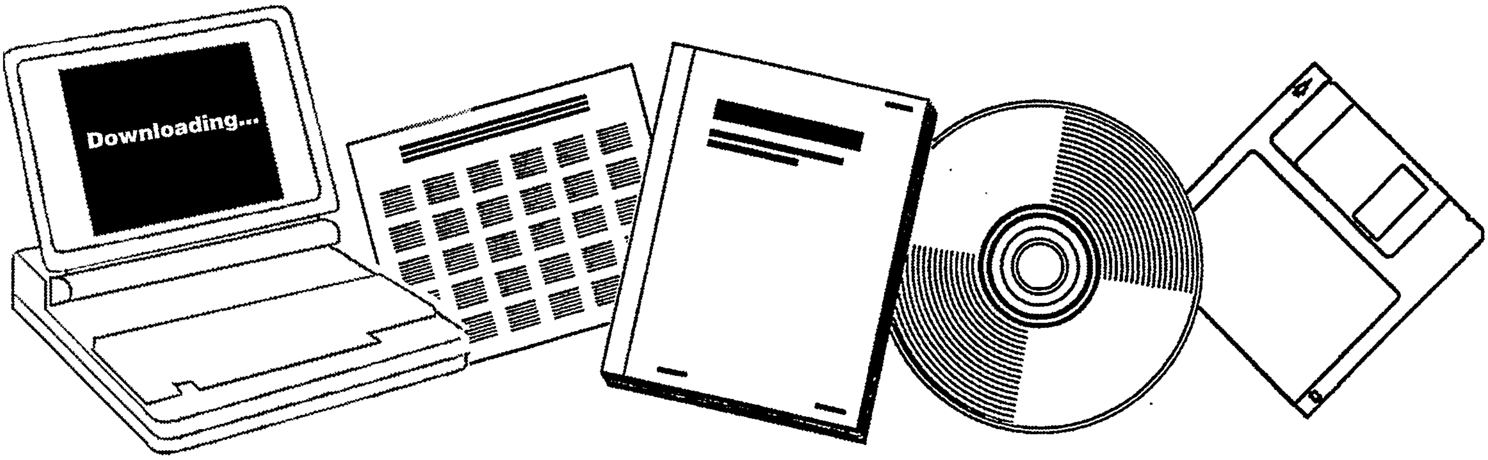
FUNDAMENTAL SYNTHETIC FUEL STABILITY STUDY. FINAL REPORT, MAY 1, 1979-JUNE 30, 1981

EXXON RESEARCH AND ENGINEERING CO.
LINDEN, NJ

MAR 1982



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Final Report
May 1, 1979–June 30, 1981

Work Performed for the Department of Energy
Under Contract No. DE-AC19-79BC10045

Date Published—March 1982

Exxon Research and Engineering Company
Linden, New Jersey

U. S. DEPARTMENT OF ENERGY

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FUNDAMENTAL SYNTHETIC FUEL STABILITY STUDY

Final Report
May 1, 1979--June 30, 1981

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UNITED STATES DEPARTMENT OF ENERGY

PREFACE

This report was prepared by Exxon Research and Engineering Company, Linden, New Jersey, for the Department of Energy under Contract DE-AC19-79-BC10045. The program was monitored by Dr. Dennis W. Brinkman of the Bartlesville Energy Technology Center.

The program covered a two-year effort over the period from May 1, 1979 to June 30, 1981. The principal investigators were Dr. John W. Frankenfeld and Dr. William F. Taylor assisted by Mr. Robert L. Bruncati. A First Annual Report covering the work done in the period May 1, 1979 to April 30, 1980 was published in February 1981 (DOE/BC/10045-12). This Final Report contains the results of the second year of effort (May 1, 1980 to June 30, 1981) and, in addition, describes the results and conclusions of the total two-year program.

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ABSTRACT

This report summarizes a multi-year study on the storage stability of synthetic fuels derived from oil shale and coal. A variety of organic nitrogen, sulfur and oxygen compounds were evaluated for their tendencies to promote sediment in hydrocarbon fuels under accelerated storage conditions. Three types of diluents were employed in model compound studies representing fuels of increasing complexity. These were pure n-decane, petroleum-derived jet fuel of the Jet A type, and No. 2 diesel fuel. In addition, several middle distillate fuels derived from actual shale liquids were tested and the results compared to the model compound studies. The fuels and fuel mixtures were stored at 110°F (43.3°C) and 150°F (65.5°C) in the dark. Sediment formation was determined gravimetrically. During the course of this work a modified storage stability test was developed which significantly improved the accuracy of sediment determination.

The effects of nitrogen compounds on sediment formation, observed previously in pure hydrocarbon systems, were confirmed in broad range fuels. The most deleterious species to fuel stability were found to be alkylated heterocyclic nitrogen compounds. The most reactive compounds were those with two or more alkyl groups, at least one of which was situated on a carbon adjacent to the nitrogen. Substitution on the nitrogen atom or on positions remote to the nitrogen atom acted to reduce the tendency toward sediment formation. In addition, fusion of an aromatic hydrocarbon ring to the heterocyclic ring reduced reactivity. A typical, highly deleterious compound which was studied extensively is 2,5-dimethylpyrrole (DMP). Other nitrogen compounds, such as amines, amides and non-alkylated heterocycles, were non-deleterious when tested by themselves. However, several of these apparently harmless species were found to interact with reactive nitrogen compounds to promote sediment formation.

With the exception of sulfonic acids and aromatic thiols none of the sulfur or oxygen compounds studied produced sediment when tested by themselves under accelerated storage conditions. However, some of them interacted with nitrogen compounds to either enhance (carboxylic acids) or retard (aromatic thiols) sediment formation.

The nature of the diluent had a significant effect on sedimentation rate, with the most complex medium (No. 2 diesel) producing the most, and the simplest (pure n-decane) the least sediment with the same nitrogen compound under identical storage conditions. This is apparently not due to variation in hydrocarbon content. Varying the amounts of different hydrocarbon types in the diluent by blending in pure compounds had little or no influence over nitrogenous sediment formation.

Storage conditions affected the formation of sediment in varying ways. Dissolved oxygen accelerated the reaction in all cases as did increased temperature and light. Water promoted sedimentation in diesel fuel but showed little effect in other diluents. Under conditions of the study, metal surfaces exerted only a minor influence.

The sedimentation reaction with 2,5-dimethylpyrrole (DMP) followed the Arrhenius equation for temperature dependence. The apparent activation energy is in the range of 10-15 kcal/mole. The sediment itself appears to be repeating units of partially oxidized nitrogen compound most likely linked through the alkyl groups attached to the ring.

Actual shale-derived middle distillates with nitrogen contents exceeding 3000 ppm were highly unstable. Those with levels <500 ppm were stable for extended periods. However, there was no direct, quantitative correlation between total nitrogen content and the rate of sediment formation.

The sediments obtained from actual shale liquids and their mode of formation appear similar to those from model nitrogen compounds. Analysis of the fuels before and after storage indicated that the neutral heterocyclic fraction (mostly alkylated pyrroles and indoles) was the only one participating in sediment formation.

The interactive effects found in model compound studies were observed in shale liquids. However, the magnitude of the interaction varied considerably depending on the source and processing history of the fuel.

Shale liquids from various sources were successfully blended with each other, with petroleum-derived fuels and with model nitrogen and sulfur compounds. Stability tests on the resulting mixtures indicated interactions were occurring which must be taken into account in predicting the storage stability of such blends.

1. INTRODUCTION

The development of alternate sources of fuel to replace rapidly dwindling reserves of petroleum has become an increasingly important concern. Two of the most promising sources of such fuels are shale rock and coal.(1) Although processes are available for the production of synthetic liquids from both shale and coal, the investment costs associated are very high and the fuels produced will unquestionably be significantly different in chemical composition from present day petroleum-derived materials.

A major difference in composition in crudes from various sources is the nitrogen content. It is known that organic nitrogen compounds can be deleterious to fuel quality especially with respect to storage stability as manifested by the formation of sediment or sludge. However, the causes and the magnitude of the problems are not well defined. This is due to the fact that the nitrogen content of nearly all petroleum-based fuels is too low to present serious concern. As a result the problem has not been studied extensively. The situation is quite different with synthetic fuels where nitrogen levels can reach 3%. Removal of nitrogen is usually accomplished by catalytic hydrogenation. Achieving very low nitrogen levels by this process is both difficult and costly. As a result there is a great incentive for determining which nitrogen compounds must be removed to achieve a stable fuel and to what degree. The major goal of this project was to study the nitrogen problem in depth to assess its impact on future synthetic fuel processing.

1.1 PROGRAM OBJECTIVES

The overall objective of this program was to extend our knowledge of the effect of the chemical composition of petroleum fuels on storage stability to future shale oil and coal-derived fuels. In addition, the study had the following specific objectives.

- Extend the study of the effects of various nonhydrocarbon impurities, particularly nitrogen-, sulfur- and oxygen-containing compounds and metals on sediment formation to determine which species are deleterious and at what levels.
- Determine the effects of certain storage conditions on fuel stability.
- Extend studies in model systems to actual synthetic liquids, such as those derived from shale and coal liquids.
- Determine effects of certain processing conditions on storage and thermal stability of actual synthetic liquids.

1.2 GENERAL METHOD OF APPROACH

To meet the objectives detailed above, a two-year program was undertaken. The program began with a study of model compounds and progressed through more and more complex fuel systems until it culminated in a study of actual synthetic fuels derived from shale.

2. TECHNICAL DISCUSSION

2.1 TASKS TO BE PERFORMED

The objectives outlined above were accomplished by performing the following tasks:

(1) Survey and assessment of previous work impacting on the present study.

(2) Extend the study of trace impurities including nitrogen, sulfur and oxygen compounds on storage stability of model fuels.

(3) Study of the interactions between trace impurities.

(4) Study effects of hydrocarbon composition and boiling range.

(5) Study effects of water and dissolved oxygen.

(6) Study effects of metal surfaces.

(7) Study storage stability of actual shale liquids - compare with model compound work.

(8) Characterize sediment and elucidate mechanism of formation.

2.2 MATERIALS AND METHODS

2.2.1 Test Fuels

Two petroleum-based test fuels were employed. These were a jet fuel from the Bayway, New Jersey Refinery (an additive-free jet fuel meeting specifications of JP-8) and a No. 2 diesel fuel from the Baytown, Texas refinery. In order to obtain a representative, additive-free fuel, components were obtained separately and blended at Exxon Research according to a recipe furnished by Exxon Co., U.S.A. Inspections on these fuels are given in the appendix to this report (Table A-1).

In addition, some experiments were performed using *n*-decane as the diluent. This material was the highest grade available. It was purified further by treatment with activated alumina to remove traces of water and polar compounds.(2,3)

A variety of actual shale middle distillates were obtained from various sources.(4-6) They were chosen to represent a wide range of nitrogen and sulfur levels and processing techniques. The sources and inspections on these fuels are given in Appendix Tables A-2 to A-6.

2.2.2 Test Compounds

Nitrogen, sulfur and oxygen compounds were purchased from commercial sources. Where necessary these were purified by distillation or crystallization and stored in an inert atmosphere. In the cases of "active" nitrogen compounds, such as 2,5-dimethylpyrrole (DMP), monthly redistillation was required.

All test compounds were added as ppm N, S, or O (wt/vol), i.e., 150 ppm DMP means 150 mg N/1000 cc test fuel.

2.2.3 Accelerated Storage Stability Test(a)

The test fuels were filtered through glass wool, followed by a medium fritted disc filter immediately before use. Each test compound was weighed into a clean, tared, 500 ml pyrex Erlenmeyer flask fitted with a ball joint stopper. To this was added 300 ml of the test fuel. Duplicate samples were made up as well as additive-free samples. All samples were stoppered and stored in darkness at 110°F ± 2°F (43.3°C), 150°F ± 2°F or at ambient temperature for a specific period. The time periods of 14-days, 28-days and 56-days were chosen as "standard" In some cases, longer and shorter periods were also employed. After storage the contents of the flask were filtered rapidly through a tared 55 mm Buchner funnel with a glass filter pad. The filtrate was stored in brown bottles under refrigeration for further use. The Erlenmeyer flasks and the filter cakes were washed with a small amount of reagent grade iso-octane and the washings filtered and then discarded.(b) The flasks and the Buchner funnels were dried in a vacuum oven at 120°C for 1-1/2 hours, allowed to cool <u>under vacuum</u> and weighed. This resulted in two sediment weights:(c,d)

(1) Insoluble sediment (mg/100 ml) = $\frac{\text{Weight of Buchner - Tare}}{3}$

(2) Adherent sediment (mg/100 ml) = $\frac{\text{Weight of Erlenmeyer - Tare}}{3}$

Both "insoluble" and "adherent" sediment values were routinely measured in this program. However, it was found that good reproducibility can be obtained only with "total" sediment (i.e. sum of insoluble and adherent). The degree to which the sediment "adhered" to the walls of the test flasks varied

---

(a) This method is a modification of that used by Brinkman, Whisman and Bowden "Stability Characteristics of Hydrocarbon Fuels from Alternate Sources", BETC/RI-78/23 (1979). One week under these conditions at 110°F is generally considered to be equivalent to 4 weeks' storage at ambient temperature.

(b) This can be omitted for light fuels such as gasoline or some jet fuels. On the other hand, careful washing is important for heavy fuels such as some of the shale liquids.

(c) Blank corrections, obtained by applying the same measurements to the fuel without additives, are subtracted from each weight.

(d) A total sediment weight, the sum of (1) and (2), is also reported; this is perhaps, the most useful measurement.

greatly not only from test compound to test compound but also, in random fashion, from replicate to replicate. As a result only total sediment values are discussed in the body of this report although amounts of both types are tabulated in Appendix B.

In some instances, mostly in the cases of actual shale liquids (Section 2.5), soluble gum formation was also monitored. The steam jet method (ASTM D-381) was used for these determinations.

A change in accelerated storage test procedures resulted in significantly better precision among replicate samples. This change comprised a combination of thorough rinsing of samples with iso-octane and an improved drying procedure. Previously samples were transferred, hot, from drying oven to desiccators and allowed to cool before weighing. Current procedure calls for turning off the heat after 1-1/2 hours and allowing both oven and samples to return to ambient temperatures in vacuum. Reproducibility of data using the old procedure is shown in Appendix Table B-1. Results with the new technique are shown in Appendix Table B-2. The average standard error for recent experiments is 10%, a significant improvement over previous experience. Some additional examples of typical replicate data are shown in Appendix B.

2.3 LITERATURE REVIEW (TASK 1)

A literature survey of the effects of nitrogen compounds on storage stability of both shale and coal liquids was conducted. This has been described and critically reviewed in an earlier report(7) and will not be repeated here.

2.4 RESULTS OF ACCELERATED STORAGE TESTS WITH MODEL COMPOUNDS

As mentioned above a major goal of this work was to extend earlier findings on pure compound systems to additional nitrogen compounds and to broad-range fuels. This section deals with storage stability tests with various pure nitrogen, sulfur and oxygen compounds alone or in combination, dissolved in jet fuel and No. 2 diesel as well as pure *n*-decane.

2.4.1 Effects of Various Nitrogen Compounds on Sediment Formation in Broad-Range Fuels (Task 2)

Two sets of experiments were carried out with single, pure nitrogen compounds. The first, using various pyrroles and indoles was designed mainly to extend earlier model systems work(2,3) to actual broad-range fuels. The second set was aimed at expanding the current knowledge to additional, as yet untested, nitrogen compounds. The tests were conducted by adding various amounts of purified model compounds to the base fuels. The resulting mixtures were stored in the dark at 110°F or 150°F for the specified time periods then analyzed for color and sediment as described in Section 2.2.3. The classes of compounds employed in these studies and their structures are shown in Figure 1.

2.4.1.1 Color and Sediment Formation with Pyrroles and Indoles

The results of ASTM D-1500 color tests for various compounds of this type in both No. 2 diesel and JP-8 fuels for up to 56-day periods are given in Appendix B. At the start of the current program these tests were run routinely with all compounds and fuels. However, it soon became apparent that this test was a fairly tedious one, discriminated very poorly among test compounds and was later abandoned. Most pyrroles and indoles developed color on standing to some degree. The more active compounds such as 2,5-dimethylpyrrole (DMP), 1,2,5-trimethylpyrrole (TMP) and 2,4-dimethyl-3-ethylpyrrole gave colors too dark to measure in a few days. Color formation, however, was a poor indicator of potential sediment formation. Active compounds showed considerable color at once while many inactive ones exhibited little or none. Other than this, no direct correlation between color and sediment formation could be discerned.

One generalization emerged, however; color development was more rapid in No. 2 diesel fuel than in either jet fuel or pure n-decane for the same compounds and conditions.

The quantities of total sediment (insoluble plus adherent) obtained with various pyrroles and indoles in the three model fuel systems are given in Table 1. Averages of 3-15 replicates are shown. More complete data are presented in Appendix B.* These data illustrate the magnitude of the problems that could be caused by some of these compounds. As little as 150 ppm (N basis) of 2,5-dimethylpyrrole affords 50 mg/100 cc of a highly insoluble sludge in a month's time (equal to perhaps 4 months' ambient storage). It is generally agreed that the maximum tolerable sediment in jet or diesel fuels is 2-10 mg/100 cc.$^{(8)}$ Since shale or coal derived fuels can have many times this level of nitrogen heterocycles$^{(1,7)}$ their impact on stability of alternate fuels is apparent. The precipitation of sediment in the case of DMP on long storage, in fact, is nearly equal to the amount of nitrogen compound charged. Since it appears that only the nitrogen compound is involved in sediment formation (see Section 2.4.6) this amounts to an essentially quantitative reaction.

It is clear that the nature of the diluent has a significant effect on sediment formation with the quantities increasing as the model fuel becomes more complex (broader boiling range) and less pure. This is much more marked with 2,5-dimethylpyrrole (DMP) but is also noticeable with 1,2,5-trimethylpyrrole (TMP) and with some indoles, especially 3-methylindole. The reason for these variations is not yet known. It may be due to differences in the hydrocarbon content of the fuels (basically solvent effects) or, more likely, to the presence of trace impurities which promote sediment formation. Such impurities would be more prevalent in the more complex fuels.

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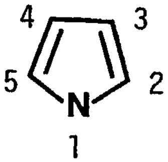
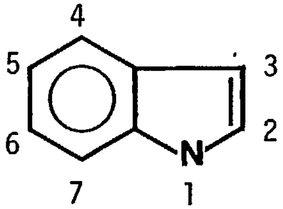
* Results in Table 1 are for 110°F; data at other temperatures are given in Section 2.4.5.1.

FIGURE 1

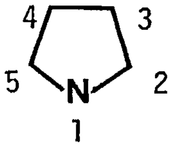
STRUCTURES AND NUMBERING SYSTEMS OF HETEROCYCLIC NITROGEN COMPOUNDS EMPLOYED IN THESE STUDIES



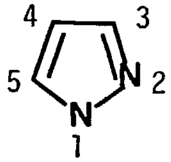
Pyrrole



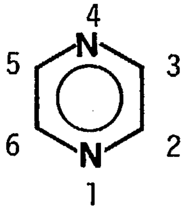
Indole



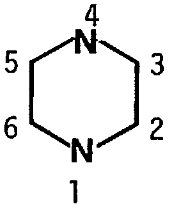
Pyrrolidine



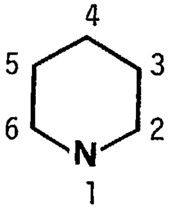
Pyrazole



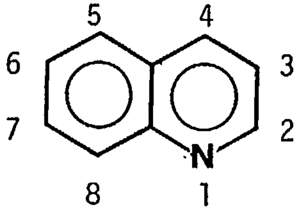
Pyrazine



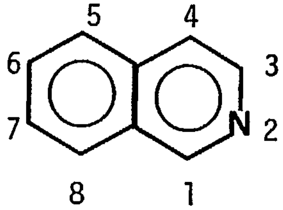
Piperazine



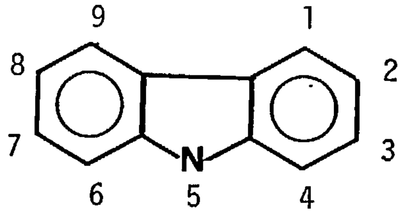
Piperidine



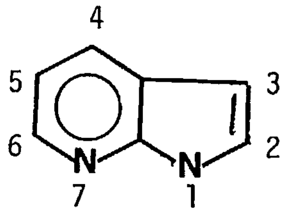
Quinoline



Isoquinoline

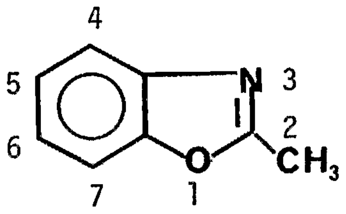


Carbazole

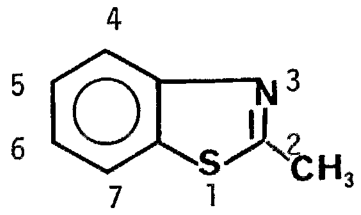


7-Azaindole

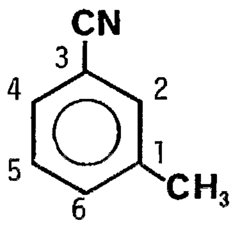
FIGURE 1 (Continued)



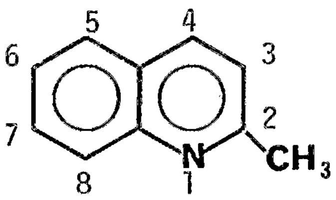
2-Methylbenzoxazole



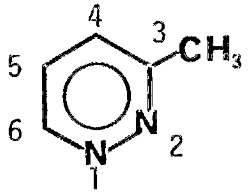
2-Methylbenzothiazole



m-Tolylnitrile



Quinaldine
(2-Methylquinoline)



3-Methylpyridazine

$(C_8H_{17})_3N$

Trioctylamine

$CH_3(CH_2)_{10}CN$

n-Undecylcyanide

TABLE 1

SEDIMENT FORMATION WITH VARIOUS PYRROLES AND INDOLES AFTER STORAGE AT 110°F IN VARIOUS TEST FUELS[a]

Nitrogen Compound	Level Added (ppm N)[c]	Total Sediment (mg/100 cc)[b] 7 Days	14 Days	28 Days	56 Days	80 Days	112 Days
		Normal Decane					
2,5-Dimethylpyrrole (DMP)	750	--	44.1	102.0	--	--	--
		Jet Fuel					
DMP	1500	--	108.5	313.7	586.3	--	--
	750	--	61.3	140.5	260.8	327.9	--
	150	--	0.8	18.3	41.2	--	--
1,2,5-Trimethylpyrrole	750	--	33.3	103.9	219.0	--	--
(TMP)	150	--	7.7	13.5	21.6	--	--
2-Methylindole	1500	--	Trace	14.6	25.9	--	--
	750	--	0.4	11.4	14.9	--	--
	150	--	0	Trace	0.5	--	--
3-Methylindole	1500	--	4.0	1.0	0.3	--	--
	750	--	1.1	0.9	0.9	--	--
	150	--	0.1	1.0	0.5	--	--
		No. 2 Diesel					
DMP	1500	--	192.8	397.0	795.8	--	--
	750	24.7	85.6	245.8	362.0	422.6	--
	150	--	23.9	40.9	74.5	89.5	--
TMP	1500	--	82.6		--	--	--
	750	--	--	117.1	--	--	--
	150	--	16.0	28.4	66.9	--	--
2,4-Dimethyl-3-ethyl-pyrrole	1500	--	19.8	26.3	--	--	--
Pyrrole	1500	--	0.7	3.0	1.0	--	--
1-Phenylpyrrole	1500	--	--	0	0	--	--
1-Methylpyrrole	1500	--	0	0	0.7	--	(d)
2-Methylindole	1500	--	Trace	13.0	26.4	--	--
	750	--	0.4	9.8	15.0	--	--
	150	--	2.0	5.0	3.2	--	--
3-Methylindole	1500	--	0.7	0.5	4.5	--	--
	750	--	0.2	0.2	1.7	--	--
	150	--	0	0.1	1.1	--	--
Indole	1500	--	Trace	1.4	1.0	--	--
1,2-Dimethylindole	1500	--	0	0	0	--	2.9
2,3-Dimethylindole	1500	--	0	Trace	6.4	--	22.0
2,5-Dimethylindole	1500	--	0	Trace	3.2	--	8.6
Carbazole	1500	--	0	0	0	--	--

(a) Dark storage; average of 2-10 replicates; more complete data in Appendix B.

(b) Sum of insoluble and adherent sediments - see Appendix B; corrected for blanks (diesel only); blank corrections: 14-Day 0, 28-Day 0.5; 56-Day 0.5 mg/100 cc.

(c) Based on Nitrogen, i.e. 150 ppm means 150 ppm nitrogen not 150 ppm pyrrole; wt/volume basis, i.e., 150 ppm mg N/100 cc diluent.

(d) Affords about 9 mg/100 cc on 120 days' storage.

Plots of sediment formation vs time for DMP stored in JP-8 at 110°F are given in Figure 2 and for No. 2 diesel in Figure 3. Figure 4 shows similar plots for TMP. The range of replicates for each point is shown to indicate the spread in the data. Good reproducibility is especially true for storage in jet fuel. These plots illustrate the linear response invariably obtained in these experiments. This is consistent with earlier observations with DMP and various other compounds under dark storage conditions.(2,3) Light storage affords quite different curves(2,3) and indicates a different reaction mechanism.

2.4.1.2 Studies with Other Nitrogen Compounds

The results of accelerated storage tests with nitrogen compounds other than pyrroles and indoles are summarized in Table 2. Structures for the compounds are presented in Figure 1. Shown in Table 2 are the total sediments formed; color tests and a breakdown of total sediment into insoluble and adherent are given in Appendix B. The sediments from these compounds tended to be more tacky than those obtained from pyrroles and indoles. Consequently most of the sediment obtained was of the adherent type. Most of the compounds tested produced some sediment, at least at long-storage times. However, none with the possible exception of 3,5-dimethylpyrazole approached the levels of sediment afforded by the more active pyrroles. Many of these compounds are basic. Once again it is worthwhile to point out that they are not nearly so active as the non-basic pyrroles and indoles.

2.4.1.3 Correlation of Chemical Structure and Reactivity in Sediment Formation

Figure 5 illustrates our current knowledge concerning the relative activities of nitrogen heterocycles. The various compounds studied so far are clustered in groups according to their realtive tendencies toward sediment formation under storage conditions. These range from extremely reactive (Group I) to essentially inactive (Group IV). Several things must be borne in mind when making these comparisons: (1) of all material studied only heterocyclic nitrogen compounds have afforded measurable sediment under these conditions; aromatic and aliphatic amines, amides, and nitriles, tested by themselves, were uniformly inactive; (2) these generalizations apply to compounds tested by themselves (see Section 2.3.2 for interactions); (3) these results apply to low temperature storage in the dark; heat and especially light can significantly change the order of reactivity. Although isolated exceptions occur the trends run clear. The most active compounds are non-basic nitrogen heterocycles with one or more alkyl groups, at least one of which is located on a carbon adjacent to the nitrogen atom.

The influence of various structural features is further illustrated by comparing the relative activities of various compounds within the same class. This is shown in Figure 6 where representative pyrroles, indoles and quinolines are given in descending order of reactivity. The following generalizations can be drawn:

FIGURE 2

SEDIMENT FORMATION FROM 2,5-DMP IN JET FUEL STORED AT 110°F

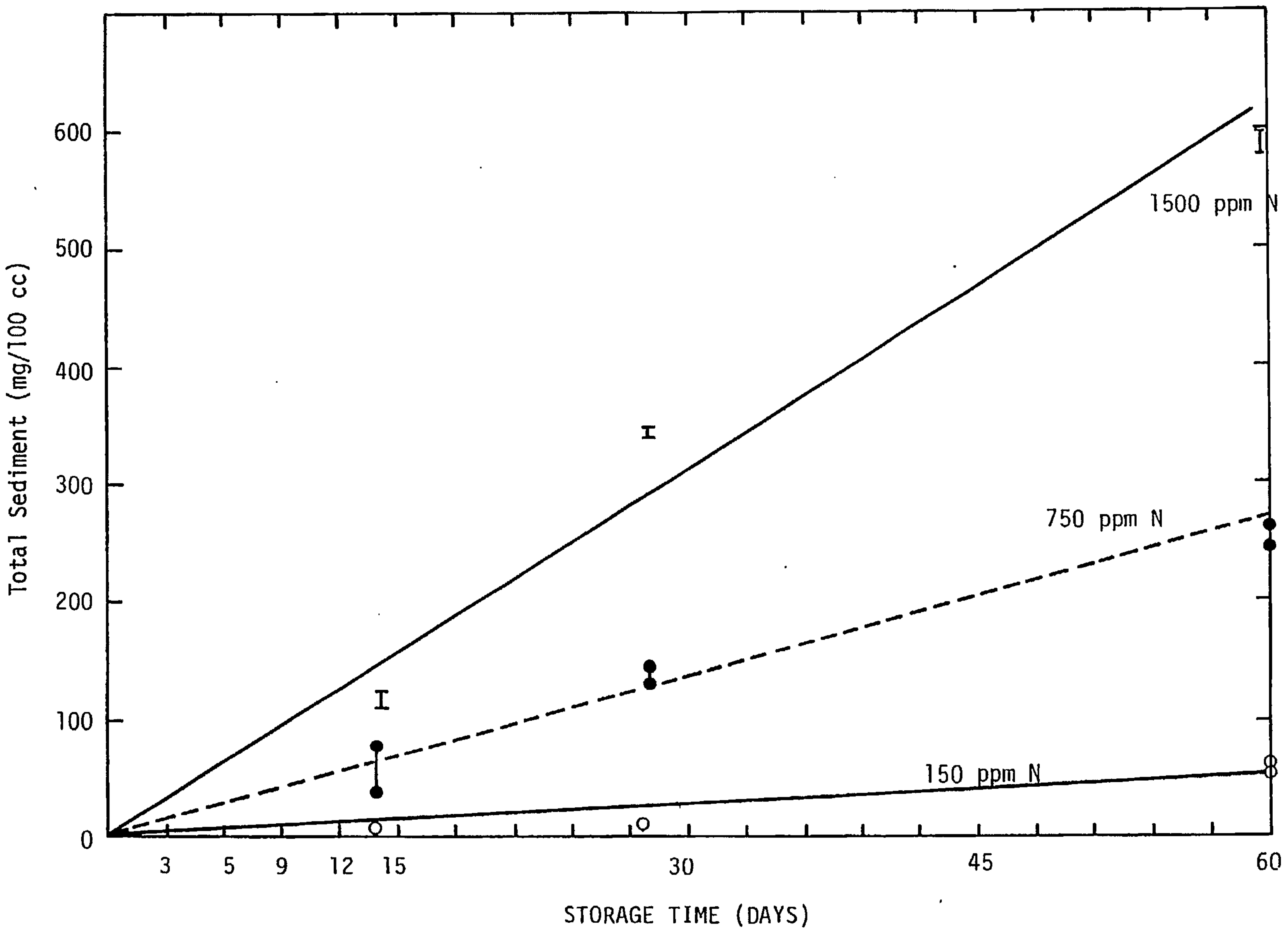


FIGURE 3

SEDIMENT FORMATION WITH 2,5-DMP IN NO. 2 DIESEL STORED AT 110°F

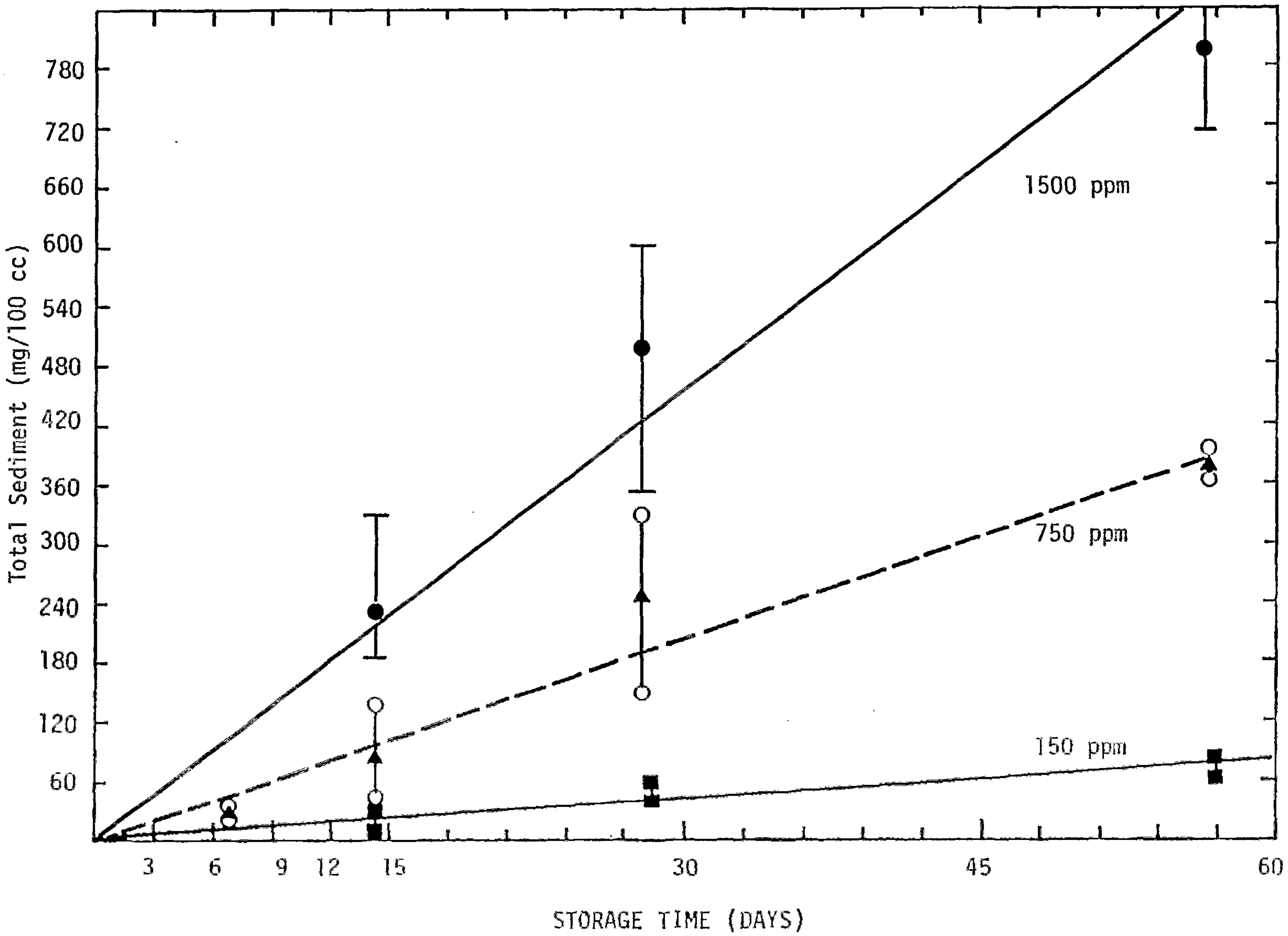


FIGURE 4

SEDIMENT FORMATION WITH 1,2,5-TRIMETHYLPYRROLE (TMP) IN NO. 2 DIESEL AT 110°F

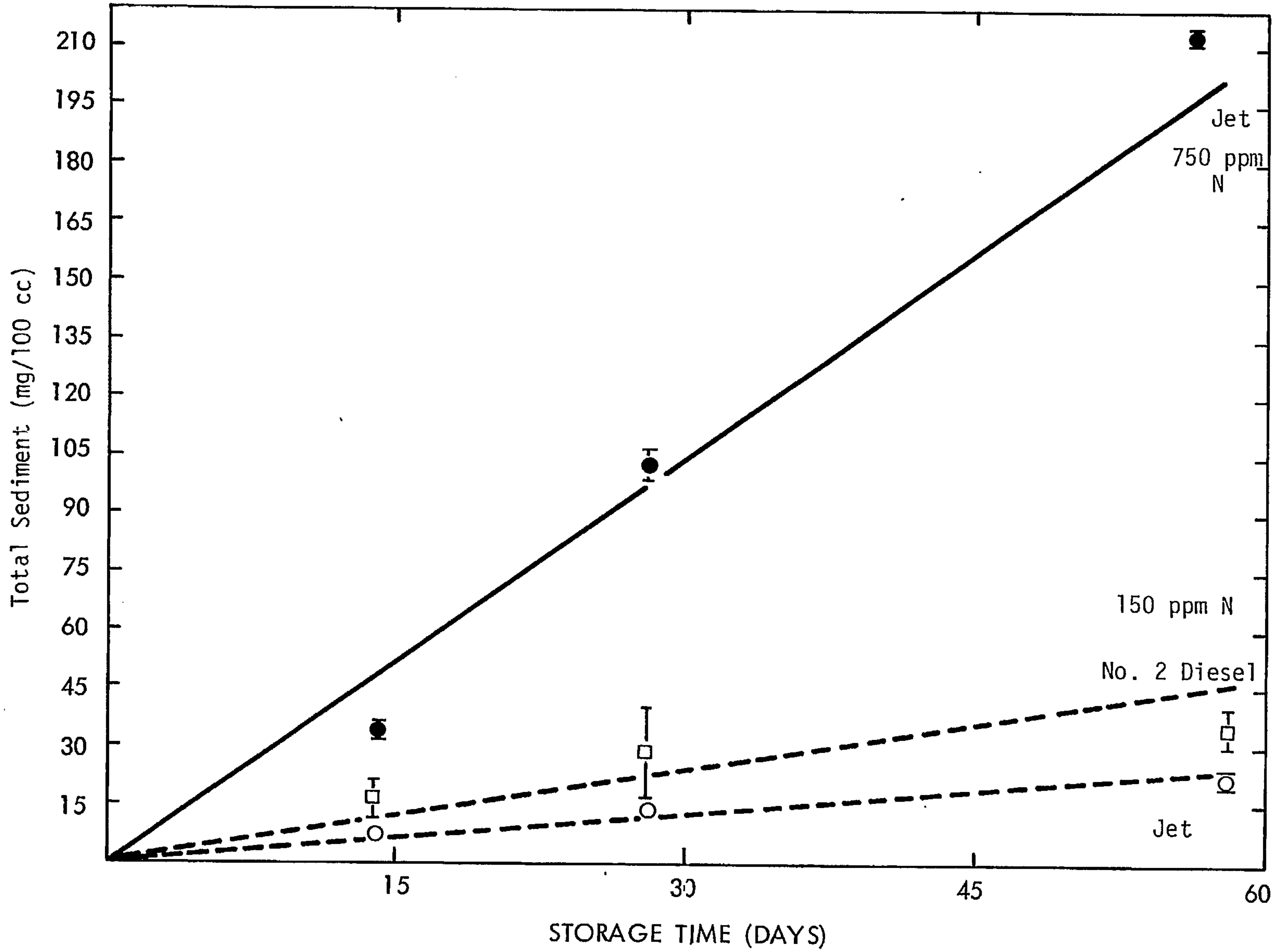


TABLE 2

EFFECTS OF VARIOUS ALKYLATED NITROGEN HETEROCYCLES ON SEDIMENT FORMATION IN NO. 2 DIESEL FUEL(a)

Nitrogen Compound(c)	Total Sediment (mg/100 cc) After(b)		
	28 Days	56 Days	112 Days
I. Pyrazole			
3-Methyl(d)	Trace	1.0	1.0
4-Methyl	0	0	0.2
3,5-Dimethyl(d)	0	Trace	80.9
II. Pyrazine			
2-Methyl (e)	0	1.0	--
2,3-Dimethyl	0	Trace	0.7
2,5-Dimethyl	0	Trace	2.0
2,6-Dimethyl	0	Trace	0.6
III. Pyrrolidine			
N-Methyl(e)	0	0	30.0
2,5-Dimethyl	0	Trace	11.5
IV. Piperazine			
N-Methyl	0	0	5.1
N,N-Dimethyl	0	0	1.2
2-Methyl	4.0	7.0	--
2,5-Dimethyl	0	Trace	17.9
2,6-Dimethyl	0	Trace	24.3
V. Isoquinoline	0	0	0
VI. Quinoline			
2-Methyl (Quinaldine)	1.8	4.0	5.0
2,6-Dimethyl	0	Trace	5.7
1,2-Dihydro-2,2,4-trimethyl	Trace	16.6	--
VII. Piperidine			
2-Methyl	Trace	Trace	13.2
3-Methyl	Trace	Trace	15.7
2,5-Dimethyl	0	0	2.1
2,6-Dimethyl	0	0	3.8
VIII. Misc. Heterocycles			
7-Azaindole	0.3	8.7	--
2-Methylbenzoxazole	0	Trace	Trace
2-Methylbenzothiazole	0	Trace	Trace
3-Methylpyridazine	4.2	4.0	--
IX. Non-Heterocyclic N Compounds			
n-Undecylcyanide	0	0	Trace
Trioctylamine	0	0	0
m-Tolylnitrile	0	0	Trace

(a) See Figure 1 for structures and numbering systems; storage at 110°F in dark; more details in Appendix B.

(b) Sum of insoluble plus adherent sediment; corrected for blank; average of 3 replicates unless otherwise noted.

(c) Added at 1500 ppm N level (wt/vol).

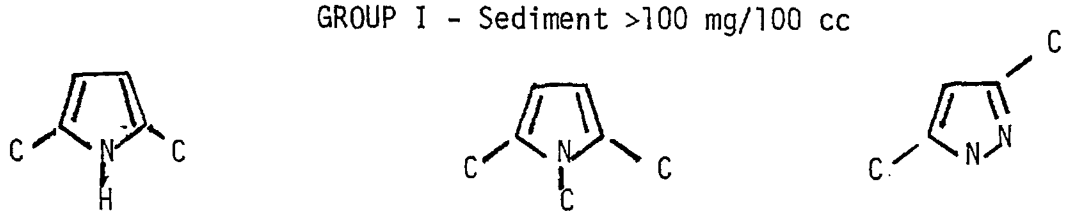
(d) Six replicates.

(e) Two replicates.

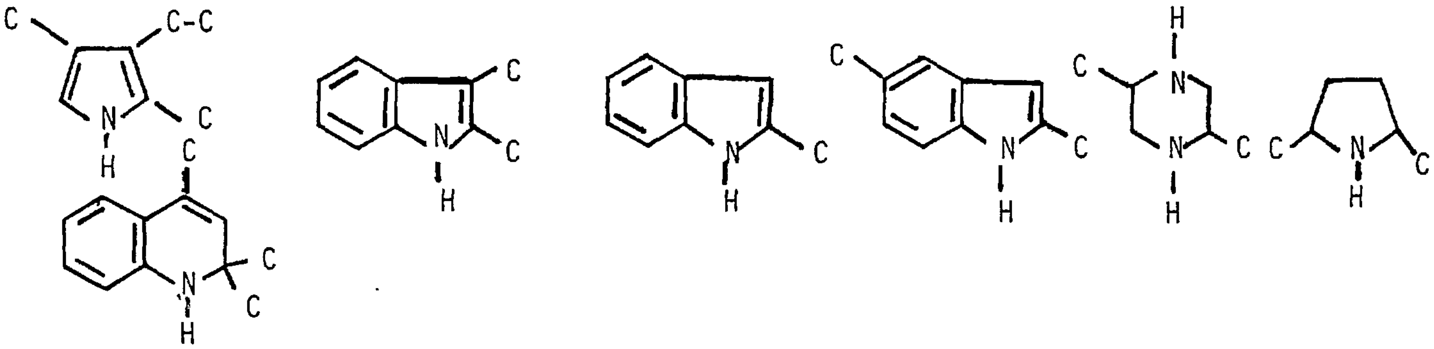
FIGURE 5

STRUCTURAL EFFECTS ON SEDIMENT FORMATION

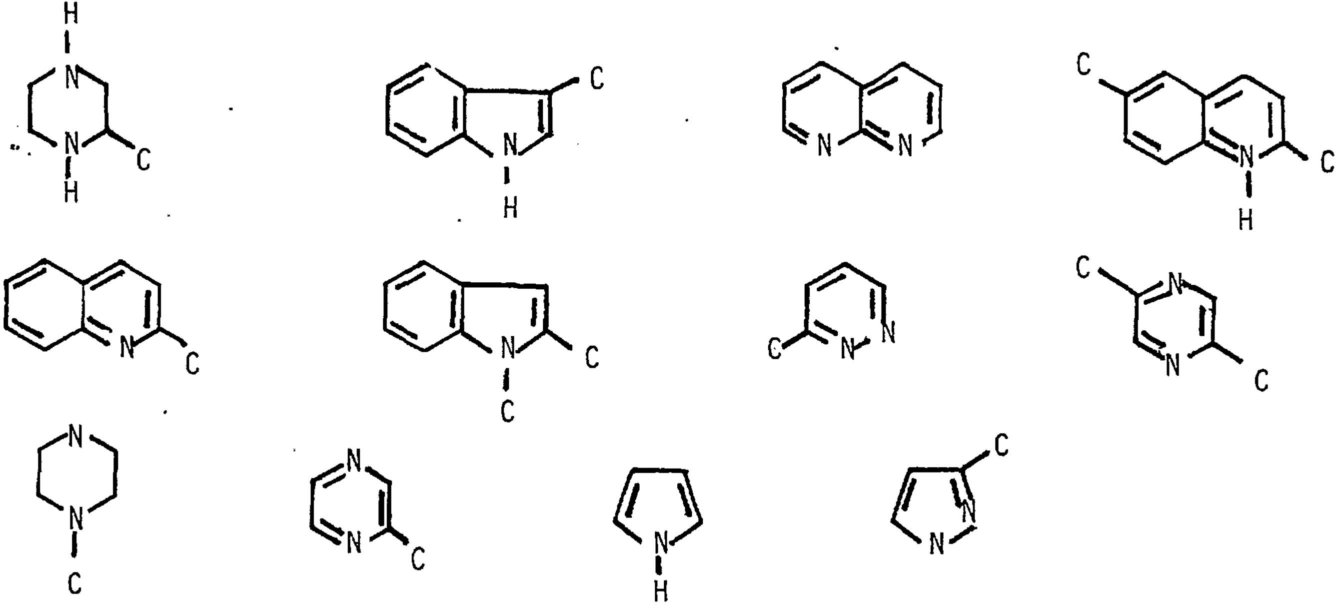
GROUP I - Sediment >100 mg/100 cc



GROUP II - Sediment >10 mg/100 cc



GROUP III - Sediment Level 2-10 mg/100 cc



GROUP IV - Sediment <2 mg/100 cc

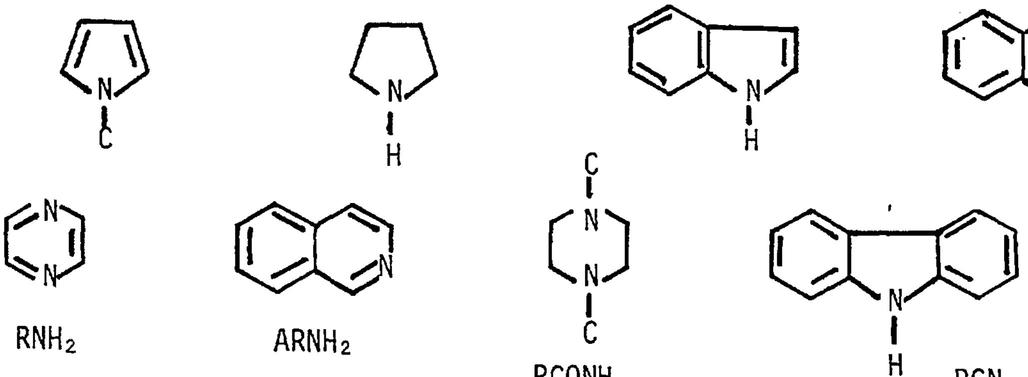
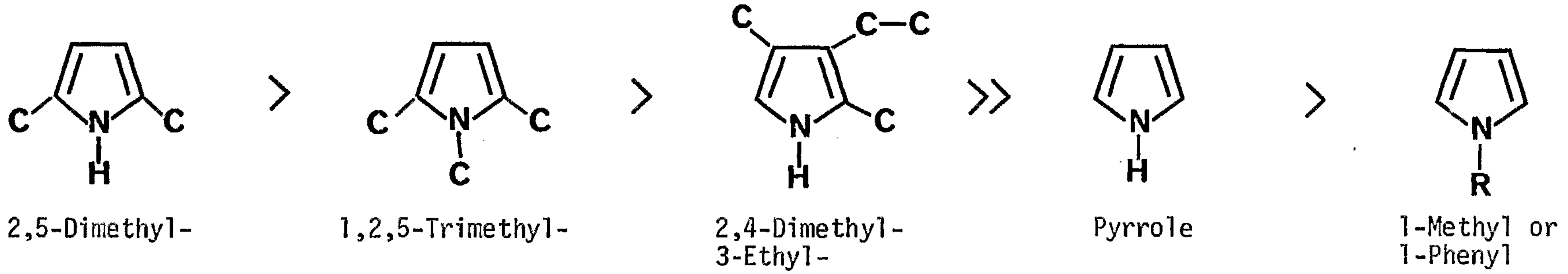


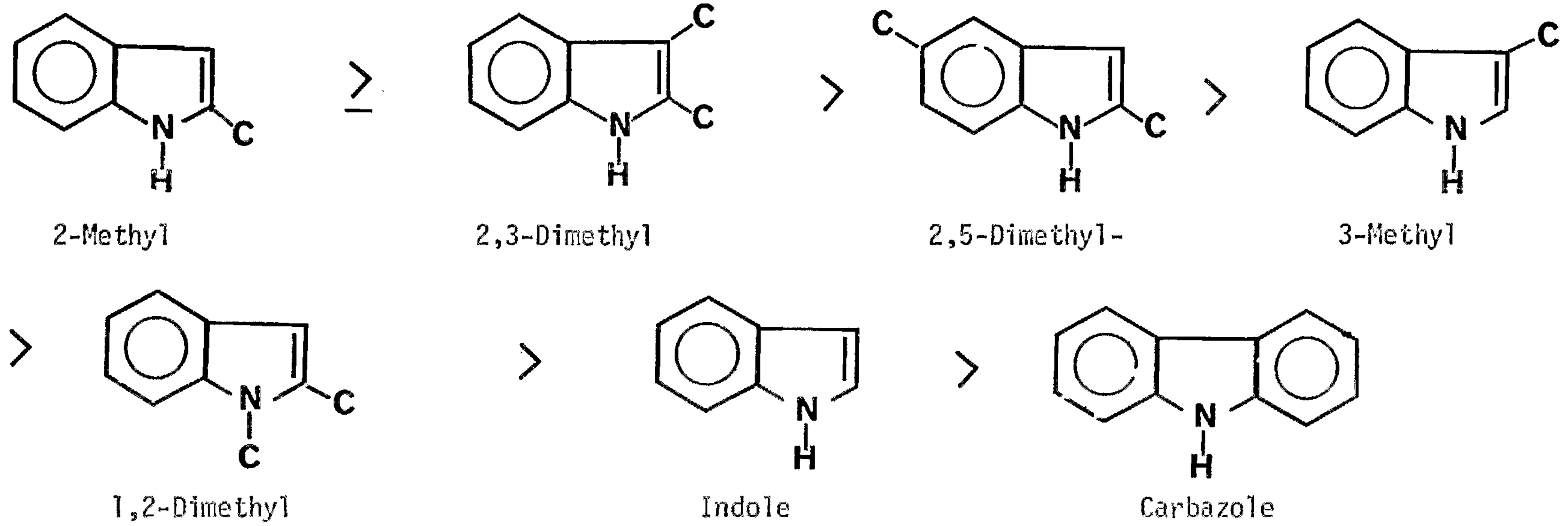
FIGURE 6

STRUCTURAL EFFECTS IN SEDIMENT FORMATION

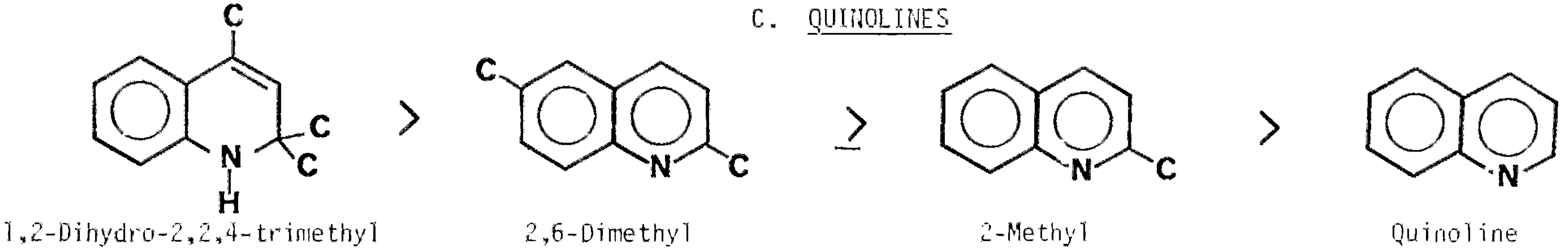
A. PYRROLES



B. INDOLES



C. QUINOLINES



- Alkyl groups are essential for significant reactivity in model compounds; unsubstituted heterocycles invariably gave negligible amounts of sediment in these tests.
- The positions adjacent to nitrogen are by far the most reactive. Compare 2,5-dimethylpyrrole to all other pyrroles and 2-methylindole to 3-methylindole.
- More than one alkyl group generally increases reactivity, especially if two or more are on carbons adjacent to nitrogen.
- Substitution on the nitrogen decreases activity; compare 2,5-dimethylpyrrole with 1,2,5-trimethylpyrrole, 1-methylpyrrole with pyrrole itself, 1,2-dimethylindole with 2- or 2,3-dimethylindole, etc.
- Unsaturation in the molecule seems to enhance reactivity but is not an essential prerequisite. Pyrroles are definitely more reactive than the corresponding pyrrolidines.
- Symmetrical, highly aromatic compounds, appear less reactive than their hydrogenated or partially hydrogenated counterparts (compare piperazines and piperidines and 1,2-dihydro-2,2,4-trimethylquinoline with alkylated quinolines). In addition, condensed aromatic structure (e.g. indoles) are much less active than noncondensed heterocycles such as pyrroles and pyrazoles.

Overall, it is clear that the most reactive compounds are unsaturated nitrogen heterocycles with multiple alkyl groups with at least one group being located adjacent to but not on the nitrogen atom.

2.4.2 Studies with Oxygen and Sulfur Compounds

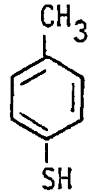
A variety of sulfur and oxygen compounds are known to be present in shale and coal liquids.(7) Representatives of the most prevalent types were investigated to determine whether (1) they could form sediment by themselves or (2) they could interact to enhance or retard sediment formation by nitrogen compounds. The compounds studied are shown in Figure 7.

None of the purely oxygen-containing species, tested by themselves, exhibited any tendency toward sediment formation; nor was any color developed with any of these compounds.

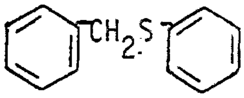
A summary of accelerated storage tests performed with sulfur compounds is given in Table 3. Even at levels up to 3000 ppm S, only *p*-thiocresol and *p*-toluenesulfonic acid afforded measurable sediments even on long-term storage.

FIGURE 7

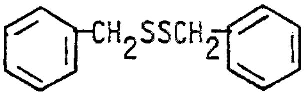
SULFUR AND OXYGEN COMPOUNDS USED IN SEDIMENT FORMATION STUDIES



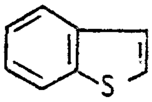
p-THIOCRESOL



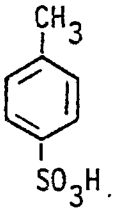
BENZYLPHENYL SULFIDE



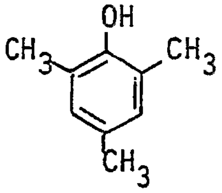
BENZYLDISULFIDE



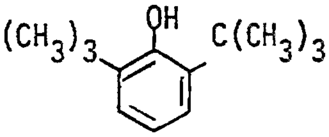
THIANAPHTHENE



p-TOLUENESULFONIC ACID



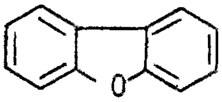
2,4,6-TRIMETHYLPHENOL



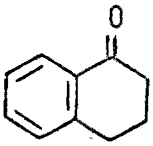
2,6-DI-t-BUTYLPHENOL

$CH_3(CH_2)_{11}SH$ n-DODECANETHIOL

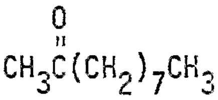
$CH_3(CH_2)_8CO_2H$ n-DECANOIC ACID



DIBENZOFURAN

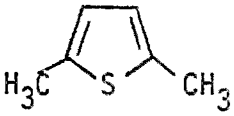


α-DECALONE

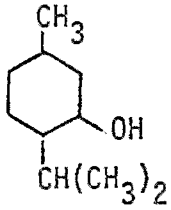


$CH_3\overset{O}{\overset{\|}{C}}(CH_2)_7CH_3$

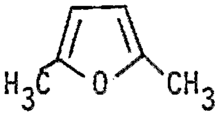
2-DECANONE



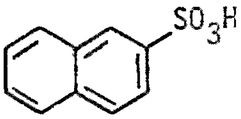
2,5-DIMETHYL-THIOPHENE



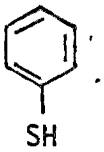
MENTHOL



2,5-DIMETHYLFURAN



2-NAPHTHALENE-SULFONIC ACID



THIOPHENOL

TABLE 3

ACCELERATED STORAGE TESTS WITH SULFUR COMPOUNDS(a)

Sulfur Compound(b)	Total Sediment(c) (mg/100 cc) in Fuel				
	No. 2 Diesel			Jet Fuel	
	28 Day	56 Day	160 Day	28 Day	56 Day
Benzylphenyl Sulfide	0	0	0	0	0
Benzyl Disulfide	0	0	0	0	0
t-Butyl Sulfide	--	--	--	0	0
Dodecanethiol	0	0	0	--	--
Thianaphthene	0	0	0	--	--
p-Thiocresol	0	0	20.7	--	--
p-Toluenesulfonic Acid	15.5	1609.6	--	20.0	

(a) Storage at 110°F.

(b) Present at 3000 ppm S level (wt/vol).

(c) Sum of insoluble and adherent deposits; average of 3 replicates.

The former gave a small amount of sediment after 5 months at 110°F but none prior to that time. The p-toluenesulfonic acid however, afforded copious amounts of black tar after 56 days' storage. These results are quite different from those from thermal stability studies which have shown that most of the compounds in Table 3 can produce significant amounts of carbonaceous deposits at temperatures above 300°F.(9) Thus, it appears that sulfur compounds of the type studied are relatively inert at 110°F, but much more reactive at higher temperatures. Sulfides, disulfides and thiols are known to decompose to form reactive free radicals at temperatures >200°F.(9,10) As a result, appreciable sediment <u>may</u> be produced at higher temperatures (>200°F) or, perhaps, on prolonged storage (>5-6 months) at 110°F which would be equivalent to approximately two years at ambient temperatures.

It appears from these studies that most common oxygen and sulfur compounds are not <u>by themselves</u> deleterious to fuel stability when present as trace impurities (i.e. at 3000 ppm or less). However, interaction experiments have indicated that some of these compounds can influence nitrogenous sediment formation. These studies are described in Section 2.4.3 below.

2.4.3 Interactions Between Pure Compounds (Task 3)

Interactions may be quite important to storage stability of synthetic fuels, especially those derived from shale and coal liquids. Previous work(2,3,11) has indicated that certain compounds, which do not produce sediment by themselves, can contribute to or stimulate sediment formation in others ("positive" interaction). In some instances, some materials interact to inhibit sediment formation ("negative" interaction). Interaction studies were conducted with both model compounds and with actual shale-derived fuels. The latter are discussed in the section on shale liquids below.

2.4.3.1 Interactions Between Pairs of Nitrogen Compounds

The results of a study to determine whether N-N interactions can occur under conditions of dark storage are given in Tables 4 and 5. These results are summarized and their significance analyzed in Table 6. In order to determine whether an interaction actually occurred the data were analyzed by means of 2 x 2 factorial experiments. A typical design involving DMP and isoquinoline is shown in Figure 8. The analysis shown in Figure 8 indicates a likely positive interaction after 28 days and clear cut interaction after 56 days. Thus, after 56 days the total sediment obtained with both nitrogen compounds together (127.5 mg/100 cc) was more than double the <u>sum</u> of the two which would be expected if they acted independently (61.8 mg/100 cc). To determine the significance of the results, the data were subjected to Students "t" test.(12) Results of significance tests are also summarized in Table 6. Plots of typical positive interactions are shown in Figure 9. Those shown are DMP interacting with isoquinoline and trioctylamine. Although significant, these interactions are relatively mild compared to interactions between two species both of which are deleterious (e.g., DMP and TMP).

TABLE 4

NITROGEN-NITROGEN INTERACTION STUDIES WITH PYRROLES DURING 110°F STORAGE IN NO. 2 DIESEL AND JET FUELS

Nitrogen Compound	Level Added (ppm N)(a)	Fuel	Total Sediment (mg/100 cc)(b)			
			14 Days	28 Days	56 Days	73 Days
2,5-Dimethylpyrrole (DMP)	150	Diesel	23.9	40.9	74.5	97.1(c)
"	750		85.6	245.8	362.0	410.0(c)
"	150	Jet	--	18.3	--	53.7(c)
"	750		--	140.5	--	330.7(c)
1,2,5-Trimethylpyrrole (TMP)	150	Diesel	16.0	28.4	34.6	--
"	750		--	117.1	--	--
"	150	Jet	--	13.5	--	--
Pyrrole	1500	Diesel	--	3.0	5.0(d)	6.0(d)
1-Methylpyrrole	1500	Diesel	--	0	0.7	
DMP	150	Diesel	64.9	98.1	164.3	--
Plus TMP	150					
DMP	150	Jet	--	56.3	--	--
Plus TMP	150					
DMP	150	Diesel	--	21.8	57.2	71.2
Plus Pyrrole(e)	1350					
DMP	150	Diesel	--	31.3	--	
Plus 1-Methylpyrrole	1350					

(a) Wt/vol basis; see Figure 1 for structures.

(b) Sum of insoluble plus adherent; corrected for solvent blanks; average of 3 replicates unless otherwise noted.

(c) Extrapolated.

(d) Estimated.

(e) Six replicates.

TABLE 5

INTERACTIONS INVOLVING PYRROLES, INDOLES AND OTHER NITROGEN COMPOUNDS(a)

Nitrogen Compound(b)	Level Added (ppm N)(b)	Fuel	Total Sediment (mg/100 cc)(c) 14 Days	28 Days	56 Days	73 Days
2-Methylindole	1500	Diesel	--	13.0	26.4	
	750		0.4	9.8	15.0	19.5(d)
	750	Jet	--	11.4	--	27.0(d)
3-Methylindole	1500	Diesel	--	0.5	4.5	
	750			0.2	1.7	
Trioctylamine	1500	Diesel	0	0	0	0
		Jet	--	0	0	0
Tripropylamine	1500	Diesel	0	0	0	0
		Jet	--	0	0	0
Isoquinoline	1500	Diesel	0	0	0	0
		Jet	--	0	0	0
DMP Plus 2-Methylindole	150 1350	Diesel	--	15.0(e)	27.3(f)	
DMP Plus 2-Methylindole	750 750	Diesel	91.7	103.3	--	83.3
DMP Plus 2-Methylindole	750 750	Jet	--	139.7	--	441.0
2-Methylindole Plus 3-Methylindole	750 750	Diesel	--	0.2(f)	0.3(f)	
DMP Plus 3-Methylindole	150 1350	Diesel	--	48.2(e)	94.0(e)	--
DMP Plus Isoquinoline	150 1350	Diesel	--	54.9(e)	127.5(e)	--
DMP Plus Isoquinoline	150 1350	Jet	--	32.9	--	94.3
DMP Plus Trioctylamine	150 1350	Diesel	--	49.8(e)	115.8(e)	--
DMP Plus Trioctylamine	150 1350	Jet	--	17.5	--	--
DMP Plus Tripropylamine	150 1350	Diesel	--	38.9	--	97.4
DMP Plus Tripropylamine	150 1350	Jet	--	17.8	--	62.7
TMP Plus Isoquinoline	150 1350	Diesel	--	35.5(e)	--	67.8

(a) See Table 4 for storage details.
(b) See Tables 1 or 4 for sediment from DMP and TMP tested alone. Levels are on N basis (wt/vol).
(c) Average of 3 replicates unless otherwise noted; total sediment is sum of insoluble plus adherent.
(d) Extrapolated.
(e) Six replicates.
(f) Two replicates.

TABLE 6

SUMMARY OF N-N INTERACTION STUDIES(a)

Fuel	Compound A	Compound B	Time (Days)	Type(b)	Significance(c)
Diesel	DMP	TMP	14	Pos.	Highly significant (t = 30; p <.005)
			28	Pos.	Significant (t = 6.7; p <.01)
			56	Pos.	Highly significant (t = 33; p <.005)
Diesel	DMP	1-Methylpyrrole	28	Neg.	Significant (t = 19; p <.05)
Diesel	DMP	Pyrrole	28	Neg.	Highly significant (t = 15; p <.005)
			56	Neg.	Significant (t = 10; p =.05)
			17	Neg.	Highly significant (t = 26; p <.005)
Diesel	DMP(d)	2-Methylindole(d)	28	Neg.	Highly significant (t = 52; p <.005)
			56	Neg.	Significant (t = 6.5; p =.05)
Diesel	DMP(e)	2-Methylindole(e)	14	None	--
			28	Neg.	Significant (t = 3.2; p <.05)
			73	Neg.	Highly significant (t = 132; p <.005)
Diesel	DMP	3-Methylindole	28	Pos.	Doubtful (t = 1.9; p =.01)
			50	Pos.	Significant (t = 5.2; .0257 > p > .01)
Diesel	DMP	Trioctylamine	28	Pos.	Doubtful (t = 0.6; p <0.1)
			56	Pos.	Significant (t = 4.5; p =.01)
Diesel	DMP	Tripropylamine	28	None	--
			73	None	--
Diesel	TMP	Isoquinoline	28	Pos.	Doubtful (t = 5.5; p = .025)
			73	Pos.	Highly significant (t = 34; p <.005)
Diesel	2-Methylindole	3-Methylindole	28	Neg.	Highly significant (t >100; p <.005)
			56	Neg.	Highly significant (t = 86; p <.005)
Jet	DMP	TMP	28	Pos.	Highly significant (t = 18; p <.005)
Jet	DMP	2-Methylindole	28	None	--
			73	Pos.	Doubtful (t = 8; p = .05)
Jet	DMP	Tripropylamine	28	None	--
			73	Pos.	Doubtful (t = 3; p = .05)
Jet	DMP	Isoquinoline	28	Pos.	Highly significant (t = 20; p <.005)
			73	Pos.	Highly significant (t = 20; p <.005)
Jet	DMP	Trioctylamine	28	None	--

(a) Three or more replicates; 110°F storage; DMP = 2,5-dimethylpyrrole, TMP = 1,2,5-trimethylpyrrole (see Tables 4 and 5 for storage data).

(b) Pos = "positive" interaction, two compounds together give more sediment than sum of same compounds tested separately; neg = "negative", two compounds together give less than sum of same compounds separately.

(c) Students' "t" test (Ref. 12, Sec. 4).

(d) DMP at 150 ppm N; 2-methylindole at 1350 ppm N.

(e) Both at 750 ppm N.

FIGURE 8

2 x 2 FACTORIAL ANALYSIS OF AN INTERACTION BETWEEN 2,5-DIMETHYLPYRROLE (A, 150 ppm) AND ISOQUINOLINE (B, 1350 ppm) IN NO. 2 DIESEL(a)

		PRESENCE OF COMPOUND A	
		NO	YES
PRESENCE OF COMPOUND B	NO	0.5	40.9(b)
	YES	0.0(c)	54.9

28-DAYS STORAGE AT 110°F

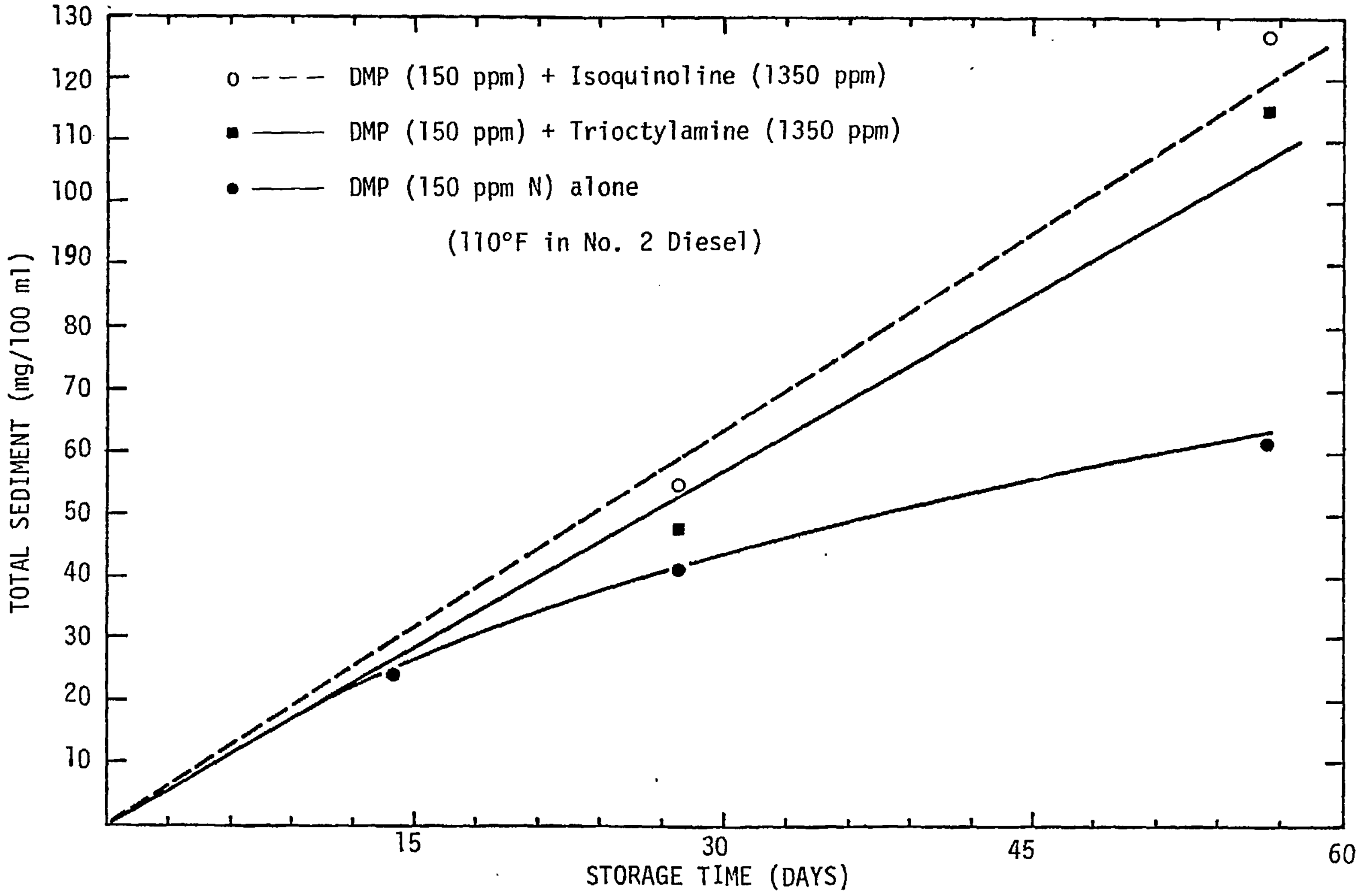
		PRESENCE OF COMPOUND A	
		NO	YES
PRESENCE OF COMPOUND B	NO	0.5	61.3(b)
	YES	0.0(c)	127.5

56 DAYS STORAGE AT 110°F

(a) Sediment shown as mg/100 cc.
(b) Amount expected from 150 ppm DMP alone.
(c) Amount from 1350 ppm Isoquinoline alone.

FIGURE 9

N-N INTERACTIONS



These results suggest that interactions can occur between various nitrogen-containing species. These have important implications for fuel stability. Certain compounds, for example trioctylamine and isoquinoline, while relatively innocuous when present alone can contribute significantly to sediment formation in the presence of compounds such as DMP. On the other hand, some materials, such as 2-methylindole, may actually have a stabilizing effect. The results of the tests with 2-methylindole are especially interesting and surprising. They indicate a statistically significant "negative" or stabilizing effect. This includes the interaction between 2-methylindole and 3-methylindole. Other "negative" interactions include those between DMP and both pyrrole and 1-methylpyrrole. In nearly all cases interactions which were originally discovered in No. 2 diesel were confirmed by studies in jet fuel. The few exceptions were of doubtful significance.

The causes of these interactions are, as yet, unknown; nor can one find any correlation between the structures or properties of compounds and their tendency to interact. However, since interactions are also observed in actual shale liquids (see Section 2.5) they are important and should not be overlooked.

2.4.3.2 Interactions Between Nitrogen Compounds and Sulfur or Oxygen Compounds

Previous work suggested that important interactions can occur between nitrogen and sulfur or oxygen compounds.(2,3,7,11) Several of these interactions were "negative" (i.e., stabilizing). A number of experiments were performed in the present program to test for these interactions in broad range fuels. Results of these are given in Table 7. The interactions discovered and their significance are summarized in Table 8. The thiols, especially the aromatic thiols, gave significant negative interactions with DMP even during long-term storage (see also Figure 10). Such interactions were observed in earlier work, but the effect was reversed on long-term storage especially in the light.(2,3) It has been suggested that this was due to oxidation of the thiols to sulfonic acids; the former being inhibitors and the latter accelerators.(3) This view is supported by a considerable body of literature(8,13-15) in which data are presented which show that aromatic thiols are accelerators of sediment formation, probably *via* their oxidation products, sulfonic acids. Since the results of this program were quite different, a series of experiments were performed to confirm the preliminary data shown in Tables 7 and 8. These are described in Section 2.4.3.3.

Surprisingly, no effects were observed with either decanoic acid or 2,6-di-*t*-butylphenol when tested with DMP in No. 2 diesel fuel (Tables 7 and 8). Work in purified decane indicated a significant accelerating effect with most organic acids including decanoic while phenols were inhibitors.(2,3) This seeming discrepancy was investigated and is described in Section 2.4.3.4. It would appear from these preliminary studies that important N-S and N-O interactions can occur in broad-range fuels, and they must be taken into consideration when processing shale liquids (see Section 2.5.3 on shale liquid interactions).

TABLE 7

INTERACTIONS BETWEEN NITROGEN COMPOUNDS AND VARIOUS SULFUR AND OXYGEN COMPOUNDS IN NO. 2 DIESEL FUEL[a]

Nitrogen Compound (ppm N)[b]	Sulfur or Oxygen Compound (ppm S or O)[b]	Total Sediment (mg/100 cc)[c]			
		7 Days	14 Days	28 Days	56 Days
DMP (750)	--	24.7	85.6	245.8	362.0
--	n-Decanoic Acid (100)	0	0	0	0
DMP (750)	Pyrrole-2-carboxyaldehyde (100)	9.2			
Pyrrole (1500)	--	--	0.7	3.0	
Pyrrole (1350)	Pyrrole-2-carboxaldehyde (100)	--	Trace	Trace	Trace
2-Methylindole (750)	--	--	0.4	9.8	15.0
2-Methylindole (750)	n-Decanoic Acid (100)	--	--	3.0	Trace
--	2,6-Di-t-butylphenol (100)	0	0	0	0
DMP (750)	2,6-Di-t-butylphenol (100)	--	107.7	293.5	--
DMP (750)	n-Decanoic Acid (100)	--	90.2	256.0	376.5
--	Thiophenol (3000)	0	0	0	
DMP (750)	Thiophenol (3000)	13.1	14.4	70.7	160.0
--	p-Thiocresol (3000)	0	0	0	
DMP (750)	p-Thiocresol (3000)	12.6	20.3	62.4	
--	Pyrrole-2-carboxaldehyde (100)	0	0	0	
--	Benzylphenyl Sulfide (3000)	0	0	0	0
DMP (750)	Benzylphenyl Sulfide (3000)	--	95.6	216.1	--
--	n-Dodecanethiol (3000)	0	0	0	0
DMP (750)	n-Dodecanethiol (3000)	--	71.6	373.2	--
--	p-Toluenesulfonic Acid[d]	0	0	15.5	
DMP (750)	p-Toluenesulfonic Acid[d]	--	71.5	233.4	--

(a) Storage at 110°F.
(b) DMP = 2,5-Dimethylpyrrole; for structures see Figures 1 and 7.
(c) Sum of insoluble plus adherent sediment; average of 3 replicates.
(d) Solubility problems; saturated solution was employed.

TABLE 8

SUMMARY OF INTERACTIONS BETWEEN 2,5-DIMETHYLPYRROLE (DMP) AND S AND O COMPOUNDS IN NO. 2 DIESEL FUEL[(a)]

Compound A (ppm)[(b)]	Compound B (ppm)[(c)]	Storage Time (days)	Type of Interaction[(d)]	Significance of Test[(e)]
DMP (750)	Decanoic Acid (100)	14	None	
DMP (750)	Decanoic Acid (100)	28	None	
DMP (750)	Decanoic Acid (100)	56	None	
DMP (750)	Benzylphenyl Sulfide (3000)	14	None	
DMP (750)	Benzylphenyl Sulfide (3000)	28	None	
DMP (750)	p-Thiocresol (3000)	7	Negative	Significant ($t = 60$; $p = 05$)
DMP (750)	p-Thiocresol (3000)	14	Negative	Highly Significant ($t = 13.0$; $p < .005$)
DMP (750)	p-Thiocresol (3000)	28	Negative	Highly Significant ($t = 19.1$; $p < .005$)
DMP (750)	Thiophenol (3000)	7	Negative	Highly Significant ($t = 11.1$; $p < .005$)
DMP (750)	Thiophenol (3000)	14	Negative	Highly Significant ($t = 71.0$; $p < .005$)
DMP (750)	Thiophenol (3000)	28	Negative	Highly Significant ($t = 28.3$; $p < .005$)
DMP (750)	Dodecanethiol (3000)	14	None	
DMP (750)	Dodecanethiol (3000)	28	Positive	Not Significant
DMP (750)	2,6-Di-t-Butylphenol (100)	14	None	
DMP (750)	2,6-Di-t-Butylphenol (100)	28	None	
DMP (750)	Pyrrole-2-carboxaldehyde (100)	7	None	
DMP (750)	Pyrrole-2-carboxaldehyde (100)	14		
DMP (750)	p-Toluenesulfonic Acid[(g)]	14	None	
DMP (750)	p-Toluenesulfonic Acid[(g)]	28	None	
Pyrrole (1350)	Pyrrole-2-Carboxaldehyde (100)	14	None	
Pyrrole (1350)	Pyrrole-2-carboxaldehyde (100)	28	Negative	Not Significant
2-Methylindole (750)	n-Decanoic Acid (100)	28	None	
2-Methylindole (750)	n-Decanoid Acid (100)	56	Negative	Doubtful

(a) Storage at 110°F.
(b) DMP = 2,5-dimethylpyrrole.
(c) See Figure 7 for structures.
(d) Pos = "positive" interaction, two compounds together give more sediment than sum of same compounds tested separately; neg = "negative", two compounds together give less than sum of same compounds separately.
(e) Students "t" test (Ref. 12, Sec. 4)

2.4.3.3 Interactions Involving Nitrogen Compounds with Thiophenols and Sulfonic Acids

Nixon,(8) Sauer,(3) Mosher(15) and others have reported that aromatic thiols strongly accelerate sediment formation, including nitrogenous sediment, in petroleum derived heating fuels as evidenced by high temperature (212°F) or long-term (one year) storage tests. It was assumed that the thiols were first oxidized to sulfonic acids which were the actual catalysts. The results of experiments described in the preceeding section, however, indicate that thiols are inhibitors of sediment formation at least in the case of DMP*. At least two reasons can account for these seeming discrepancies: (1) at the levels first employed in this study (3000 ppm S) and at fairly short storage periods, thiols are inhibitors since they are acting as antioxidants (for the importance of dissolved oxygen to sediment formation see Section 2.4.5.3); (2) low levels of thiols may act as accelerators, especially at long-storage periods; (3) the mechanism of sediment formation in the case of DMP is different from that described by others. The results of experiments designed to check these theories are summarized in Table 9. The data indicate a highly significant inhibiting effect (negative interactions) for thiophenol at all levels studied at least up to 14 days at 110°F. For higher levels this extends to at least 28 days for 1000 ppm S and in excess of 120 days for 3000 ppm S (Table 9 and Figure 10). It appears that the effect is roughly proportional to concentration. This is illustrated by the curves in Figure 11. No evidence for accelerating effects has yet been obtained under dark storage conditions.

Sulfonic acids appear to be mild accelerators at best (Table 9). Significant positive interactions were observed with DMP and *p*-toluenesulfonic acid in both jet fuel and decane. However, the magnitude of the effect was small. No significant interaction could be detected in No. 2 diesel.

Thus, it appears that thiophenols are active inhibitors of nitrogenous sediment formation with DMP, probably acting as antioxidants, at least so long as appreciable quantities of the unchanged thiol remain. On long-term storage, especially in the presence of light, the inhibitor may be consumed or converted to a catalyst and the reaction pursues a different course.

2.4.3.4 Effects of Decanoic Acid

Experiments using purified n-decane as the diluent at ambient temperatures have shown that organic acids, especially *n*-decanoic have a strong accelerating effect on sediment formed from DMP.(2,3) The effects were observed in both light and dark storage conditions. Since no interaction could be detected in the present studies (which employed No. 2 diesel as the model fuel under accelerated (110°F) storage conditions), a separate study was undertaken to investigate these seemingly contradictory results. Three diluents, No. 2 diesel, jet fuel and purified *n*-decane were used and samples were stored both at ambient temperatures and at 110°F. The results are presented in Table 10

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* It is noteworthy that similar inhibitions are observed in actual shale liquids (see Section 2.5.3 below).

TABLE 9

INTERACTION STUDIES WITH DMP AND AROMATIC SULFUR COMPOUNDS[a]

Fuel	DMP (ppm N)[b]	Sulfur Compound	ppm S	Total Sediment (mg/100 cc)[c]						
				7 Days	14 Days	28 Days	56 Days	80 Days	112 Days	128 Days
Diesel	750	None	--	24.7	85.6	245.8	362.0	422.6	--	600.0
	750	Thiophenol	3000	13.1	14.4	70.7	160.0	166.5	191.1	
	750	Thiophenol	1000		22.4	55.5				
	750	Thiophenol	500	12.4	36.4					
	750	Thiophenol	100	20.5	41.6					
	750	p-Thiocresol	3000	12.6	20.3	62.4				
	None	p-Toluenesulfonic Acid	(d)	--	0	15.5	>1000			
	750	p-Toluenesulfonic Acid	(d)	--	71.5	233.4				
Jet	750	None	--	--	61.3	140.5	253.7			
	750	p-Thiocresol	3000	--	--	58.8	83.9			
	750	Thiophenol	3000	--	49.8	88.4				
	750	p-Toluenesulfonic Acid	(d)		59.8	168.1[e]				
Decane	750	None	--	--	44.1	102.0				
	750	p-Toluenesulfonic Acid	(d)	--	53.2[e]	125.9[e]				

(a) Stored at 110°F.

(b) DMP = 2,5-Dimethylpyrrole; added as ppm N.

(c) Sum of insoluble plus adherent deposits; ave. of 3 or 4 replicates.

(d) Saturated solution (>3000 ppm S).

(e) This represents a statistically significant (Student's test) positive interaction.

FIGURE 10

NEGATIVE INTERACTION BETWEEN DMP AND THIOPHENOL IN NO. 2 DIESEL AT 110°F

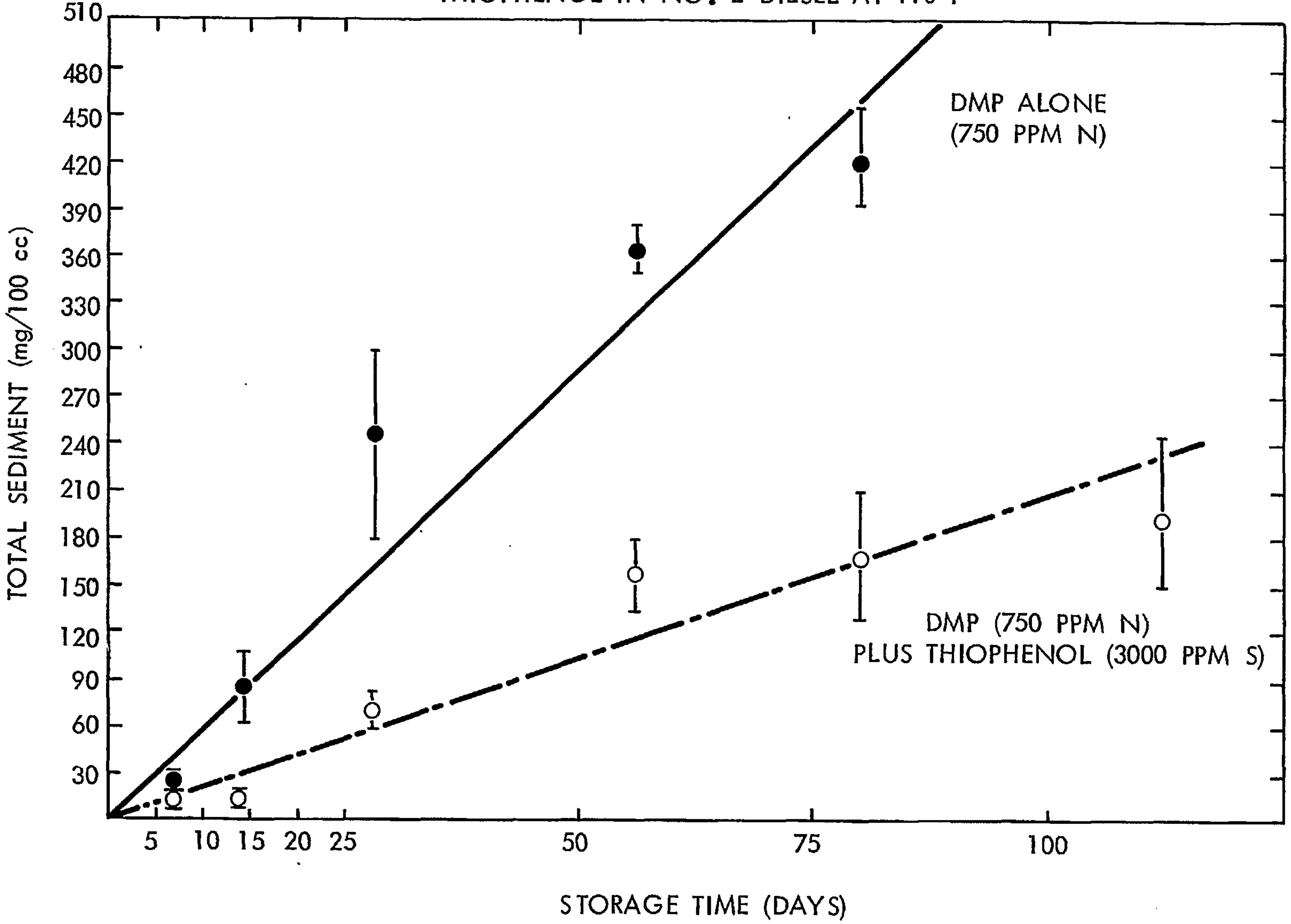


FIGURE 11

EFFECTS OF VARIOUS CONC. OF THIOPHENOL ON SEDIMENT FORMATION WITH DMP

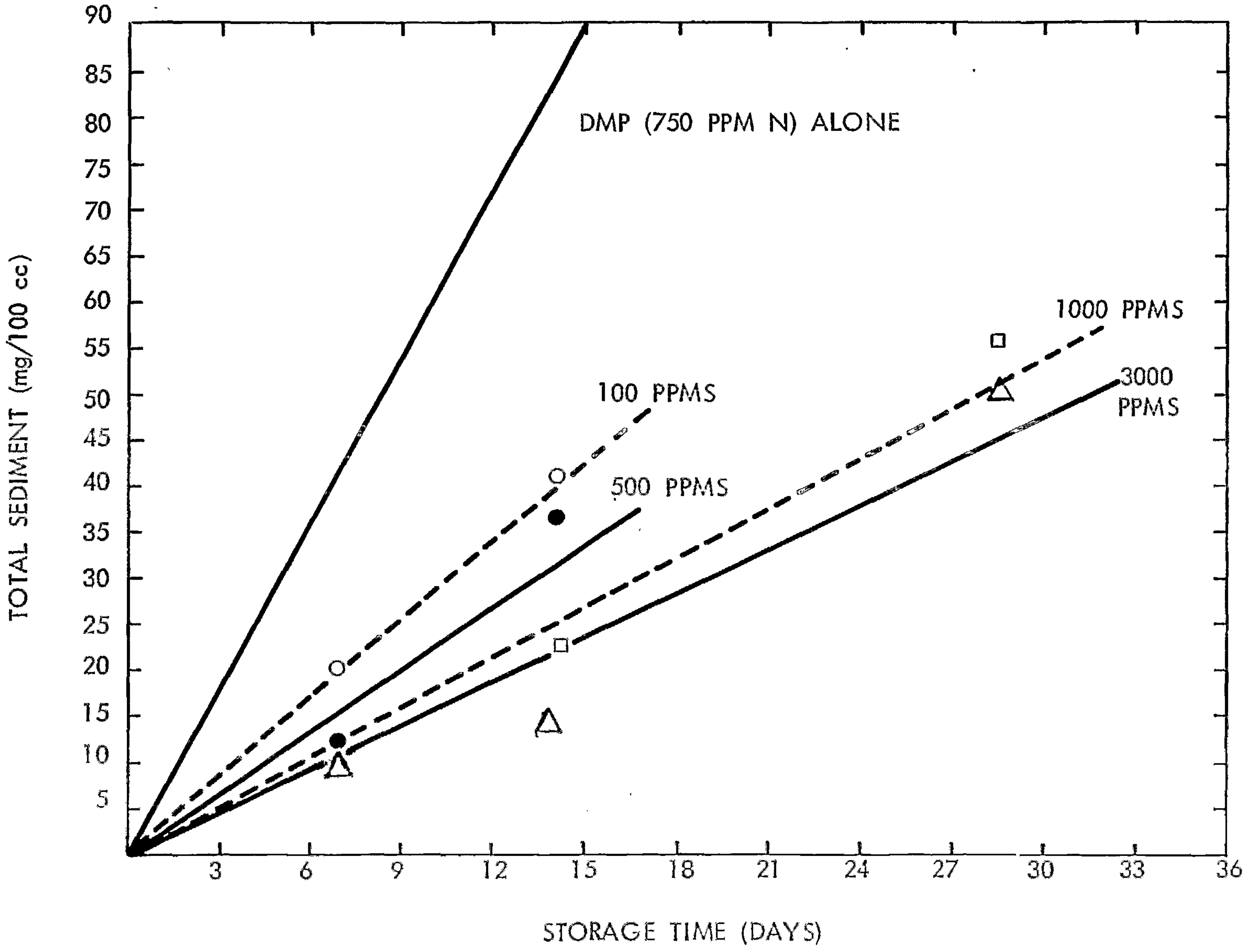


TABLE 10

EFFECTS OF n-DECANOIC ACID ON SEDIMENT FORMATION WITH 2,5-DIMETHYLPYRROLE (DMP) IN VARIOUS MODEL FUEL SYSTEMS(a)

FUEL	STORAGE Temp (°F)	ppm DMP(c)	ppm R CO_2H(d)	Total Sediment(b) (mg/100cc) After 14 Days	28 Days	50 Days
Diesel	72	750	---	18.6	42.6	-----
		750	100	16.1	46.1	-----
	110	750	---	88.5	245.8	380.1
		750	100	88.0	245.0	500.0
Jet	72	750	---	7.0	-----	-----
		750	100	12.7	-----	-----
	110	750	---	61.3	140.5	253.7
		750	100	84.7	227.0	432.9
n-Decane(e)	72	750	---	18.3	38.1	-----
		750	100	69.2	103.9	-----
	110	750	---	44.1	101.5	-----
		750	100	92.8	225.2	375.0

(a) Some data from reference 2.

(b) Sum of insoluble and adherent sediments adjusted for blanks (sec. table 12).

(c) Nitrogen basis.

(d) R CO_2H = n-decanoic acid; ppm on oxygen basis.

(e) Purified over silica gel and activated alumina.

and illustrated by the plots in Figure 12. Previous work has shown that decanoic acid alone afforded no sediment or color change in hydrocarbon fuels.

These results confirmed the observation that decanoic acid interacts strongly with DMP in decane to promote sediment formation. A significant positive interaction also exists in jet fuel. In diesel, however, no interaction occurs. A possible explanation for these results lies in the fact that the base No. 2 diesel has an appreciable acid titer (Appendix Table A-1) while both the jet fuel and *n*-decane were acid free. It is interesting that the curves for DMP in diesel with and without added acid are virtually superimposable with those of both jet fuel and decane *with* added acid (Figure 12). This suggests that acid, present normally in diesel fuel, may contribute to the enhanced sediment formation in that fuel.

2.4.4 Effects of Hydrocarbon Content of Base Fuel on Sediment Formation (Task 4)

The differences in sediment formation rates observed with various diluents (see Section 2.4.1.1) indicates the chemical characteristics of the base fuels can exert a significant influence on the amounts of nitrogenous sediment obtained. This may be due to differences in solubility characteristics of the base fuels or to the presence of trace impurities which accelerate or inhibit sediment formation. The effects of the hydrocarbon content of the base fuels was studied by adding representatives of the most prevalent hydrocarbon types, *n*-paraffins, branched paraffins, naphthenes (cycloparaffins), aromatics and olefins to the base fuels and determining their influence on sediment formation with various nitrogen compounds. The hydrocarbons were added at levels approximating their normal occurrence in most distillate fuels.(15) The more highly refined jet fuel was used for the experiments using olefins, because adding small quantities of olefins to a complex fuel such as No. 2 diesel would likely lead to equivocal results.

The results of the hydrocarbon study are summarized in Tables 11 and 12. DMP at the 1500 ppm N level was employed as the nitrogen compound. The results shown in Table 11 suggest that the major hydrocarbon types, aromatics, naphthenics and monoolefins, have little influence on nitrogenous sediment. Even the reactive mono-olefin, *α*-methylstyrene, showed no tendency to promote sediment formation.

Somewhat different results were obtained with certain representative diolefins and vinyl compounds which may be present in small quantities in shale-derived fuels. Results of some experiments with these diolefins are given in Table 12 while those with some vinyl compounds are shown in Table 13. These experiments were carried out by adding two volume % olefins to the base fuels along with 750 ppm (wt/vol) N as DMP.

Surprisingly, the data shown in Table 12 suggest that these diolefins have essentially no influence on total sediment formation with DMP in the more highly purified fuels (jet and pure n-decane). The sediment after 28 days was within experimental error of that obtained with the diluent plus DMP

FIGURE 12

EFFECTS OF DECANOIC ACID ON SEDIMENT FORMATION WITH DMP (750 ppm) IN VARIOUS DILUENTS AT 110°F

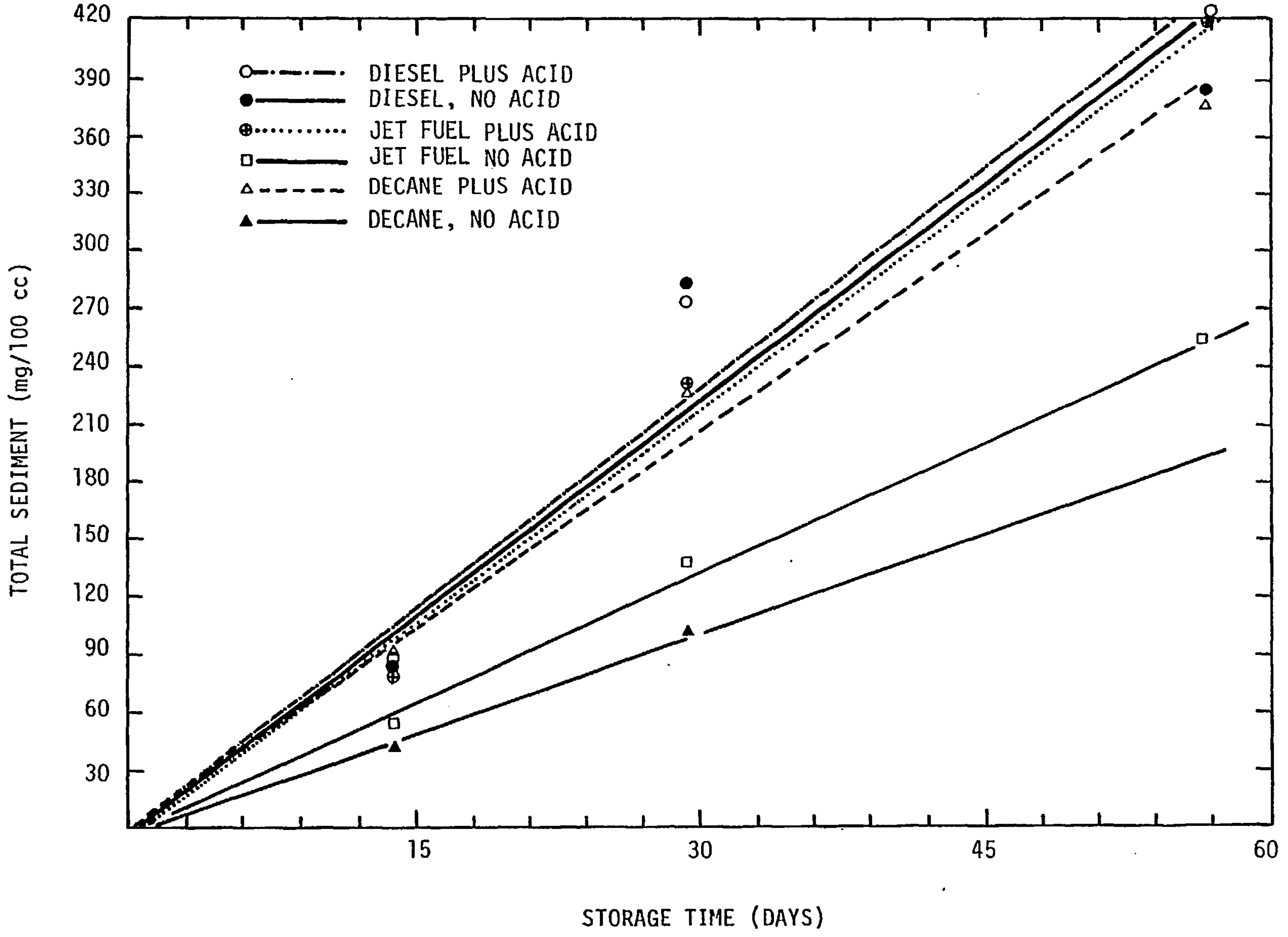


TABLE 11

EFFECTS OF HYDROCARBON TYPES ON SEDIMENT FORMATION WITH 2,5-DIMETHYLPYRROLE (DMP)(a)

Base Fuel	Hydrocarbon Added	Vol. % Added	Total Sediment (mg/100ml)(b) 14 Days	28 Days	After 56 Days
No. 2 Diesel(3)	None	--	217.5	572.8	795.8
	s-Butylbenzene	15	176.1	833.3	-----
	Cyclohexane	20	152.0	888.0	-----
JP-8	None	--	108.5	313.7	586.3
	s-Butylbenzene	15	93.5	313.2	630.5
	1-Dodecene	5	112.0	311.2	685.5
	α-Methylstyrene	5	118.1	327.8	676.0

(a) DMP Level: 1500 ppm N; storage temp: 110°F.

(b) Ave. of 2 or more replicates; "total sediments" is sum of insoluble, and adherent sediments.

TABLE 12

EFFECTS OF DIOLEFINS ON SEDIMENT FORMATION WITH DMP[(a)]

Base Fuel	Olefin Added	Vol % Added	Sediment (mg/100 cc) After 28 Days at 110°F[(b)] Insol.	Adherent	Total
Diesel	None	--	65.3	180.5	245.8
	1,7-Octadiene	2	106.2	10.4	117.0
	1,3-Octadiene	2	56.8	3.0	59.8
	2,4-Octadiene	2	153.4	5.5	158.9
	2,6-Octadiene	2	178.9	8.7	187.6
	2,5-Dimethyl-2,4-hexadiene	2	121.0	8.0	129.0
Jet	None	--	6.6	133.9	140.5
	1,7-Octadiene	2	14.6	127.1	141.7
	1,3-Octadiene	2	33.1	98.6	131.7
	2,4-Octadiene	2	16.5	124.7	141.2
	2,5-Dimethyl-2,4-hexadiene	2	56.2	80.2	136.8
n-Decane[(c)]	None	--	28.3	73.7	102.0
	1,7-Octadiene	2	15.8	102.5	118.3
	1,3-Octadiene	2	11.2	91.6	102.8

(a) 750 ppm DMP (N basis) in all cases.

(b) Avg. of 3 replicates.

(c) Dried and purified over activated silica gel and alumina.

TABLE 13

EFFECTS OF REACTIVE VINYL OLEFINS ON SEDIMENT FORMATION WITH DMP IN JET FUEL[a]

Olefin	Vol % Added	Sediment (mg/100 cc) After 28 Days[b]		
		Insoluble	Adherent	Total
None	--	6.6	133.9	140.5
4-Vinyl-1-cyclohexene	2	24.5	92.5	117.0
Vinylcyclohexane	2	5.7	132.6	138.3
4-Vinylpyridine	2	206.5	32.7	239.2
2-Vinylpyridine	2	154.5	89.3	243.8

(a) DMP present at 750 ppm N level in all cases; storage at 110°F.

(b) Average of 3 replicates.

alone. On the other hand, most diolefins significantly retarded nitrogenous sediment formation in No. 2 diesel. This is noteworthy for 1,3- and 1,7-octadienes where results were clearly outside the range of probable error. This, if real, might be due to some sort of solvent effect or a complicated interaction.

On the other hand, vinylpyridines appear to stimulate sediment formation with DMP in jet fuel (Table 13). Almost double the amount was obtained in 28 days at 110°F as compared to controls. This may be due either to olefin-nitrogen or nitrogen-nitrogen interactions although the latter seems most likely since neither vinylcyclohexane nor vinylcyclohexene had any effect.

2.4.5 Effects of Storage Conditions on Sediment Formation (Tasks 5 and 6)

The effects of several important storage conditions on sediment formation were investigated using model compounds, mostly DMP. The conditions studied were temperature, light, dissolved oxygen, dissolved and dispersed water and metal surfaces. An in-depth study of these parameters was beyond the scope of this program. However, the results presented here point up the areas in which potential problems may exist. In general, temperature, dissolved oxygen and light strongly accelerate the rate of sediment formation, water has a variable effect while metal surfaces appear to exert only minor influences, if any.

2.4.5.1 Effects of Storage Temperature - Estimation of Apparent Activation Energy

The effects of storage temperature on sediment formation were studied using DMP as the model compound. Results of tests with DMP in No. 2 diesel, jet fuel, and decane are given in Table 14. Arrhenius plots of the same data are shown in Figures 13 and 14. This permits an estimation of the apparent activation energy of the reaction from the equation:(17)

$$\ln V_T - \ln V_{T_0} = \frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

Where V_T and V_{T_0} are the amounts of sediment formed at temperature T and temperature T_0, E is the activation energy and R is the ideal gas constant. From the plots in Figures 13 and 14, apparent activation energies for sediment formation:

E_{ACT} = 10.7 and 10.9 Kcal/mole in No. 2 diesel

E_{ACT} = 14.4 Kcal/mole in jet fuel

E_{ACT} = 9.6 Kcal/mole in decane

TABLE 14

TEMPERATURE STUDY WITH 2,5-DIMETHYLPYRROLE (DMP)

				Temperature			Total Sediment (mg/100 cc)[a]				
Replicate	DMP (ppm N)	Time (Days)	Fuel	°F	°C	°K	Repl.	Mean ($\bar{x}$)	Std. Dev. (σ)	$\frac{\sigma}{\bar{x}}$ (%)	E_{ACT} (Kcal/Mole)
1 2 3	1500 " "	14 " "	Diesel Blank	150			2.0 1.5 1.5	1.7	.29	16.9	
1 2 3	1500 " "	14 " "	Diesel	74	23.3	296.3	42.7 42.1 43.9	42.9	.92	2.1	
1 2 3	1500 " "	14 " "	Diesel	115	46.1	319.1	158.3 199.8 228.2	195.4	35.2	18.0	
1 2	1500 "	14 "	Diesel(b)	155	68.3	341.3	373.2 342.2	375.4	22.3	6.2	10.7
1 2 3 4	750 " " "	14 " " "	Diesel	74	23.3	296.3	27.1 26.6 19.7 20.5	23.5	3.9	16.6	
1 2 3 4	750 " " "	14 " " "	Diesel	110	43.3	316.3	59.9 106.3 120.6 56.1	85.7	32.5	38.0	10.9
1 2 3	1500 " "	14 " "	Jet	74	23.3	296.3	20.8 19.5 18.7	19.7	1.06	5.4	
1 2 3	1500 " "	14 " "	Jet	115	46.1	319.1	38.4 129.8 138.0	135.4	4.88	3.6	
1 2 3	1500 " "	14 " "	Jet	155	68.3	341.3	307.0 338.4 326.5	324.0	15.9	4.9	14.4
1 2	750 "	14 "	Decane	74	23.3	296.3	17.7 19.0	18.3	0.91	5.1	8.4
1 2	750 "	14 "	Decane	110	43.3	316.3	45.4 42.8	44.1	1.8	4.1	
1 2	750 "	28 "	Decane	74	23.3	296.3	38.8 38.3	38.6	0.35	0.9	9.6
1 2	750 "	28 "	Decane	110	43.3	316.3	102.0 102.0	102.0	0	0	

(a) Sum of insoluble plus adherent sediments, corrected for blank; no blank correction for jet or decane.

(b) Two replicates only

FIGURE 13

ARRHENIUS PLOT DMP (1500 ppm N) IN JET (14-DAYS)

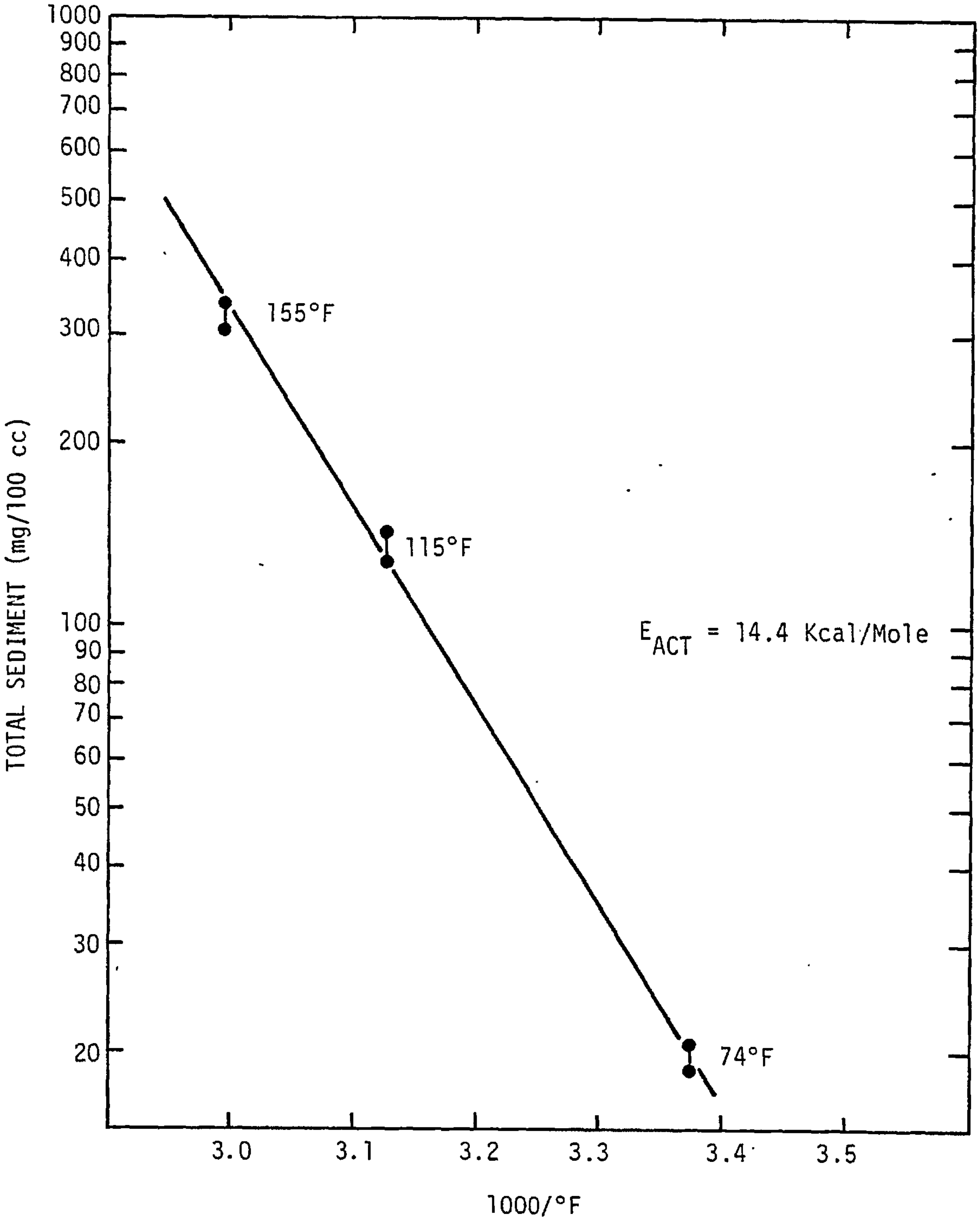
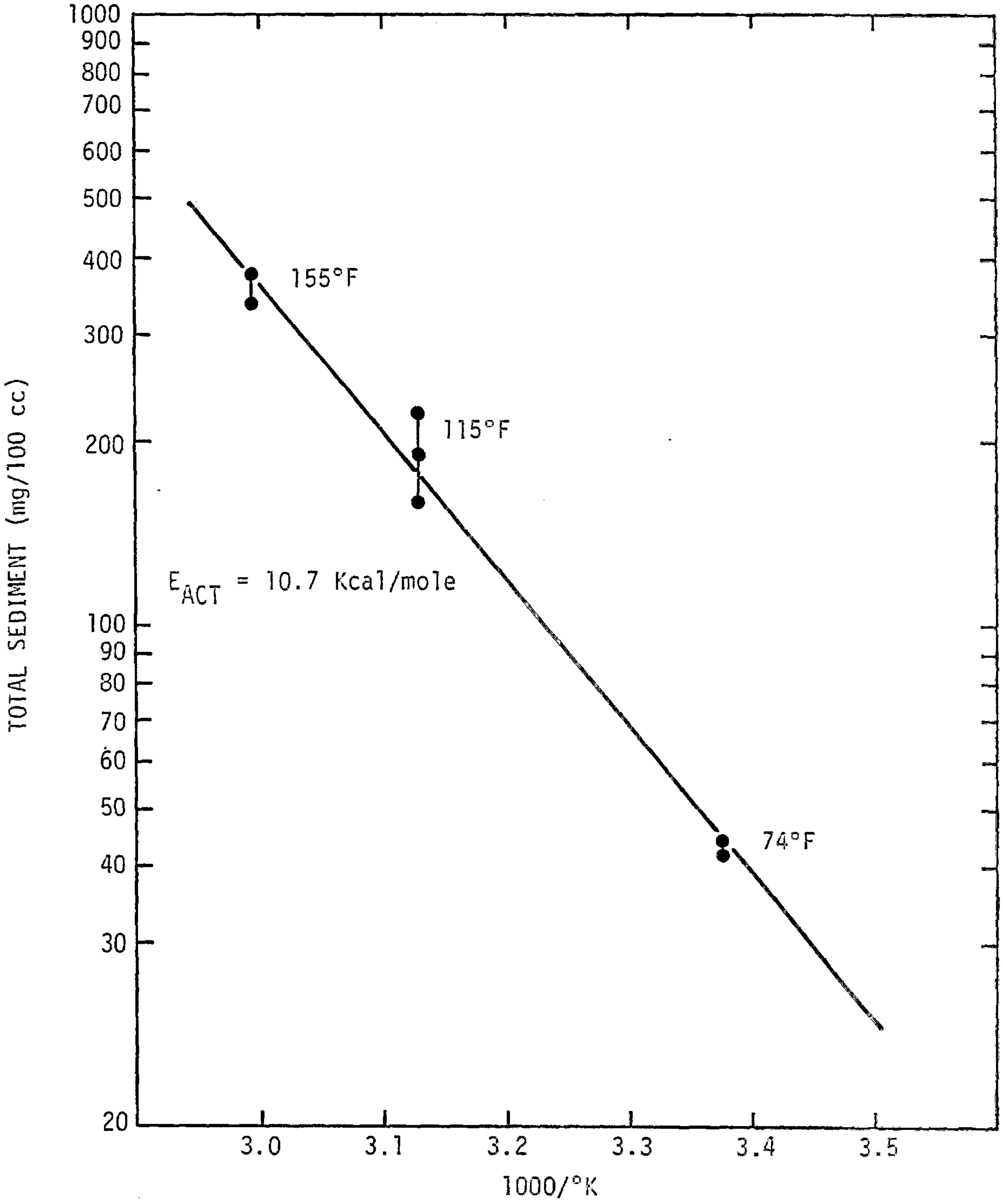


FIGURE 14

ARRHENIUS PLOT OF DMP (1500 ppm N) IN NO. 2 DIESEL AFTER 14-DAYS' STORAGE (RANGE OF REPLICATES ARE INDICATED)



are obtained. These are rather low for most organic reactions, but are similar to those obtained previously for jet fuel deposit formation rates at high temperatures.(18,19) Temperature data for the reaction of DMP in decane are also given in Table 14. However, only two temperature points are available. Thus, the data are less accurate than for diesel and jet fuel. However, the results confirm the low activation energy of the sediment forming reaction.

2.4.5.2 Effects of Light on Sediment Formation

In a previous study(2,3) light was used to accelerate sediment formation with model nitrogen compounds in purified decane. It was found that not only was light a strong promoter but it also affected the course of the reaction although apparently not the characteristics of the sediments obtained. This is illustrated by the curves in Figure 15 (taken from Ref. 2). Plots of sediment formation vs time for reactions in the dark are invariably linear even to long-term periods (see Figures 2, 3 and 10 for example) while curves obtained from storage tests in the light are sharply curved. It is now clear that light is something more than simply a promoter. Since fuels are routinely stored in the dark the problem of light is not serious. However, two things should be borne in mind: (1) light must be carefully excluded in storage of synfuels and (2) storage conditions must be specified in discussing the mechanism of the sediment forming reaction. Reactions carried out in the dark cannot be compared directly to light catalyzed reactions.

2.4.5.3 Effects of Dissolved Oxygen

The characteristics of the sediments obtained from DMP here as well as in previous work(3) indicate that the reaction involves oxidative self-condensation (see Section 2.4.6). Thus, the dissolved oxygen content may play a significant role in the rate and extent of sediment formation. The results of experiments with DMP in various solvents at different levels of dissolved oxygen are given in Table 15. It appears that dissolved oxygen has a significant influence. The data are very sketchy but the effect appears to vary with the diluent. The effect is much greater in diesel than in jet fuels or pure decane (deoxygenation brings about an 80-fold decrease in sediment in diesel, a 5-8-fold decrease in decane and only about a 30% decrease in jet fuel). Such differences have been observed in studies with organic acids, dissolved water and N-N interaction studies. However, they are rather surprising in the case of dissolved oxygen.

2.4.5.4 Influence of Metal Surfaces

It has been widely shown in the literature that both soluble and insoluble metals can catalyze autoxidation reactions in petroleum.(8,20-21) Copper is especially active(8,20) although vanadium alloys(20) and, to some extent, iron(20) are also active. These effects are especially important on

FIGURE 15

EFFECTS OF UV RADIATION ON SEDIMENT FORMATION BY 2,5-DMP IN N-DECANE[2,3]

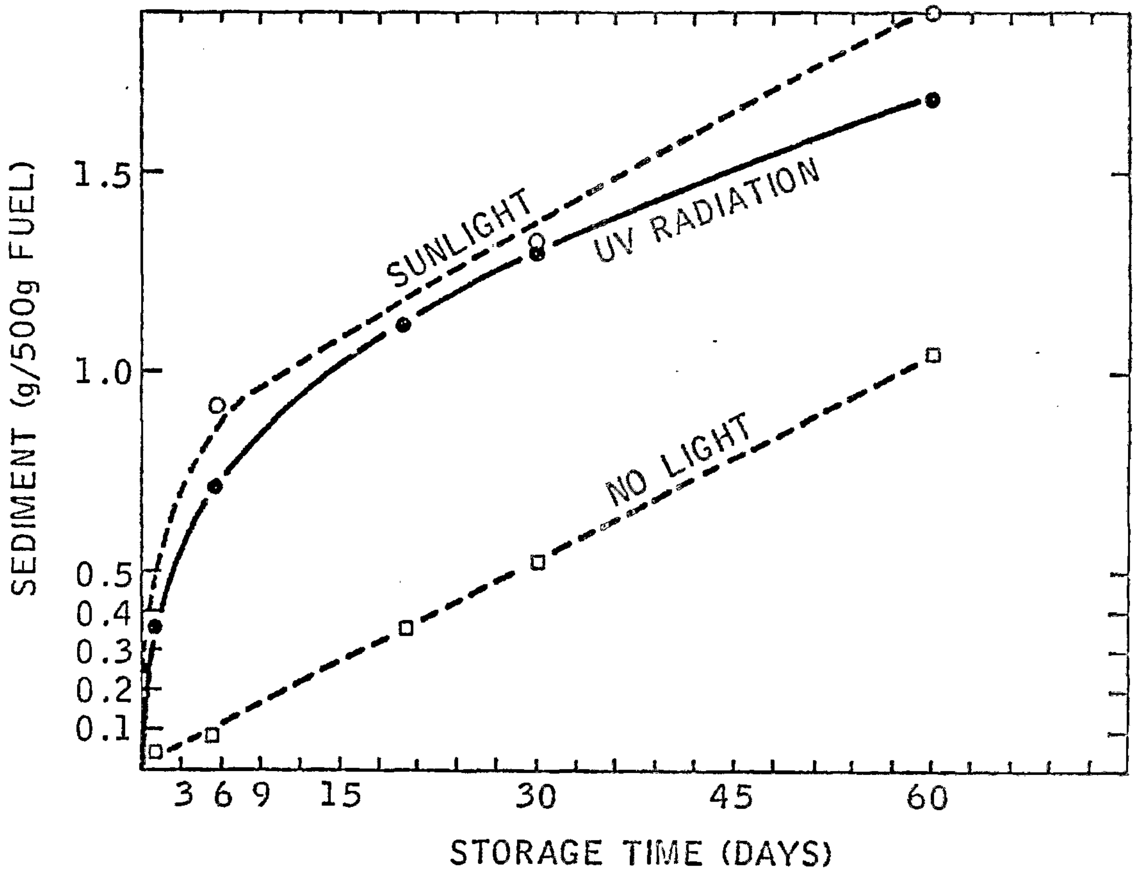


TABLE 15

EFFECTS OF DISSOLVED OXYGEN ON SEDIMENT FORMATION WITH DMP

Fuel	ppm DMP(b)	Storage Temperature (°F)	Conditions Time (Days)	Total Sediment (mg/100 cc)(a)		
				Deoxygenated(c)	Untreated	Air Saturated(d)
Diesel(e)	750	110	14	1.1	85.6	81.7
Jet(f)	750	110	14	43.7	61.3	64.1
Decane(g)	2000	74	15	0.5	4.5	5.5
Decane(g)	2000	74	30	1.0	8.0	9.5
Decane(g)	2000	74	60	3.5	16.5	18.0

(a) Sum of insoluble plus adherent sediments; storage in dark.

(b) N basis (wt/vol).

(c) Achieved by sparging with high purity nitrogen; contain <1 ppm O_2.

(d) Air sparged, previously determined as about 70 ppm O_2.

(e) Six replicates.

(f) Three replicates.

(g) Two replicates; see reference 3.

short-term storage and may be involved in overcoming an induction period.(8,20) A comprehensive study of the effects of metal surfaces was beyond the scope of the present program. However, a preliminary experiment with copper, steel and tin-coated steel was conducted using DMP as the model compound. Two strips measuring 20 mm x 50 mm each were added to each flask containing 750 ppm DMP in either diesel or jet fuel. The samples were stored for short-time periods at 110°F. The results are summarized in Table 16. No clear-cut trends were observed. The sediment in the case of copper was higher than with steel in every case but the difference was very small. Adding the strips, if anything, decreased sediment formation but by an insignificant amount.

2.4.5.5 Effects of Dissolved and Dispersed Water

The presence of moisture is a nearly unavoidable fact of life so far as storage of fuel is concerned. It is, therefore, important to determine its effect on nitrogenous sediment formation. Preliminary experiments(3,22) had suggested that water had a significant but variable effect on sediment formation depending on the nature of the test fuel or diluent. A follow-up experiment confirms this as shown in Table 17 and Figure 16 (results shown are for ambient temperature storage). Considerable difficulty was encountered both in introducing and maintaining known amounts of water into the fuel mixtures and in measuring the water actually present. The data, therefore, are rather imprecise. However, the trends are clear; in diesel, water has a significant accelerating effect on sediment formation with DMP at both 28 and 56 days' storage periods while no measurable effect was encountered in either jet fuel or n-decane. Two possible explanations suggest themselves: (1) No. 2 diesel, with natural emulsifiers present, holds water possibly in the form of reverse micelles which may stimulate sediment formation while water in both jet fuel and decane is nearly exclusively dissolved; (2) the water in diesel reacts with some trace impurity (e.g., acids, Ref. 7) to enhance their catalytic effect, such impurities being absent in the other fuels.

2.4.6 Composition of the Sediment and Characteristics of the Reaction

Continued progress has been made toward elucidating the mechanism of nitrogenous sediment formation with model compounds in both narrow and broad range fuels. The goal of this work is a better understanding of sediment formation in hopes of eventually finding economical ways of preventing it. Critical features of this growing body of knowledge include the identification of the types of nitrogen compound most prone to form sediment, the conditions under which sediment is most readily formed and the various interactions effects which accelerate or retard the reaction.

TABLE 16

EFFECTS OF METAL SURFACES ON SEDIMENT FORMATION WITH DMP[(a)]

		Sediment (mg/100 cc) After							
		7 Days				14 Days			
Metal[(b)]	Fuel	Metal Surface	Insol	Adherent	Total	Metal Surface	Insol	Adherent	Total
None	Diesel	--	24.1	0.6	24.7	--	57.2	28.4	85.6
None	Jet	--	--	--	--	--	7.3	54.0	61.3
Copper	Diesel	0.3	22.5	0.7	23.5	1.7	67.0	3.1	71.8
Steel[(c)]	Diesel	0.3	20.6	0.7	21.6	--	--	--	--
Coated Steel[(d)]	Diesel	--	--	--	--	0.6	51.0	1.4	53.0
Copper	Jet	0.2	14.3	0.8	15.3	3.0	36.9	1.6	41.5
Steel[(c)]	Jet	0.1	10.9	1.4	11.4	--	--	--	--
Coated Steel[(d)]	Jet					4.3	33.4	1.9	39.6

(a) DMP present at 750 ppm N (wt/vol); storage at 110°F in dark; 3 replicates at 14 days; 2 replicates at 7 days.

(b) Two strips 20 mm x 50 mm added to each sample.

(c) Cold rolled steel plate.

(d) Tin plated.

TABLE 17

EFFECTS OF WATER ON SEDIMENT FORMATION WITH DMP IN VARIOUS FUELS STORED AT AMBIENT TEMPERATURE[a]

Fuel	Water Level[b] (ppm)	Total Sediment[c] (mg/100 cc) 28 Days	56 Days
Diesel	<10	34.7	92.8
	71	47.0	--
	79	44.0	125.0
	99	81.9	220.8
	131	62.2	292.5
	169	110.6	336.0
Jet	1	20.1	63.6
	<10	19.2	55.9
	6	18.0	62.1
	52	36.0	108
	83	20.1	64.5
Decane	4.4	28.6	61.5
	4.7	29.0	71.6
	6.7	38.5	--
	16.8	25.8	62.6

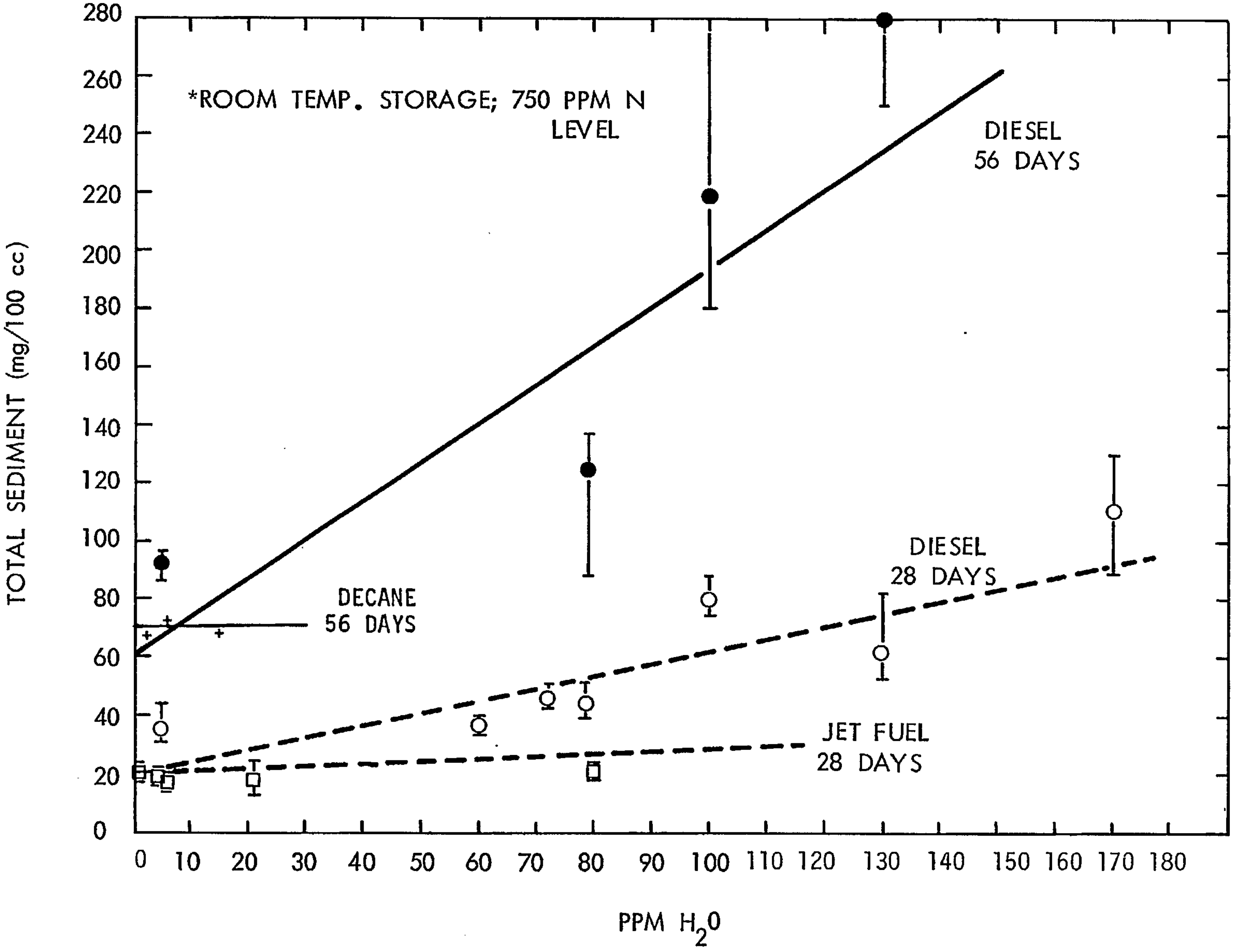
(a) DMP present at 750 ppm N levels; storage in dark at ambient temperature.

(b) As determined by Karl Fischer titration.

(c) Sum of insoluble plus adherent deposits; ave. of 3 replicates.

FIGURE 16

EFFECTS OF WATER ON SEDIMENT FORMATION WITH DMP*



2.4.6.1 Characteristics of the Sediments Produced by Model Nitrogen Compounds

The elemental analyses from a number of sediments from DMP under a variety of storage conditions are given in Table 18. These values are exceptionally consistent no matter what the diluent or storage conditions. It appears, that, although conditions may affect the rate of formation and quantity of sediment, they do not 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:

$$C_{6.3}H_{7.0}\ N\ O_{1.67}$$

while that of dimethylpyrrole is:

$$C_6H_9\ N$$

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 infrared spectrum of a DMP sediment is shown in Figure 17 and contrasted with that of fresh DMP. Carbonyl absorption at 1650-1700 cm^{-1} is clearly present and there appears to be more than one type. Methyl absorption is present along with some methylene. It also appears that the N-H absorption is retained. In addition some hint of C-O stretch is given by weak absorption at about 1090-1150 cm^{-1}. This absorption shows up much stronger in raw shale sediments (see Section 2.5.4).

This analysis confirms that the pyrrole ring is intact and suggests that oxygen has been introduced in the form of one or more carbonyl groups. The strong $-CH_3$ absorption relative to $-CH_2$ indicates that some of the methyl groups remain intact and that no long chain $-CH_2-$ units (from other components of the media) have been introduced. The possible presence of ether groups or carboxylates cannot be ruled out.

The extreme insolubility of the DMP sediments precludes taking solution IR and NMR spectra. This is especially troublesome in the case of proton NMR where techniques using solid are only now becoming available. The use of solid state ^{13}C NMR is feasible, however. Two traces, obtained by this technique of sediments from DMP and TMP (1,2,5-trimethylpyrrole) are shown in Figure 18 along with possible assignments of peaks. The results tend to support conclusions made by infrared analysis: (1) the pyrrole ring is intact (2) at least two types of carbonyl groups are present, (3) both $-CH_3$ and $-CH_2$ carbons are present and the low values for $-CH_2$ indicate the absence of any long hydrocarbon chain (from the diluent), (4) the possibility of an ether linkage to carbon is also suggested.

TABLE 18

ANALYSIS OF SEDIMENTS FROM DMP UNDER VARIOUS STORAGE CONDITIONS(a)

Additive(s)	Storage Conditions	Fuel(b)	Storage Time	% C	% H	% N	% O(c)	% S
DMP	Light - 72°F	n-Decane	5 days	62.28	5.33	11.86	20.53	(d)
DMP	Light - 72°F	n-Decane	60 days	63.89	5.09	12.31	18.71	(d)
DMP	Light - 72°F	JP-5	80 days	59.71	5.54	11.29	23.28	.18
DMP & Decanoic Acid	Light - 72°F	JP-5	80 days	62.30	5.88	10.95	20.07	.80
DMP & Decanoic Acid	Dark - 72°F	JP-5	80 days	61.09	5.88	10.84	22.04	.15
Average of 11 Samples from decane (all conditions			--	61.30	5.67	11.29	21.51	(d)
DMP	Dark - 110°F	Diesel	120 days	67.22	6.99	9.24	16.55	(d)
DMP	Dark - 110°F	Diesel	160 days	63.28	6.32	10.50	19.90	(d)
DMP + Thiophenol	Dark - 110°F	Jet	160 days	65.05	6.07	9.08	19.80	(d)

(a) Decane and JP-5 results from Ref. 3; light was uv light at 366 nm except for JP-5 samples which were irradiated with sunlight.

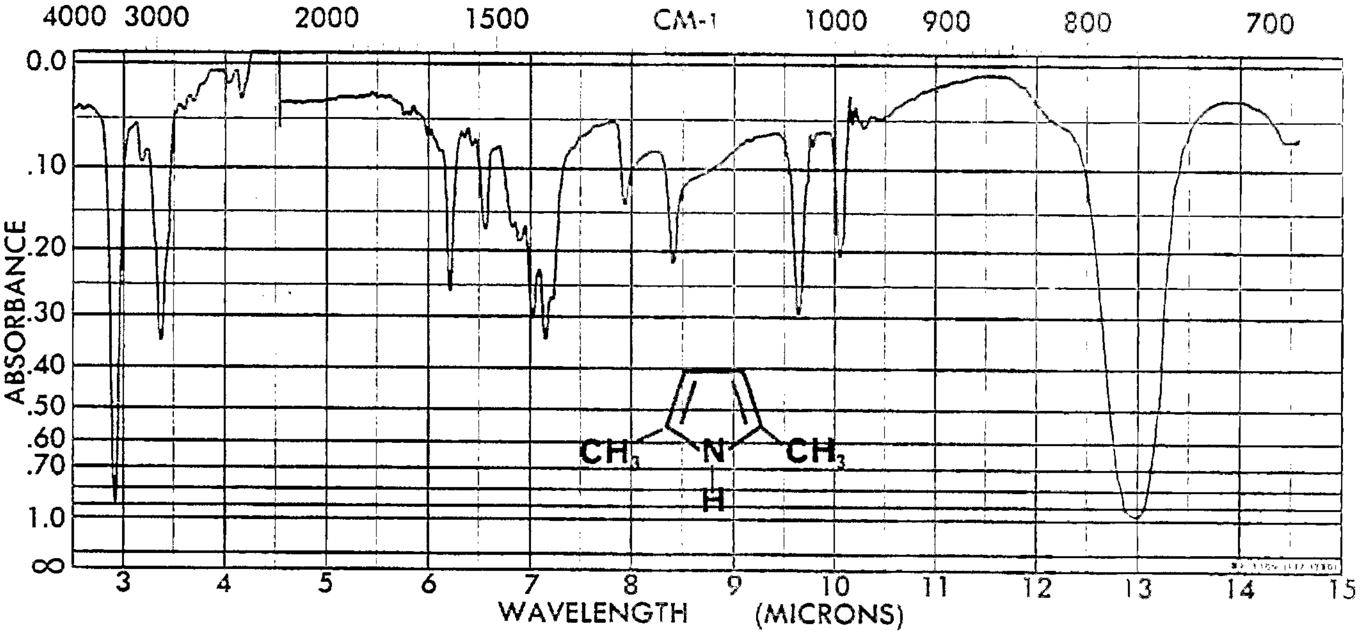
(b) Decane was specially purified (Ref. 3). Other fuels used as received.

(c) By difference.

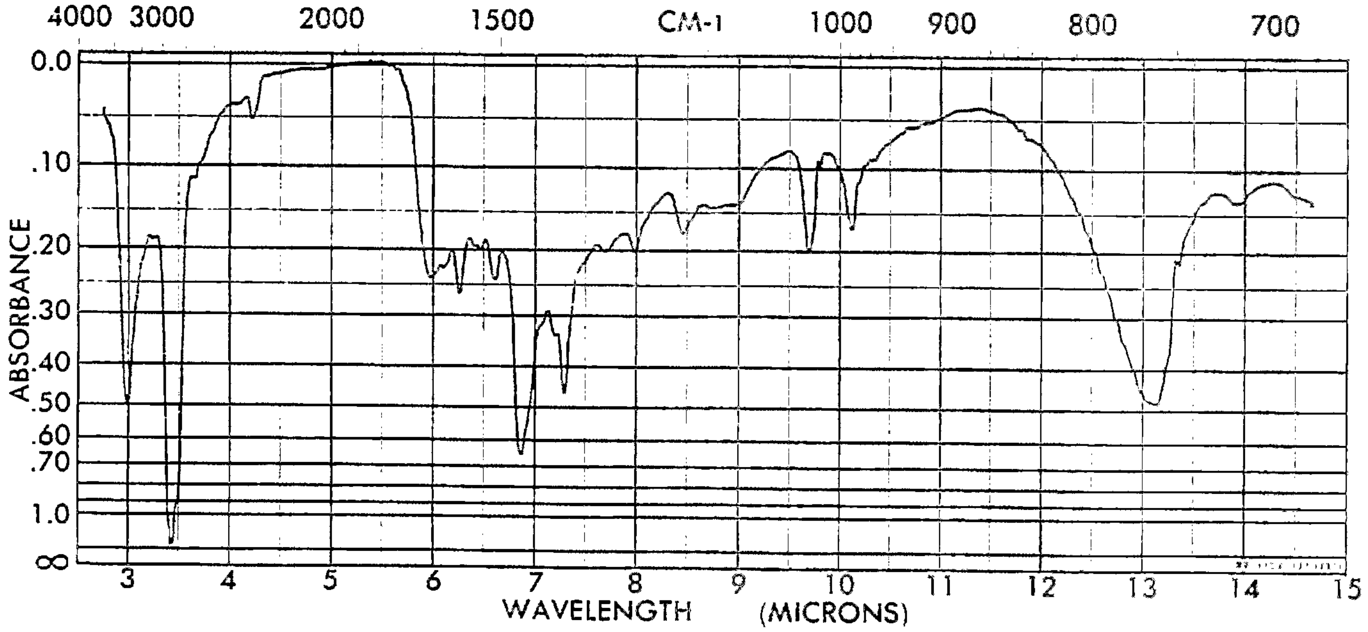
(d) Not determined.

FIGURE 17

IR SPECTRA OF SEDIMENT FROM 2,5-DIMETHYLPYRROLE IN NO. 2 DIESEL FUEL (60 DAYS' STORAGE AT 110°F)



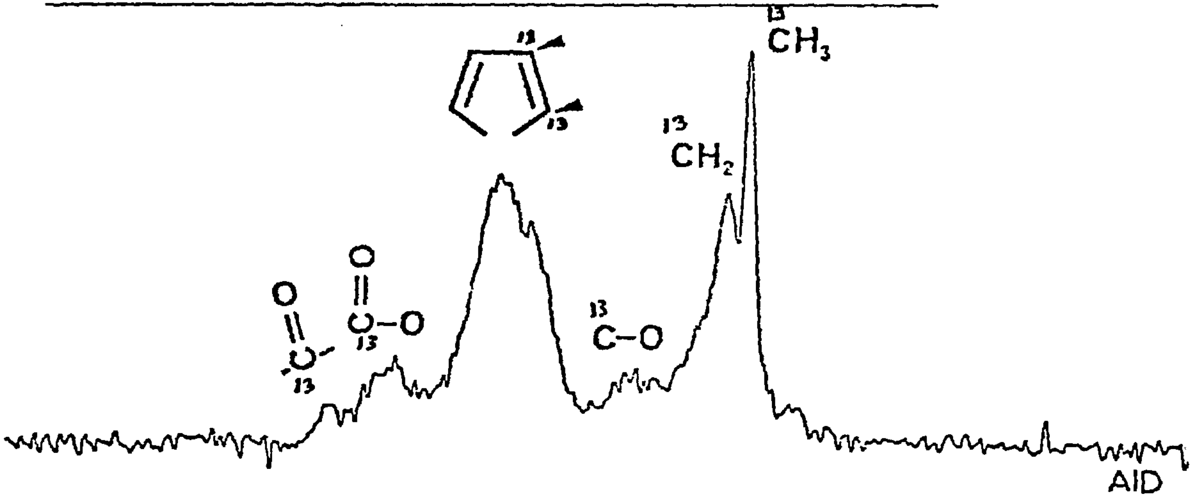
A. FRESH DMP (NEAT)



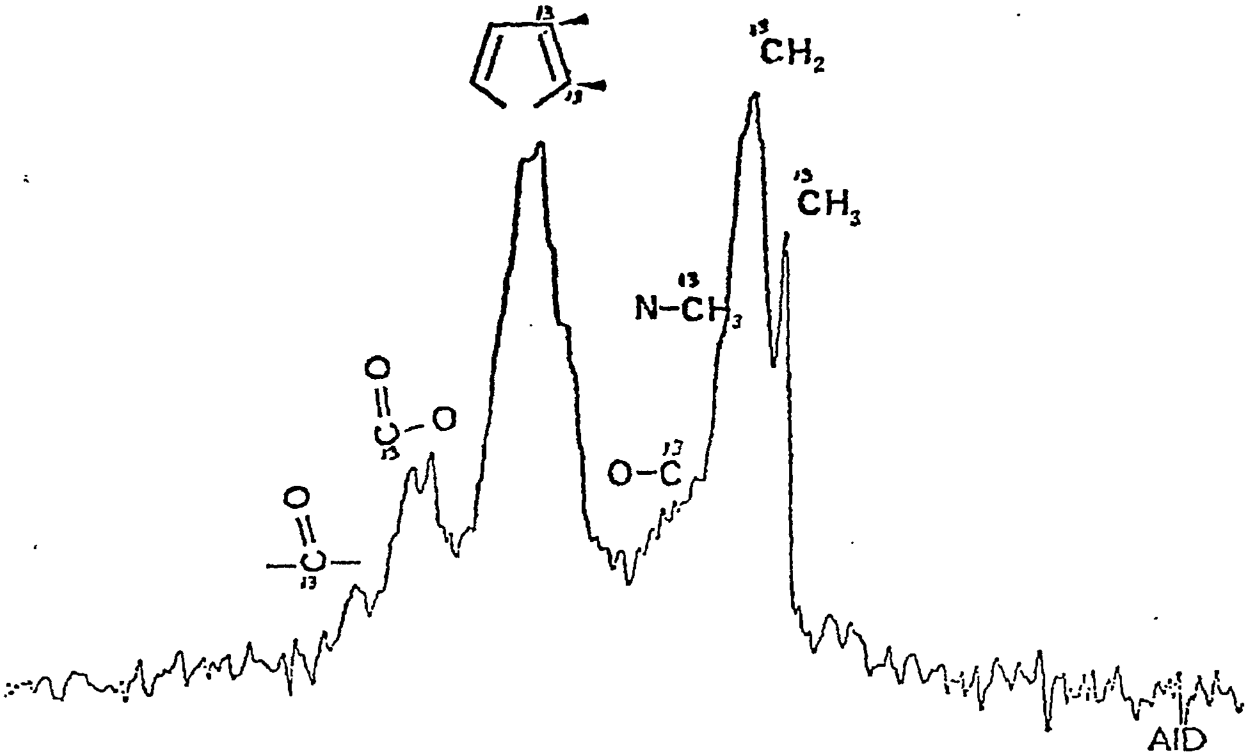
B. SEDIMENT (MULL)

FIGURE 18

SOLID STATE ^{13}C NMR TRACES FOR SOME NITROGENOUS SEDIMENTS



A. SEDIMENT FROM DMP IN NO. 2 DIESEL (110°F - 56 DAYS)



B. SEDIMENT FROM TMP IN NO. 2 DIESEL (110°F - 56 DAYS)

The more important mass spectral peaks and their possible fragment assignments are given in Scheme I. From the elemental analysis, ^{13}C NMR, IR and mass spectral data one can begin to draw partial structures for the sediment obtained in the current program. These are shown as partial structures (Scheme II). If a single structure is present, the representation best fitting a 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. That is, peaks 122 and 123, due to oxygenated structures II, 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.

Figure 19 gives the mass spectra of sediments from DMP in decane obtained under deoxygenated and air saturated conditions. The ratios of the 94 peak to the 122 peak are 11.3 for the deoxygenated sample (18A) and 3.7 for the air saturated case (18B). 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 and V.

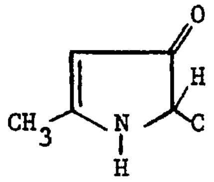
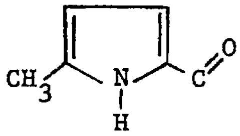
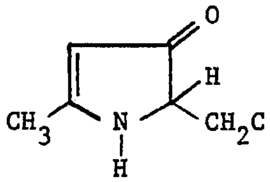
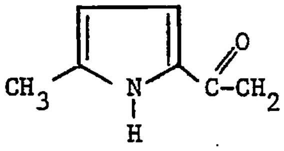
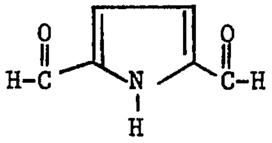
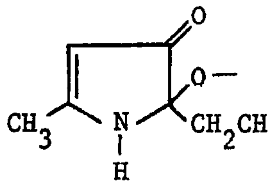
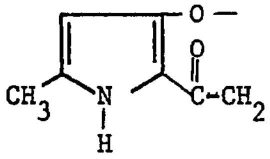
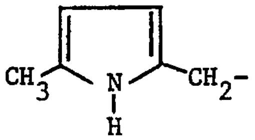
The ester, partial structure VI,has been proposed by Sauer, Weed and Headington for sediments formed on oxidation of heating oils.(8,13) In addition it is a structure easily rationalized (see Section 2.4.6.2). The current data cannot rule out such structures. In fact, the possible presence of carboxylate groups as shown in the ^{13}C NMR and IR spectra would be consistent with such a partial structure. At the present time it appears most likely that several structures, similar to I-VI,are all contributing to the average properties observed.

2.4.6.2 Characteristics of the Sediment-Forming Reaction

Figure 20 shows a plot of total sediment vs nitrogen content for self-condensation of DMP in jet fuel. A linear plot is obtained. Although a rigorous kinetic analysis cannot be made on the basis of these limited data, it appears that sediment formation is first order in DMP.

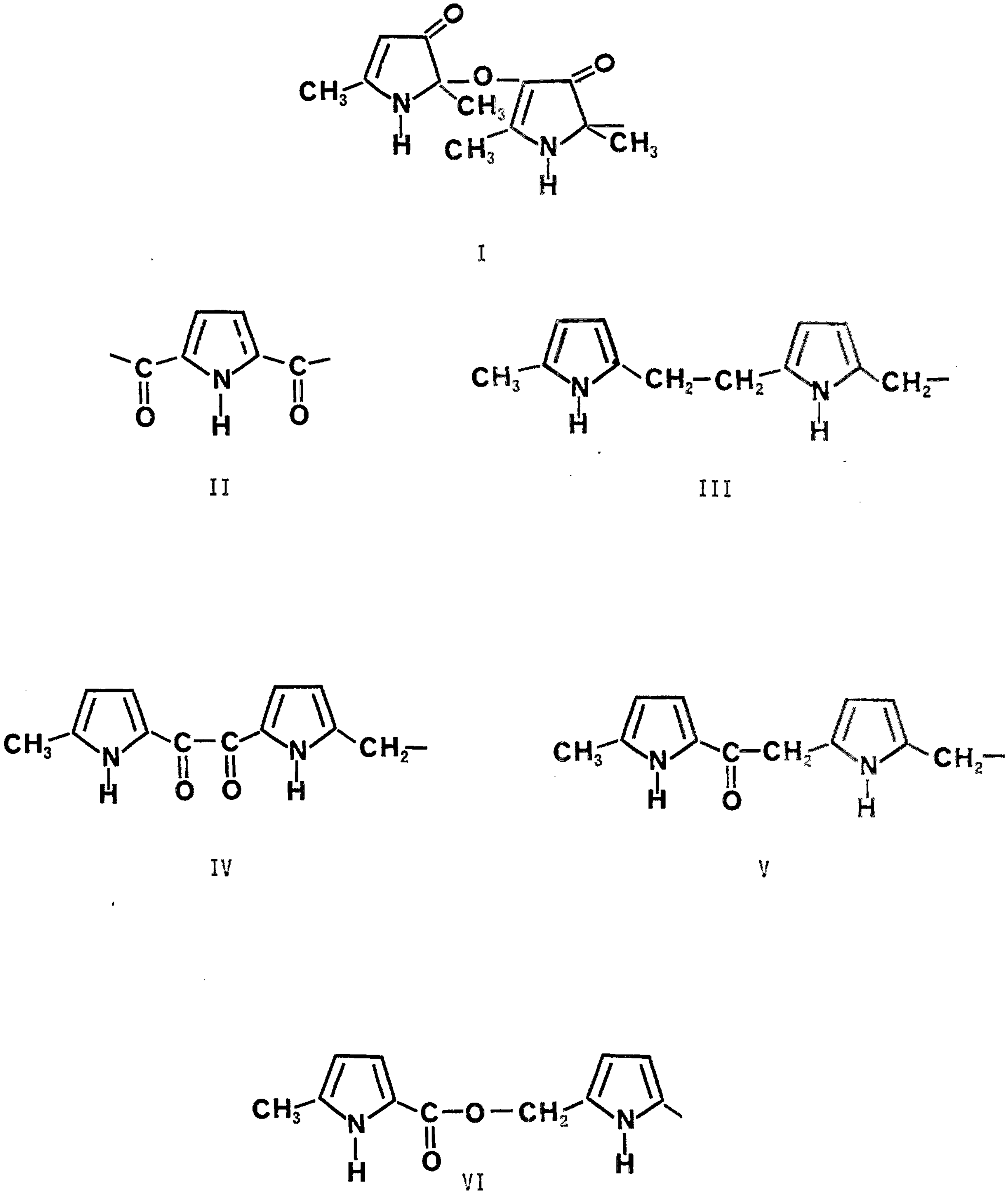
SCHEME I

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	 or 
122	 or 
123	
138	 or 
94	

SCHEME II

POSSIBLE PARTIAL STRUCTURES FOR DMP SEDIMENT



I

II

III

IV

V

VI

FIGURE 19

EFFECTS OF DISSOLVED OXYGEN ON MASS SPECTRUM OF DMP SEDIMENT (OBTAINED IN DECANE AT ROOM TEMPERATURE)

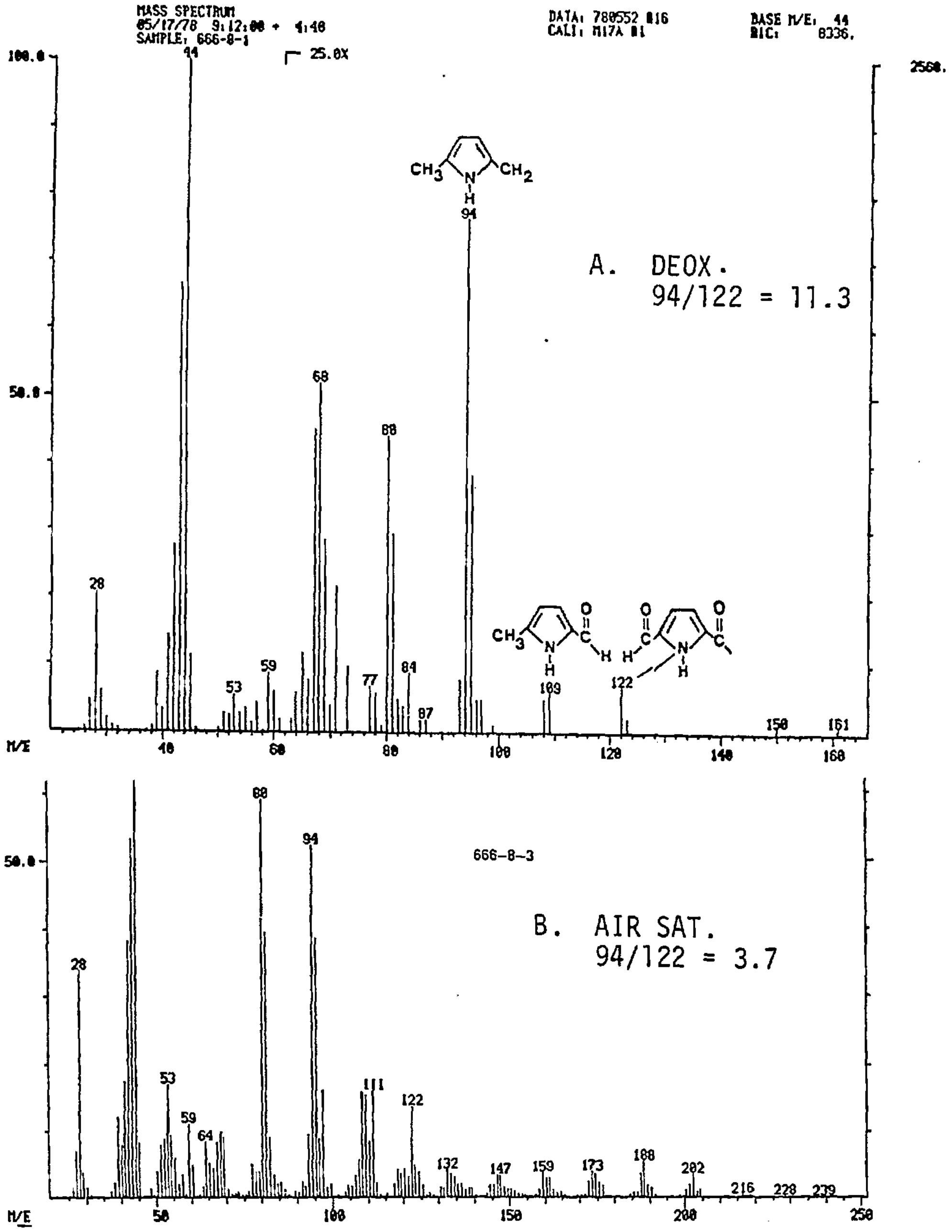
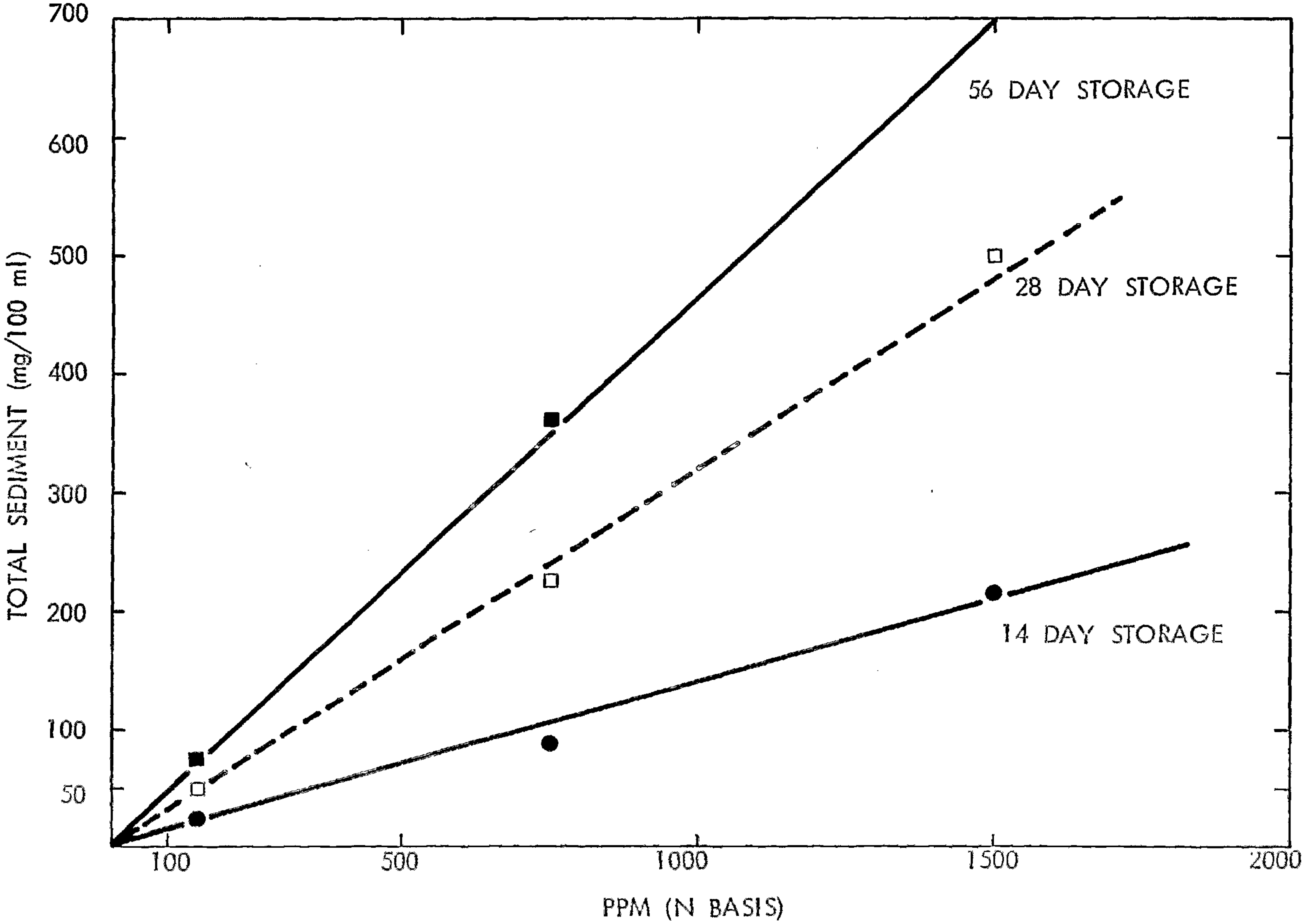


FIGURE 20

EFFECT OF CONCENTRATION ON SEDIMENT FORMATION WITH 2,5-DMP IN JET FUEL AT 110°F



From this observation and those described in previous sections, the following generalizations can be made, tentatively, about the formation of nitrogenous sediments in model systems in the dark at temperatures up to 110°F.

- Only alkylated, heterocyclic nitrogen compounds actively undergo the reaction.
- The reaction appears first order in the nitrogen compound.
- Oxygen is required.
- The diluent affects the rate of reaction but not the characteristics of the sediment.
- The activation energy is quite low.
- The sediment obtained appears to be repeating units of partially oxidized nitrogen compound with an average of 1 1/2 oxygen atoms introduced accompanied by a loss of 2-3 hydrogen atoms.
- The oxygen atoms are present at least partially as one or more types of carbonyl functions with ether linkages also a possibility.

Sedimentation thus appears to be a free radical, autoxidative reaction. A possible reaction scheme which could lead to the formation of partial structures II-VI is shown in Figure 21. It must be recognized that other pathways and structures exist and, in fact, are probably involved under certain conditions.

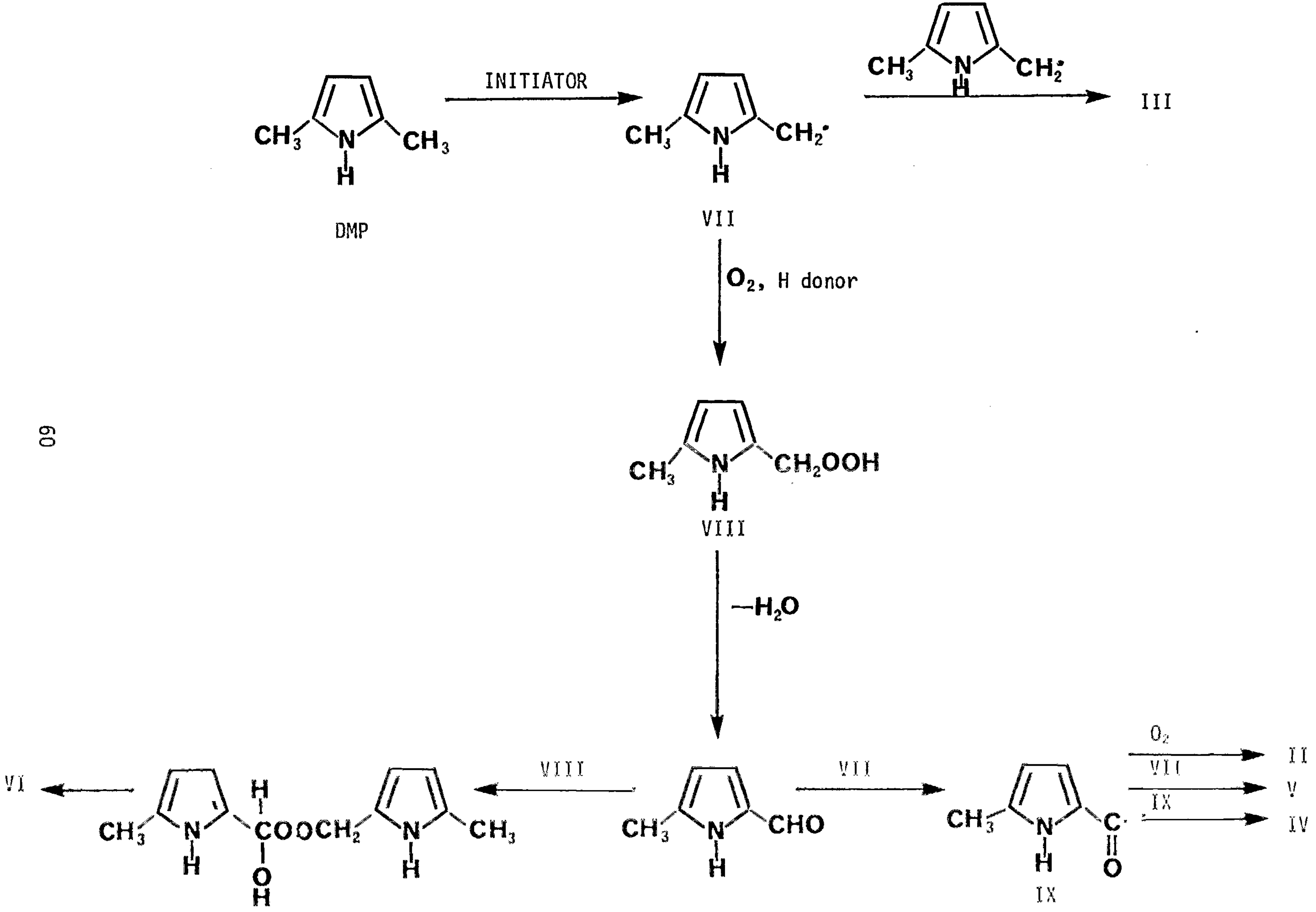
2.5 STORAGE STABILITY OF ACTUAL SHALE LIQUIDS

The studies with model compounds, described in the preceeding sections, were expanded to include various actual shale liquids in order to establish that the results obtained in model systems could be extended to "real world" fuels. Three approaches were explored:

(1) Well characterized shale liquids were subjected to accelerated storage tests to determine whether sediments, similar to those in model systems, could be obtained and whether the amounts and types of sediment can be correlated with the amounts and types of nitrogen compounds in the original shale liquid.

FIGURE 21

POSSIBLE REACTION PATHS TO DMP SEDIMENT



(2) The same liquids were spiked with pure nitrogen and sulfur compounds to determine whether the same tendency toward sediment formation and interactive effects is observed in the shale matrix as in the model diluents.

(3) Shale liquids were studied as blends with both petroleum-derived fuels and other shale middle distillates. Such studies provide insight both as to the compatibility of shale blends and to their storage behavior as compared to model compounds.

The results of these studies outlined in the following sections suggest that shale liquids afford nitrogen-rich sediments resembling those obtained in model compound studies. Considerable differences between various shale-derived fuels exist but these appear to be explainable based on the known compositional differences of the fuels.

2.5.1 Characteristics of Shale Liquids Employed in This Study

A variety of shale distillates with different properties were studied. These included:

- Hydrotreated Middle Distillates from In Situ Shale Oil

A series of 11 shale liquids (two crude but distilled to middle distillate end points, and nine distilled and hydrotreated) have been obtained from a previously completed DOE contract dealing with a different aspect of product quality.(4) These samples were prepared by first distilling and then, in the case of the nine treated samples, hydrotreating crude *in situ* shale liquid obtained from Occidental Oil Shale Co.(4) Inspections on the two distilled but untreated liquid are given in Appendix Table A-2. These liquids are dark in color, extremely odorous and inherently unstable.

The inspection on the nine hydrotreated samples and their designations are given in Appendix Table A-3. Each of three distillation cuts was hydrotreated to three different severities yielding the matrix of nine liquids shown in Figure 22. Hydrotreating significantly improved these samples from the stability standpoint; nearly 99% of the nitrogen and sulfur were removed from most samples by even the mildest hydrotreating. An exception is the broad range fuel, C (Figure 22, Table A-3). Only the most severe hydrotreating reduced the nitrogen by 98% in this case. Most of these liquids were light in color and free of apparent sludge after several months in the cold box. However, the samples possessed a definite, pungent odor.

FIGURE 22

MATRIX OF HYDROTREATED SHALE MIDDLE DISTILLATES USED IN THIS STUDY

		Hydroprocessing Conditions[b] Total Pressure[c]		
Final BP[a]		1	2	3
Feed Identification		1500 psig	1200 psig	800 psig
640°F	(A)	A-1	A-2	A-3
670°F	(B)	B-1	B-2	B-3
700°F	(C)	C-1	C-2	C-3

(a) Initial BP = 325°F in all cases.

(b) Temp. = 710-750°F; 1.0 LHSV in all cases; catalyst: Shell Oil Co. #324 nickel molybdate on alumina; see reference 4 for details.

(c) Finished fuels identified as "A-1", "A-2" etc. Fuel A-1 for example was narrow cut distillate (325°-640°F) hydrotreated to 1500 psig.

- Partially Hydrotreated "Off Spec" Shale Distillates

Several partially hydrotreated or "off spec" shale liquids were obtained as by-products of the DOE program mentioned in the previous section.(4) These were quite useful as they were materials of intermediate to high nitrogen and sulfur contents. Their characteristics are summarized in Appendix Table A-4.

- Samples from Oak Ridge National Laboratories

A series of six middle distillate fuels, derived from Paraho Shale were obtained from Oak Ridge National Laboratories. These represented fuels not only of different nitrogen and sulfur levels but also from a different source and processing history. Inspections on these fuels are given in Table A-5.

A single sample of a shale-derived JP-5 fuel prepared some years ago.(5,23) This fuel was extensively processed to low nitrogen levels. Its characteristics are shown in Table A-6.

2.5.2 Results of Accelerated Storage Tests with Various Shale Liquids

These experiments were carried out in the same manner as with model systems except that, in some cases, soluble gum analyses were also performed. Color tests were not conducted since many of the samples were more or less colored as received.

2.5.2.1 Studies with Distilled But Not Upgraded Shale Samples

Two samples of distilled but not hydrotreated in situ shale liquids were available from a previous study.(4) These liquids are dark in color, odorous and quite unstable under storage conditions. Both liquids had significant amounts of sediment present at the start of the study but continued to produce large amounts of additional sediment. The results of these tests are shown in Table 19.

Liquid A gave nearly 6 grams/100 cc of sediment while Liquid C produced about 1.5 grams/100 cc (including the sediment present at the start of testing). This is indicative of the inherent instability of crude shale liquid. The sediments from these experiments were collected and characterized (see Section 2.5.4).

TABLE 19

ACCELERATED STORAGE STABILITY TESTS WITH CRUDE SHALE LIQUIDS

Liquid[a]	% N	Total Sediment[b] (mg/100 cc) After Start[c]	 60 Days	 84 Days
A	1.2	5,100	411.2	560.0
C	1.2	20.4	253.6	1,400

(a) Liquid A: Occidental *in situ* shale distilled to give boiling range of 325-640°F; Liquid C: boiling range of 325-700°F.

(b) Total of adherent plus insoluble; ave. of two replicates; 110°F storage.

(c) After several months in the cold; note some sediment in grams/100 cc not mg.

2.5.2.2 Studies with Partially Hydrotreated ("High Nitrogen") Middle Distillate from Occidental In Situ Shale Oil

The results of accelerated storage tests with some partially hydrotreated in situ shale middle distillates are summarized in Table 20. These samples all have nitrogen levels exceeding 1000 ppm and all produced significant quantities of sediment. Plots of sediment formation vs time for these liquids are shown in Figures 23 and 24. Figure 23 contains plots of sediment formation vs time for various hydrotreated middle distillates derived from in situ shale liquid "A" (boiling range: 325-640°F) while 24 shows similar plots for liquids derived from distillate "C" (boiling range: 325-700°F). In all cases linear plots are obtained quite similar to those observed in model compound studies. The levels of sediment obtained are roughly proportionate to nitrogen level. Generally, shale liquids with N contents >1000 ppm are unstable in this test.

2.5.2.3 Studies with Severely Hydrotreated ("Low Nitrogen") Shale Liquids - Evidence for an Induction Period

Results of long-term accelerated storage tests with severely hydrotreated middle distillates (all derived from in situ crude shale oil) are summarized in Table 21. Both insoluble sediment and, where appropriate, soluble gum levels are shown. All of the samples studied contained less than 500 ppm total nitrogen. None gave any measurable sediment through 80 days' storage at 110°F (equivalent to about 10 months at ambient temperatures) although high levels of soluble gum were occasionally observed. After approximately 120 days, however, all samples except A-1 afforded sediment which increased significantly on longer storage. Plots illustrating this phenomena are given in Figure 25. An induction period appears to exist. This suggests that these fuels may present stability problems on long-term storage.

2.5.2.4 Accelerated Storage Stability Tests with Oak Ridge National Laboratory Samples

These fuels are derived from a different shale (Paraho) by a different retorting technique (Paraho-above ground) and refined differently from those given in Tables 20 and 21. Characteristics are tabulated in Appendix Table A-5. Results of accelerated storage stability tests are shown in Table 22 and plotted in Figure 26. Like the samples from the in situ shale (Tables 20 and 21) these fuels are divided sharply into "high" and "low" nitrogen samples. The low nitrogen materials gave no sediment at storage times up to 70 days, although measurable sediment was obtained after 120 days (equivalent to over 15 months at ambient). The high nitrogen material, however, afforded significant amounts of sediment but much less than other shale liquids of comparable nitrogen contents. On the other hand, existent gum levels were somewhat higher in these fuels than from the in situ shale samples.

TABLE 20

SEDIMENT FORMATION WITH SOME SHALE MIDDLE DISTILLATES WITH MODERATE TO HIGH NITROGEN CONTENTS

Sample[a]	Nitrogen Content (ppm)		Total Sediment[b] (mg/100 cc) After					
	Total	Pyrrole	28 Days	60 Days	70 Days	84 Days	120 Days	156 Days
A-4	3,600	181	46.9	--	114		155.3	
A-6	12,000	496	297	--	506		821.5	
C-2[c]	3,900	--	48.4		131		240.7	
C-3	4,100	58	39.1	74.1	--	129.2	198	
C-4	10,000	538	79.6	191	--	--	409	500

(a) See Ref. 3 and Table 5 for inspections on samples; A-4, A-6 and C-4 are "Off Spec" samples.

(b) Adherent plus insoluble; average of 3 replicates unless noted; storage at 110°F.

(c) Single replicate due to small sample size.

FIGURE 23

SEDIMENT FORMATION WITH VARIOUS HYDROTREATED SAMPLES OF IN SITU SHALE MIDDLE DISTILLATE "A" (325-640°F)*

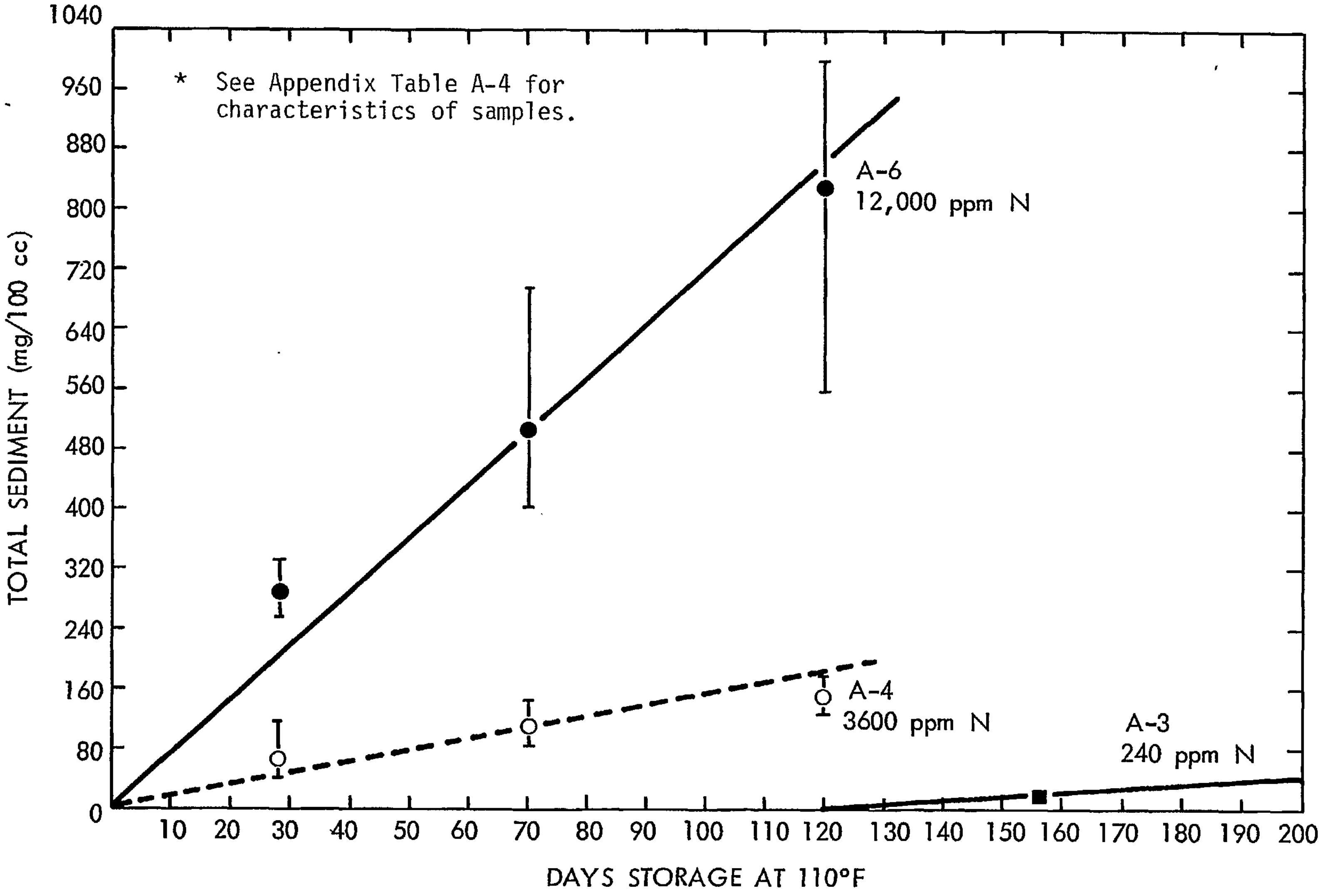


FIGURE 24

SEDIMENT FORMATION WITH VARIOUS SHALE MIDDLE DISTILLATES FROM IN SITU SHALE LIQUID "C" (325-700°F)

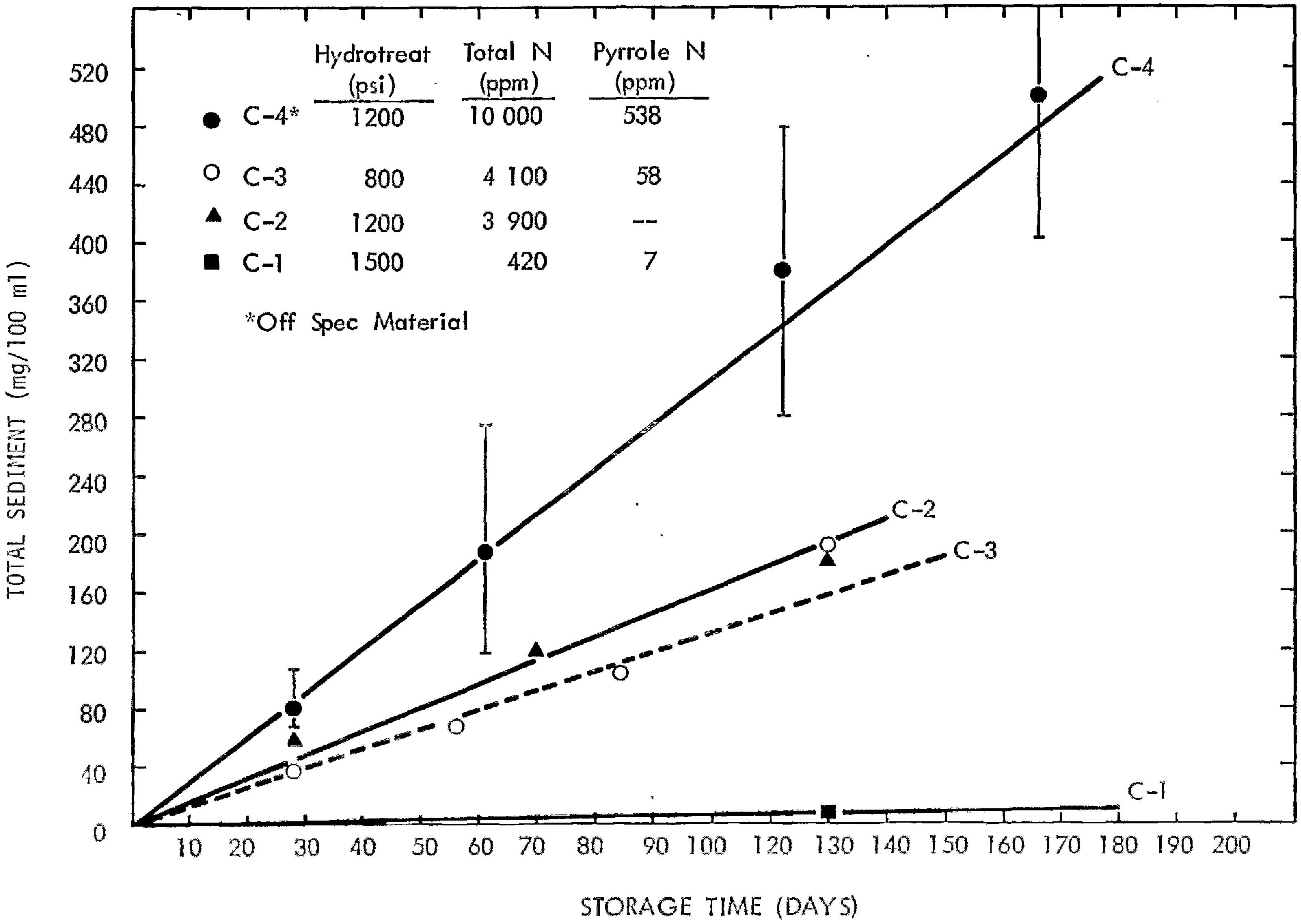


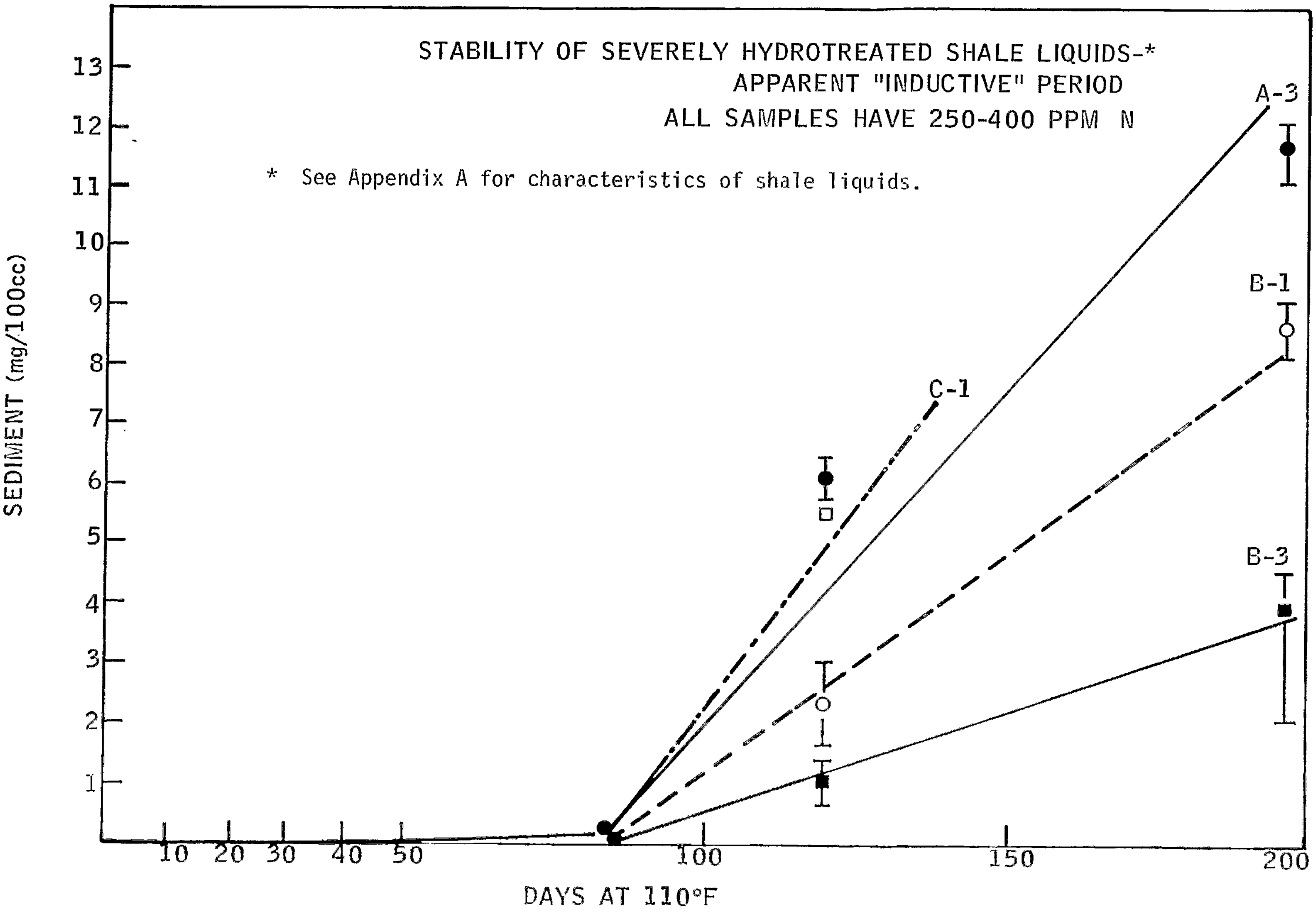
TABLE 21

SEDIMENT AND GUM FORMATION WITH SOME SHALE MIDDLE DISTILLATES WITH LOW NITROGEN CONTENTS

Sample[a]	Nitrogen Content (ppm) Total	Nitrogen Content (ppm) Pyrrole N	Steam Jet Gum[c,d] (mg/100 cc)	Replicate	Gum and Total Sediment[b] After 28 Days Gum (mg/100 cc)	28 Days Sediment (mg/100 cc)	56 Days Gum (mg/100 cc)	56 Days Sediment (mg/100 cc)	120 Days Gum (mg/100 cc)	120 Days Sediment (mg/100 cc)	187 Days Sediment (mg/100 cc)
A-1	480	9.3	4.4	1	(d)	0	(d)	0	10.6	Trace	Trace
				2		0		0	6.6	"	"
				3		0		0	11.6	"	"
				Avg.		0		0	9.6	"	"
A-3	240	10.7	2.4	1	5.8	0		0	5.4	5.1	10.5
				2	3.4	0		0	5.2	5.8	11.8
				3	--	0		0	5.0	7.0	11.6
				Avg.	4.6	0		0	5.2	6.0	11.5
B-1	340	8.76	11.8	1	15.0	0		Trace	--	1.1	9.4
				2	17.8	0		"	32.2	3.0	7.9
				3	--	0		"	24.2	2.7	8.5
				Avg.	16.4	0		"	28.2	1.8	9.0
B-3	360	5.20 (7.2)(e)	5.6	1	4.4	0		0	5.4	0.7	4.4
				2	5.8	0		0	4.8	1.4	2.1
				3	--	0		0	10.4	0.8	5.5
				Avg.	5.1	0		0	6.7	1.0	4.0
C-1	420	7.34	(d)	1	(d)	0		Trace	(d)	5.6	
				2		0		"		5.8	
				3		0		"		4.8	
				Avg.		0		"		4.5	

(a) See Ref. 3 for sample characteristics and identification.
(b) Total of insoluble plus adherent sediment.
(c) ASTM Method D-381.
(d) Steam jet gum not determined for heavy samples (C-1 or C-3), gum not determined at 56 or 187 days or at 28 days for A-1.
(e) Replicate measurement.

FIGURE 25



* See Appendix A for characteristics of shale liquids.

TABLE 22

ACCELERATED STORAGE STABILITY TESTS WITH OAK RIDGE SHALE OILS(a)

	Inspections(b)					Storage Stability Total Sediment (mg/100 ml) After(e)		
Oil	N ppm	S ppm	Pyrrole N (ppm)(c)	Exist. Gum(c,d) (mg/100 ml)	Acid # (mg KOH/g)	28 Days	70 Days	120 Days
JP-5 Precursor 4604(f)	3800(c)	0.4	71.7	12.6	0.032	1.5	4.2	7.2
JP-8 Precursor 4605(f)	3900(c)	1.0	123.2	21.0	0.070	8.0	16.0	22.0
DFM Precursor 4606(f)	3600	0.6	194	31.6	0.037	4.3	10.5	17.2
JP-5 Product 4608(f)	22	15	.02	0.0	0.000	0.0	0.0	0.8
JP-8 Product 4609(f)	0.5	0.6	8.1	1.6	0.002	0.0	0.0	1.1
DFM Product 4610(f)	15	7.0	1.3	0.6	0.001	0.0	0.0	0.6

(a) See Appendix Table A-5 for more complete inspections on these oils.

(b) Reported by Oak Ridge National Labs unless otherwise noted.

(c) Exxon values.

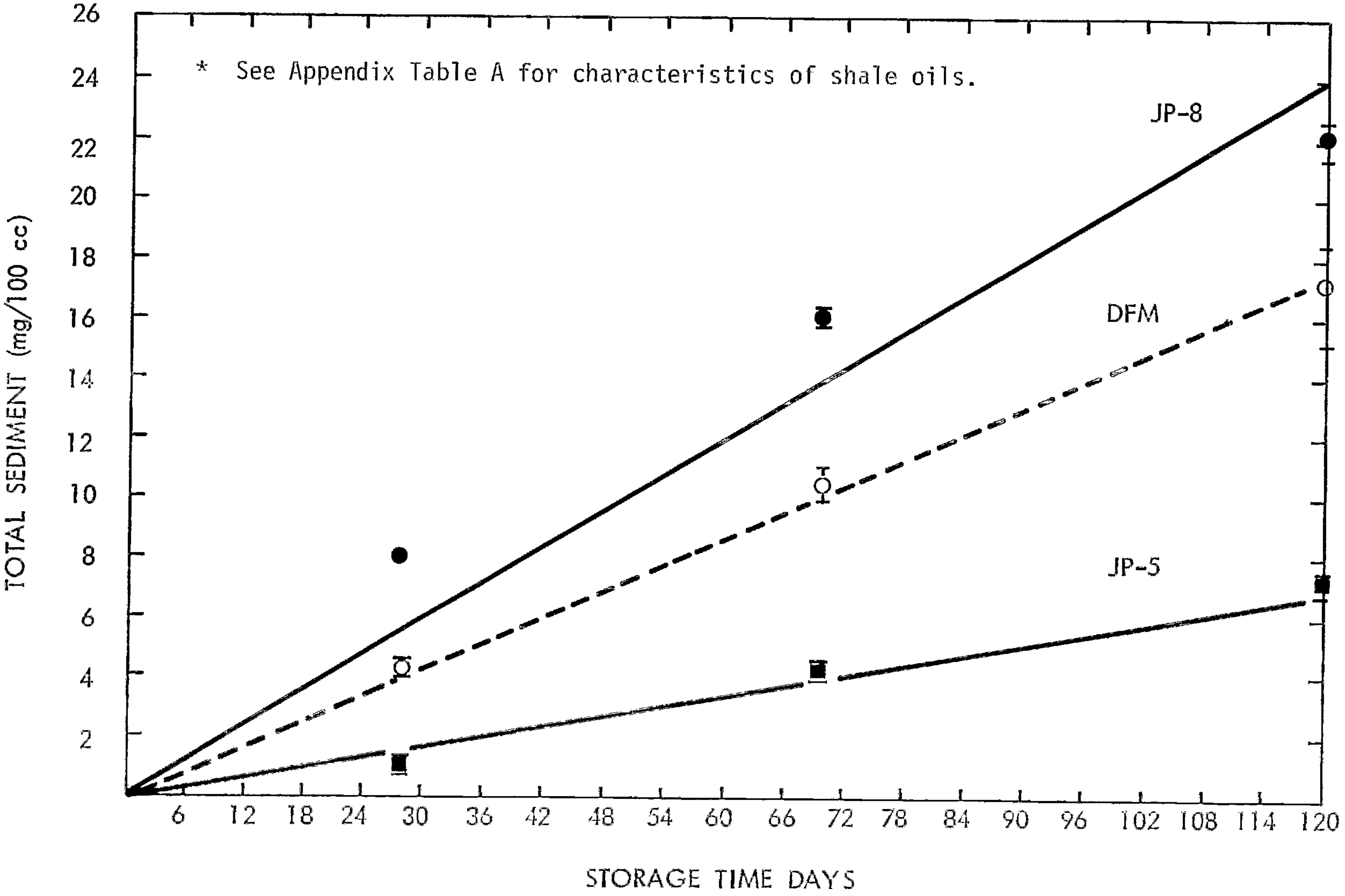
(d) Sum of adherent plus insoluble values.

(e) Sum of adherent and insoluble sediments; avg. of three replicates. storage at 110°F in dark.

(f) Oak Ridge designation.

FIGURE 26

SEDIMENT FORMATION DURING ACCELERATED STORAGE TESTS WITH OAK RIDGE PRECURSOR OILS*



* See Appendix Table A for characteristics of shale oils.

2.5.2.5 Studies with JP-5 Derived from Shale

A single sample of shale-derived JP-5, prepared some years ago by Exxon(5,23) was examined for gum and sediment formation at 110°F in the dark and at ambient temperature exposed to light. Results are shown in Table 23. This material, which was exhaustively hydrotreated, had been stored in a closed container at ambient conditions for about 4 years prior to this test. It was clear, nearly colorless and contained no sediment. The existent gum level was only 2.0 mg/100 cc, well below the JP-5 specifications of 7.0 mg/100 cc.(24) After 60 days at 110°F this sample showed no change in color nor was any measurable sediment produced. The existent gum at the end of this period had risen to 3.0 mg/100 ml. However, after 112 days on the windowsill the fuel was dark colored and contained 67.2 mg/100 cc of a brown-black sediment. In addition, the existent gum level rose to 9.2 mg/100 cc.

2.5.2.6 Correlation Between Total Nitrogen and Sediment Formation

A plot of long-term (156 days) sediment levels vs nitrogen content for various shale liquids is given in Figure 27. The long-term storage data was used in order to include the low nitrogen samples. In some cases the values used were extrapolated from shorter-term results. It appears that for shale liquids from the same source and with similar upgrading procedures (e.g., the in situ shales in Figure 27) a rough correlation between total nitrogen content and sediment formation exists. Fuels with different histories (e.g., the Oak Ridge samples in Figure 27) do not show the same correlation. This is another example of the finding that the character of the nitrogen compounds may be of greater importance to sediment formation than the total amount of nitrogen present. Clearly, simply determining the nitrogen content of a fuel is not sufficient for an accurate prediction of its stability.

2.5.3 Interaction Effects in Actual Shale Liquids

One likely option in the development of a synfuel industry is the integration or blending of syncrudes or finished products with other synthetics or with petroleum-derived materials.(1) It is, therefore, of importance to determine the compatibility of shale liquid with themselves and with petroleum fuels and to see whether the same or similar N-N or N-S interactions occurred as in the case of model fuel systems. During the present program the following blends were studied:

(1) Various shale liquids with model nitrogen compounds - test for N-N interactive effects.

(2) Shale liquids and sulfur compounds.

TABLE 23

GUM AND SEDIMENT FORMATION IN A SHALE-DERIVED JP-5 UNDER DIFFERENT STORAGE CONDITIONS(a)

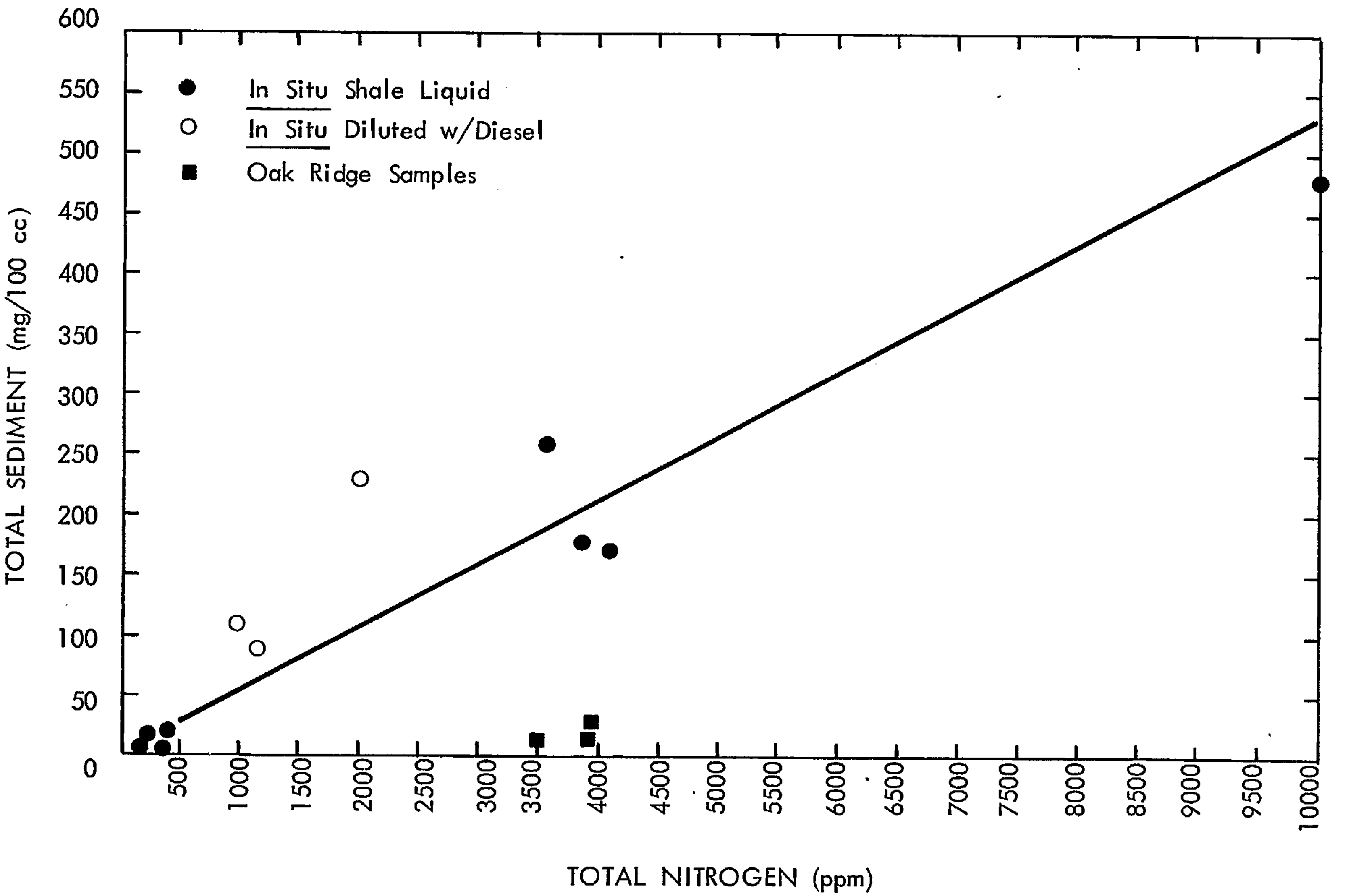
Storage	Temperature	Time (Days)	Existent Gum (mg/100 cc)	Total Sediment (mg/100 cc)
None(b)	72°F	--	2.0	0.0
Dark	110°F	60	3.0	0.0
Light	72°F	115	9.2	67.2

(a) For description of this material see Appendix Table A-6.

(b) Sample had been stored in closed container for 4 years prior to test.

FIGURE 27

PLOT OF NITROGEN CONTENT VS. SEDIMENT LEVEL IN VARIOUS SHALE LIQUIDS (AFTER 156 DAYS AT 110°F)



(3) Blends of shale liquid with petroleum-derived fuels.

(4) Mixtures of different shale liquids from similar and various sources.

2.5.3.1 Interactions Between 2,5-Dimethylpyrrole (DMP) and Various Shale Liquids

The shale liquids studied reacted in varying ways when spiked with 150 ppm of DMP. In some cases a strong positive interaction (more sediment than expected - see Section 2.4.3) resulted while in others a negative interaction was observed. These results are given in Table 24 and Figures 28 and 29. It is significant that, in all but one instance, strong positive interactions were encountered between DMP and shale liquid with high nitrogen contents (A-4, C-3, C-6 and the JP-8 precursor, all containing several thousand ppm N) while strong negative interactions were observed with liquids which had been severely processed to low nitrogen levels (A-1, B-1, C-1 and JP-8 product). These results are illustrated by the plots in Figures 28 and 29 as well as results in Table 24. Here the strong positive interactions between DMP and A-4 and JP-8 precursor are contrasted with the negative interaction with A-1 and JP-8 product.

The single exception to the observation described above is, perhaps, significant. This is the partially hydroprocessed shale liquid C-4. This material has 10 000 ppm nitrogen but gives a possible negative interaction with DMP (Table 24). A possible explanation for this is that C-4 has >3000 ppm sulfur, the only shale liquid studied in this program with anything like this much sulfur. As shown in Section 2.4.3.2 above, sulfur compounds interact negatively with DMP and this may be occurring here. Figure 30 contrasts the different responses of C-3 (103 ppm S) and C-4 (3107 ppm S) to added DMP. The low sulfur liquid C-3, interacts very strongly to added DMP while C-4 appears to interact negatively, if at all.

2.5.3.2 Sulfur-Nitrogen Interactions in Shale-Derived Fuels

The results of some limited experiments on the effects of thiophenol on sediment formation in shale liquids are summarized in Table 25 and Figure 31. The interactions between thiophenol (1000 ppm S) and the shale liquids themselves was minimal. However, when DMP was added the thiophenol exerted a strong "negative" (or stabilizing) effect similar to those obtained in model compound studies (see Figure 30).

TABLE 24

INTERACTIONS BETWEEN DMP AND VARIOUS HYDROTREATED SHALE LIQUIDS(a)

Shale Liquid(b)	N Content (ppm)(b)	DMP Added (ppm N)	Total Sediment (mg/100 cc)(c)					Interaction Type (Significance)(d)
			28 Days	56 Days	70 Days	84 Days	120 Days	
A-1	480	None	0	0	--	--	Trace	
None		150	40.9	74.5	--	--	134.3	
A-1	480	150	18.4	52.2	--	--	110.4	Neg (S)
A-4	3600	None	70.3	--	112.2	--	155.3	
None		150	40.9	--	110.0	--	134.3	
A-4	480	150	208.5	--	364.6	--	464.2	Pos (HS)
A-6(e)	1300(e)	None	41.7	89.1	--	--	--	
None		150	40.9	74.5	--	--	--	
A-6(e)	1300	150	241.6	310.1	--	--	--	Pos (HS)
B-1	340	None	0	Trace	--	Trace	--	
None		150	40.9	74.5	--	90.0	--	
B-1	340	150	22.2	50.4	--	74.0	--	Neg (HS)
C-1	420	None	0	0	--	--	4.5	
None		150	40.9	74.5	--	--	134.3	
C-1	420	150	24.1	60.5	--	--	139.3	Neg (HS at 28, 56)
C-3	4100	None	39.1	86.5	--	138.5	--	
None		150	40.9	74.5	--	90.0	--	
C-3	4100	150	143.2	275.6	--	430.0	--	Pos (HS)
C-4	10 000	None	79.6	161.8	--	--	382.1	
None		150	40.9	74.5	--	--	134.3	
C-4	10 000	150	99.4	175.3	--	--	335.2	Neg (? - S)
JP-8 Prod.	0.5	None	0	--	0	--	0.8	
None		150	40.9	--	110.0	--	134.3	
JP-8 Prod.	0.5	150	29.7	--	56.9	--	108.7	Neg (HS)
JP-8 Prec.	3900	None	4.3	--	10.5	--	22.0	
None		150	40.9	--	110.0	--	134.3	
JP-8 Prec.	3900	150	78.9	--	155.4	--	282.0	Pos (HS)

(a) Stored at 110°F in dark; DMP sediment "alone" based on No. 2 diesel studies.
(b) See Appendix Tables A-3 and A-4 for characteristics.
(c) Sum of insoluble plus adherent sediments.
(d) Students test (Ref. 17): Pos = "positive"; Neg = "negative" or stabilizing;
(HS) = highly significant; (S) = significant;
(?) = doubtful
(e) Diluted 1:10 with No. 2 diesel oil before DMP was added.

FIGURE 28

INTERACTIONS BETWEEN DMP AND TWO OAK RIDGE SHALE PRECURSOR OILS (DMP ADDED AT 150 PPM N LEVEL) (110°F STORAGE)

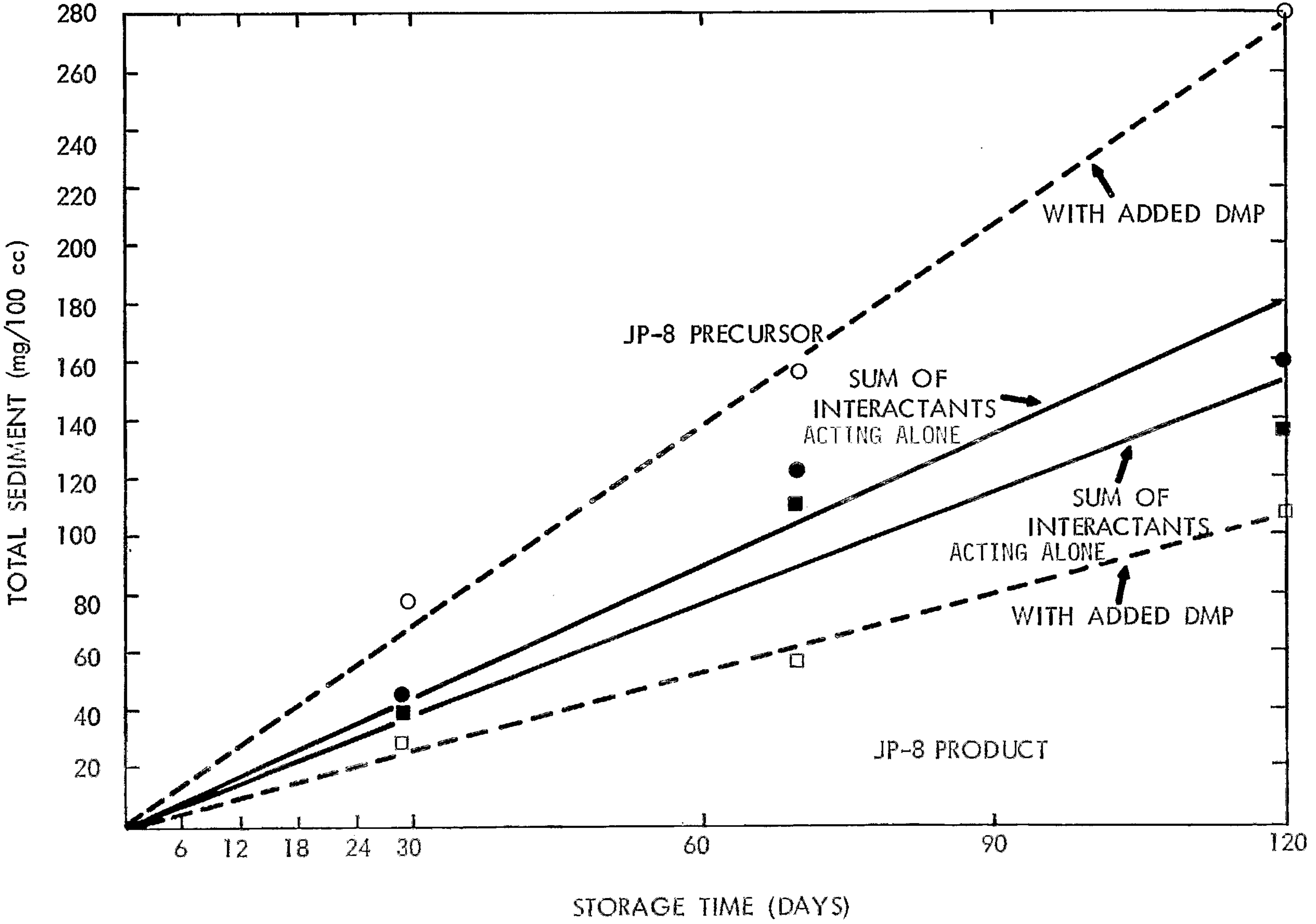


FIGURE 29

INTERACTIONS BETWEEN DMP AND SOME HYDROTREATED SHALE MIDDLE DISTILLATES AS INFLUENCED BY NITROGEN LEVEL OF SHALE LIQUID

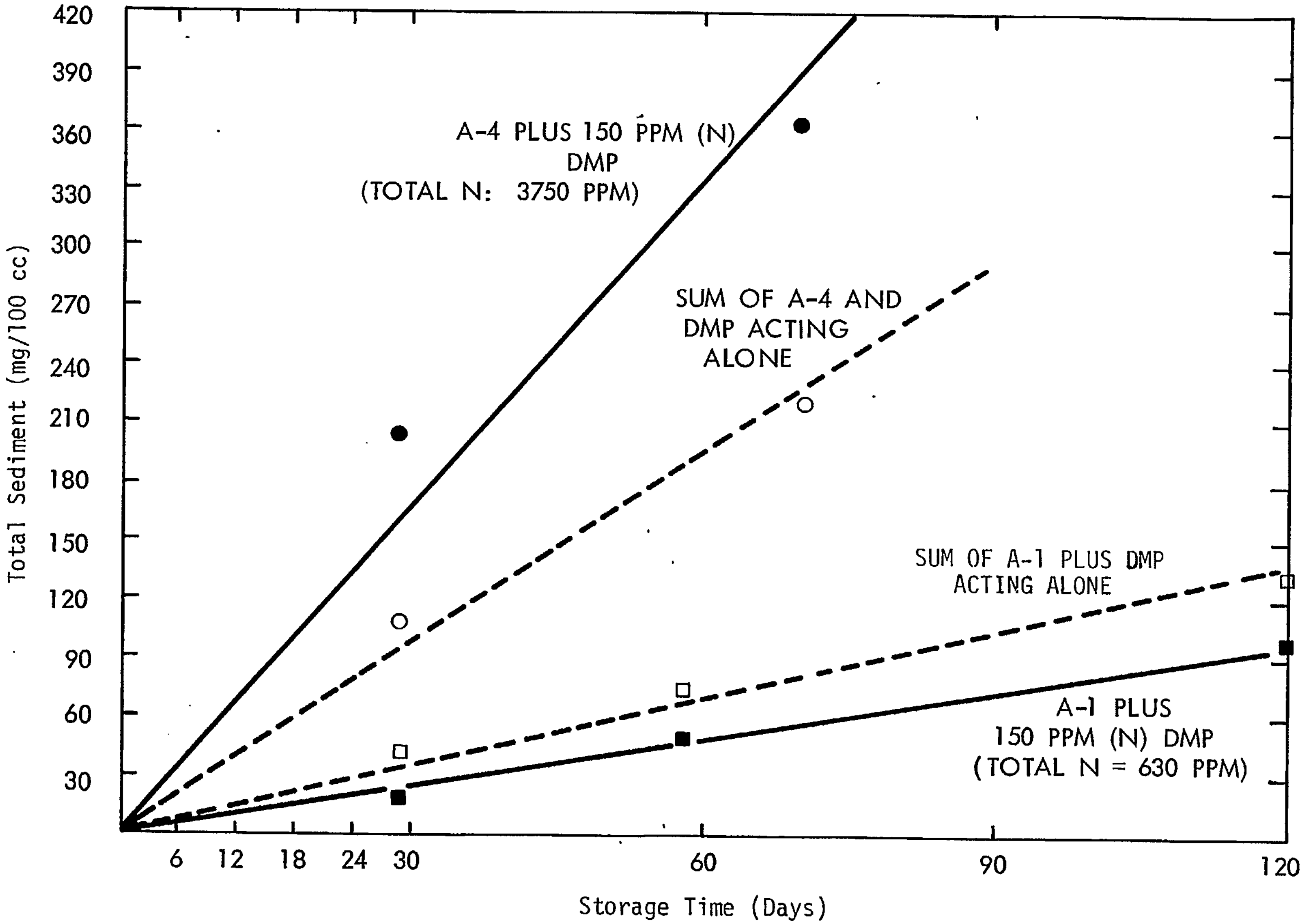


FIGURE 30

SEDIMENT FORMATION WITH VARIOUS HYDROTREATED SHALE MIDDLE DISTILLATES AS AFFECTED BY NITROGEN LEVELS, PYRROLE NITROGEN AND SULFUR

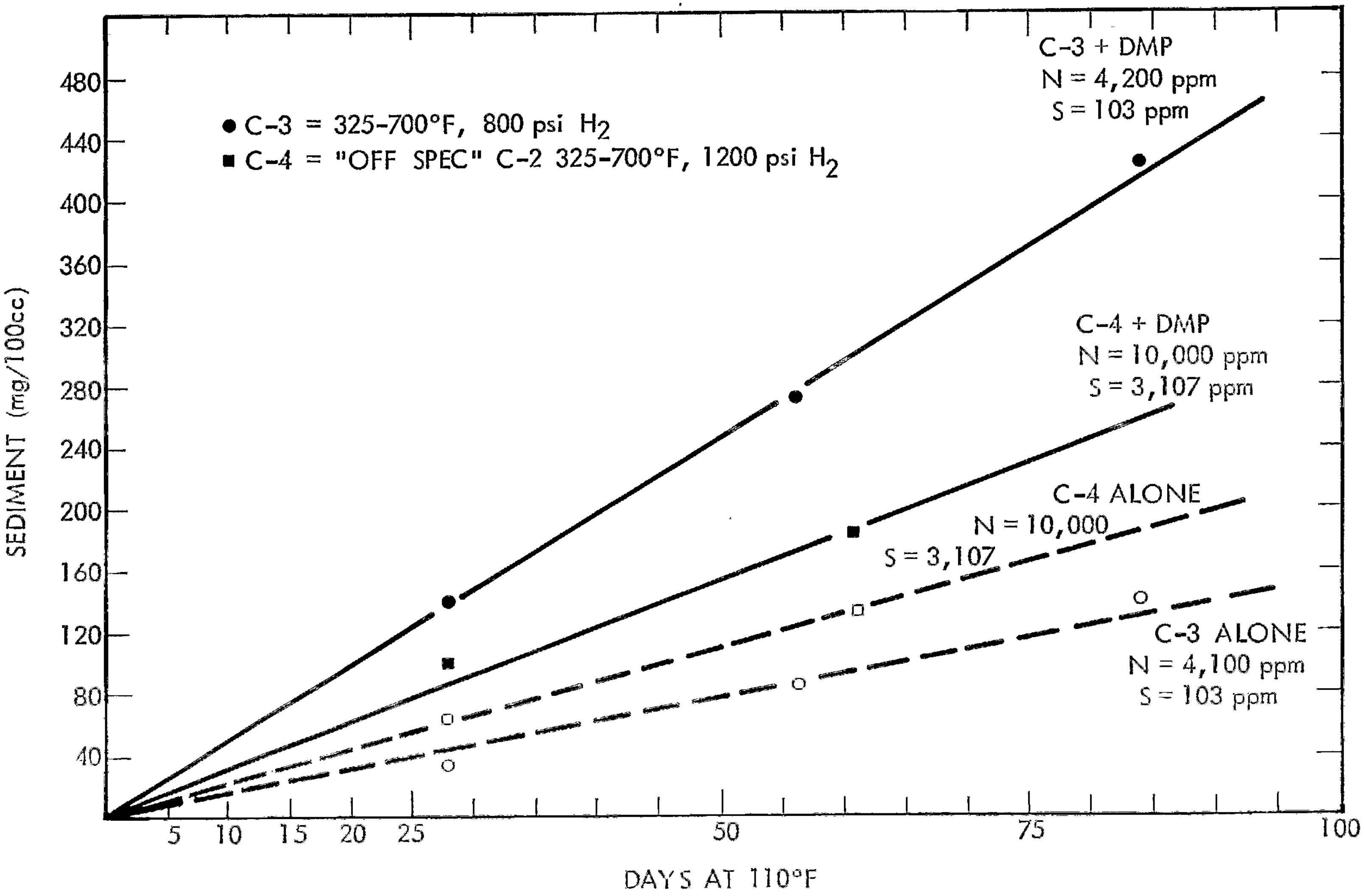


TABLE 25

INTERACTIONS BETWEEN THIOPHENOL, DMP AND SOME SHALE LIQUIDS[(a)]

Shale Liquid[(b)]	Thiophenol (ppm S)	DMP (ppm N)	Total Sediment (mg/100 cc)[(c)] After				Interactive Effect of Thiophenol (Significance)[(d)]
			28 Days	56 Days	84 Days	120 Days	
C-3	None	None	39.1	86.5	129.2	197.7	
C-3	1000	None	59.2	80.1	--	144.4	Neg (?)
C-3	None	150	143.2	276.5	--	--	
C-3	1000	150	117.8	249.4	--	--	Neg (S)
C-3	3000	150	4.8	11.3	--	--	Neg (HS)
C-4	None	None	79.6	161.8	251.7	--	
C-4	1000	None	53.6	164.7	226.5	--	Neg (?)
C-4	None	150	99.4	--	--	--	
C-4	3000	150	7.1	--	--	--	Neg (HS)

(a) Stored at 110°F in dark.

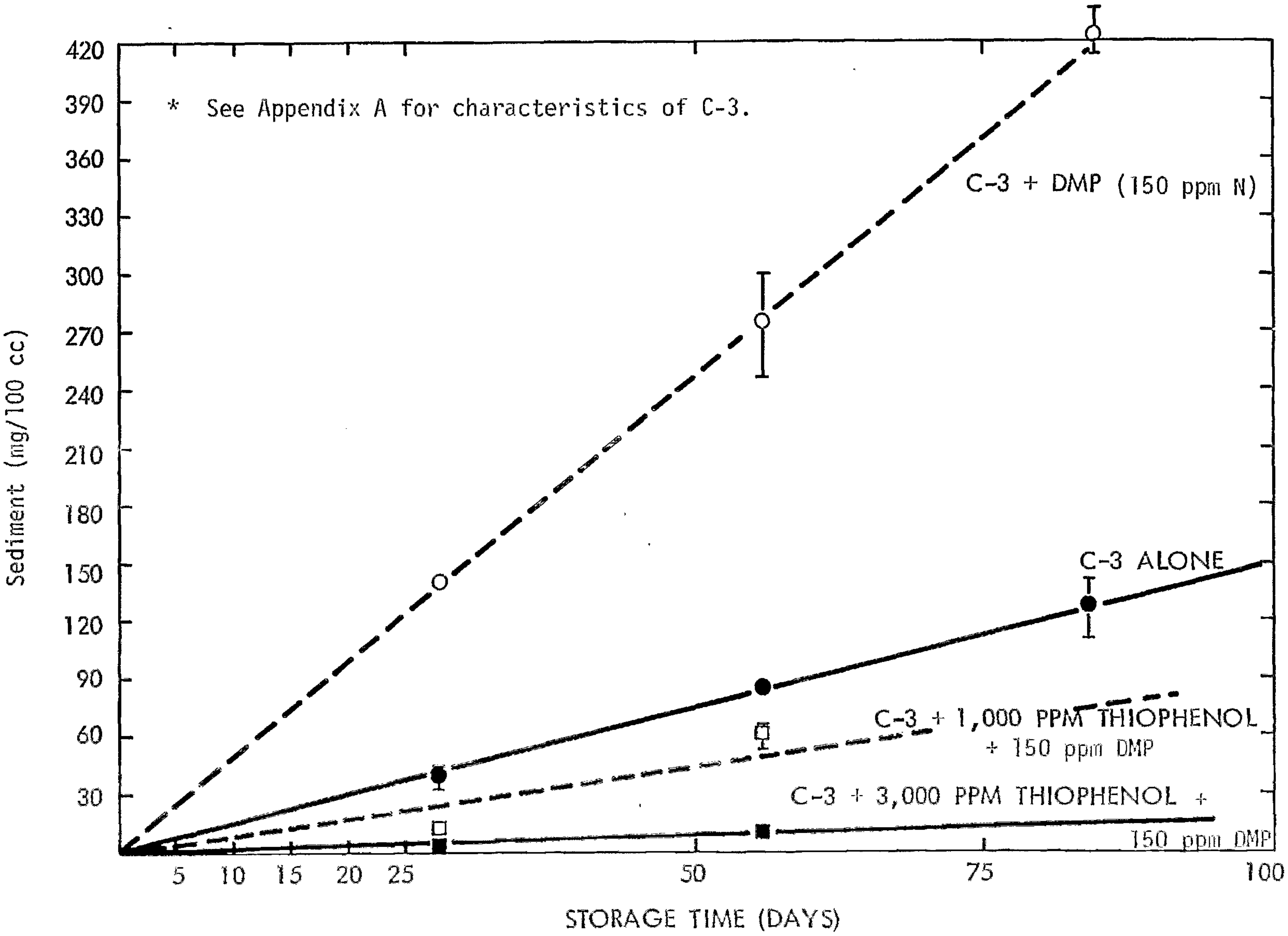
(b) See Appendix Table A-3 for characteristics.

(c) Sum of insoluble plus adherent; average of three replicates.

(d) Students test (Ref. 17); Neg = "negative" or stabilizing" (?) = doubtful; (S) = significant; (HS) = highly significant.

FIGURE 31

EFFECTS OF DMP & THIOPHENOL ON SEDIMENT FORMATION IN SHALE LIQUID C-3 (110°F STORAGE)*



2.5.3.3 Interactions Between Shale Liquids and Petroleum-Derived Middle Distillates

Blends of two shale middle distillates with No. 2 diesel fuel were studied. There appeared to be no gross incompatibility. Accelerated storage stability tests were run and are summarized in Table 26 and Figure 32. Interestingly enough it appears that sediment level may not be linearly related to the dilution (i.e. the nitrogen content) (see Figure 32). This is in contrast to what was observed with mixtures of model compounds. Thus, blending may be useful in achieving enhanced stability but a one-to-one relationship between dilution and sediment level may not be attainend.

2.5.3.4 Interactions in Blends of Shale Liquids from the Same and Varying Sources

The results of a preliminary study to determine whether interactive effects occurred when blends of different shale liquids were subjected to accelerated storage stability tests are summarized in Table 27. No incompatibilities were observed. Surprisingly, no significant interactions were detected in this study. A slight but significant negative interaction was encountered with A-6 and the DFM precursor and a small positive one with A-3 and DFM precursor. However, the data are insufficient to draw any conclusions at the present time.

2.5.4 Characteristics of Sediments Derived from Shale Liquids - Comparison with Model Compound Studies

This effort is aimed at correlating the earlier work on model compounds(1,2) with results obtained with actual shale liquids. Two approaches were taken: (1) analysis of the shale liquid before and after storage to determine which compound types are likely involved in sediment formation; (2) analysis of the sediment itself.

Analyses were performed on fresh and aged C-4 shale oil distillate. Each sample was fractionated by gradient elution on silicic acid to determine which classes of compounds were involved in sediment formation. Gas chromatographic/flame ionization analyses coupled with GC/MS indicate that the major changes occur in the alkyl pyrrole, alkyl indole portion of the neutral N-heterocyclics fractions (with the indoles predominating). The fractions obtained and their changes on storage are shown in Table 28. From these data and the appearance of the GC/FID chromatograms, only Cut III, which contains neutral nitrogen heterocycles, was reduced significantly on accelerated storage testing. This is consistent with the idea that it is these types of compounds which participate in sediment formation.

TABLE 26

EFFECTS OF BLENDING OF SHALE LIQUIDS AND PETROLEUM MIDDLE DISTILLATES(a)

Shale Liquid(b)	Blending Ratio	Resultant N Level (ppm)	Total Sediment (mg/100 cc)(c)	
			28 Days	56 Days
C-4	None	10 000	79.6	162
	1:4	2 000	41.2	73.5
	1:9	1 000	19.0	31.6
A-6	None	12 000	297	405
	1:4	2 400	124	168.7
	1:9	1 200	41.7	89.1

(a) Storage at 110°F in dark.

(b) See Appendix Table A-9 for characteristics.

(c) Sum of insoluble plus adherent; average of 3 replicates.

TABLE 27

ACCELERATED STORAGE STABILITY OF BLENDS OF SHALE MIDDLE DISTILLATES[a]

Components of Blend[b]	Total N in Blend (ppm)	Total Sediment (mg/100 cc)[c]			
		14 Days		42 Days	
		Expected	Observed	Expected	Observed
C-3 + A-6	8050	84.1	82.9	223	230
C-3 + JP-5 Prec.	3950	10.2	10.9	30.6	30.0
C-3 + DFM Prec.	3850	17.8	11.8	53.4	31.5
C-3 + DFM Prod.	2050	9.8	9.0	29.4	21.8
A-3 + A-6	6120	99.0	118.8	297	223.0
A-3 + DFM Prec.	2010	2.7	9.9	8.1	12.1
A-6 + DFM Prec.	7800	75.6	31.4	227	61.7
DFM Prec. + DFM Prod.	1800	2.7	2.5	8.1	5.7

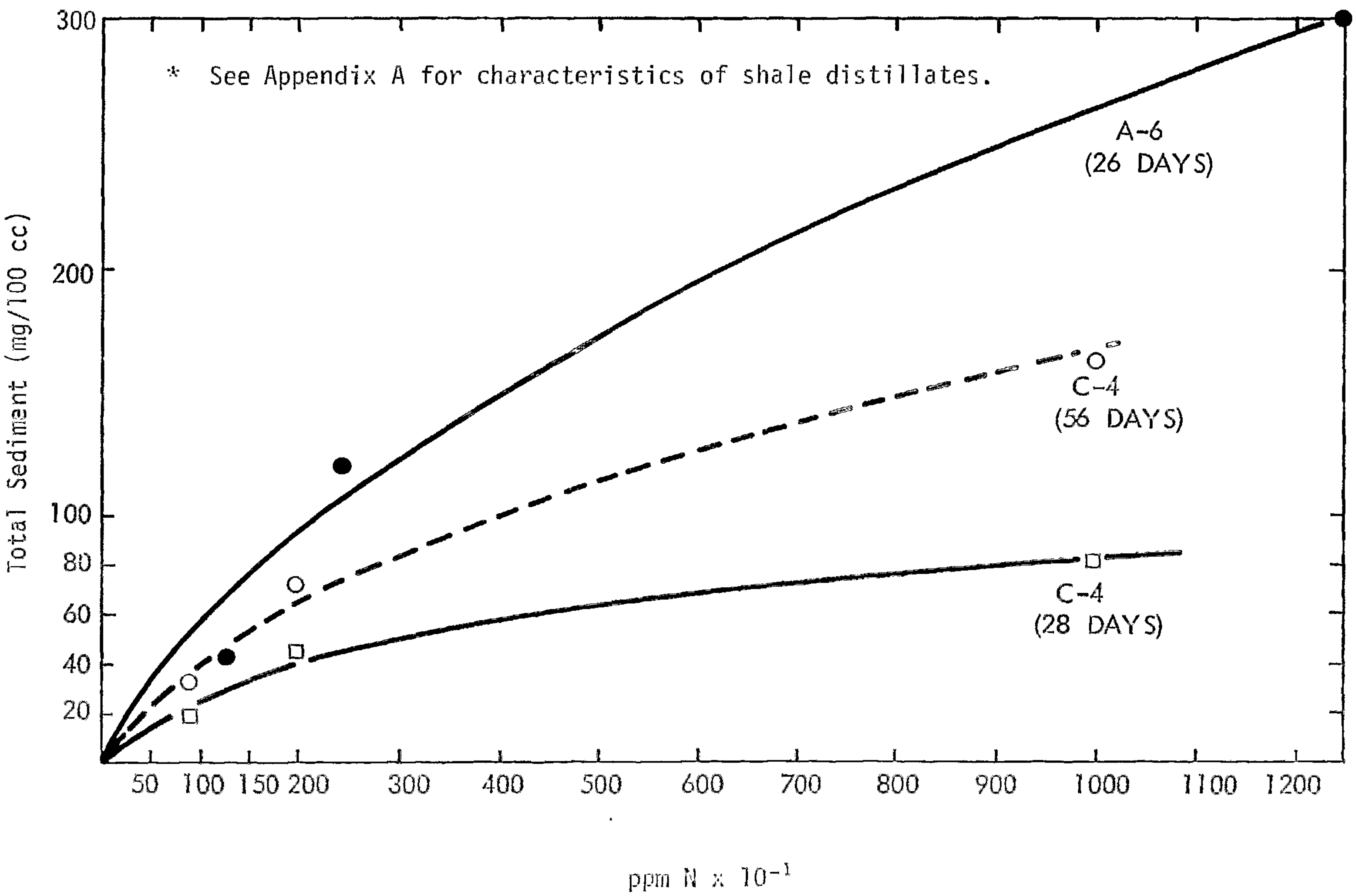
(a) Stored at 110°F in the dark.

(b) See Appendix A for characteristics of fuels; blends were all 50/50 by volume.

(c) Sum of insoluble plus adherent; "Expected" means sum of two components acting alone.

FIGURE 32

EFFECTS OF BLENDING SHALE DISTILLATES A-6 AND C-4 WITH NO. 2 DIESEL (STORAGE AT 110°F)*



* See Appendix A for characteristics of shale distillates.

TABLE 28

FRACTIONATION OF SHALE LIQUID C-4 BY CHROMATOGRAPHY AND EFFECT OF AGING ON MASS DISTRIBUTION

Cut	Name	Mass Distributions[a] by GC/FID Unaged	Aged
I	Saturates	614	546
II	Aromatics	307	319
III	Neutral N-Heterocyclics	52.6	34.7
IV	Basic N-Heterocyclics	40.6	49.9
V	Polar N	75.2	77.4

(a) Given as mg/g of sample.

The infrared spectrum for the sediment derived from shale liquid C-3 is shown in Figure 33. The spectrum shows some similarities to that obtained from DMP in No. 2 diesel (compare Figure 32). There appears to be N-H present, a complicated carbonyl group but no long methylene chain as would be expected if the hydrocarbons in the liquid were incorporated in the sediment. The most significant feature of this trace is the strong, broad band at about 1100 cm^{-1}. The band is present in some of the shale sediments but weak or absent in others. Only a hint of this band is present in the DMP sediment. No assignment can be made for this band at present but it falls roughly in the C-O stretch region.(25) In appearance and behavior the shale sediments are similar to those from DMP although the shale sediments are somewhat more soluble in organic solvents. In addition, the curves of sediment formation *vs* time follow the same pattern as those of model compounds. The reactions seem to be inhibited by aromatics that are similar to model compound reactions.

The elemental analyses from several different shale sediments are shown in Table 29. Several interesting features are apparent. These include the relatively consistent nitrogen contents and the average N/C ratios (which fall in the alkyl indole region). These ratios are much higher than expected if any of the hydrocarbons were incorporated in the sediment. Another feature is the sulfur contents. These vary from virtually none to quite high values. Especially interesting is the fact that the *lowest sediment sulfur arises from the liquids which had the highest sulfur contents*. These same liquids also had the highest nitrogen contents *and* produced the greatest amount of sediment. Again this suggests a plurality of pathways for sediment formation. If an abundance of active nitrogen compounds are present (N content >5000 ppm) the sediment consists almost exclusively of polymerized nitrogen compounds. Where less of the active compounds are present, due to more severe hydroprocessing, sulfur compounds may get involved in sediment formation to a considerably greater extent, possibly by a different reaction mechanism.

It is difficult to draw firm conclusions concerning the mechanism of sediment formation from the data obtained from the storage of actual shale liquids because of the inherent complexity of such fuel systems. However, some generalizations concerning the reaction may be made.

(1) Nitrogenous sediment formation in shale liquids, as in the case of model compounds, involves oxidative oligomerization of nitrogen compounds possibly with participation of sulfur compounds.

(2) The neutral, heterocyclic compounds (mainly alkyl pyrroles and indoles) appear to be especially reactive.

(3) As in the case of model compound studies, not all nitrogen and sulfur compounds are active. Thus, total nitrogen content is not, by itself, a sufficient predictor of storage stability.

FIGURE 33

INFRARED SPECTRUM OF SEDIMENT FROM
SHALE MIDDLE DISTILLATE C-3 (MULL)

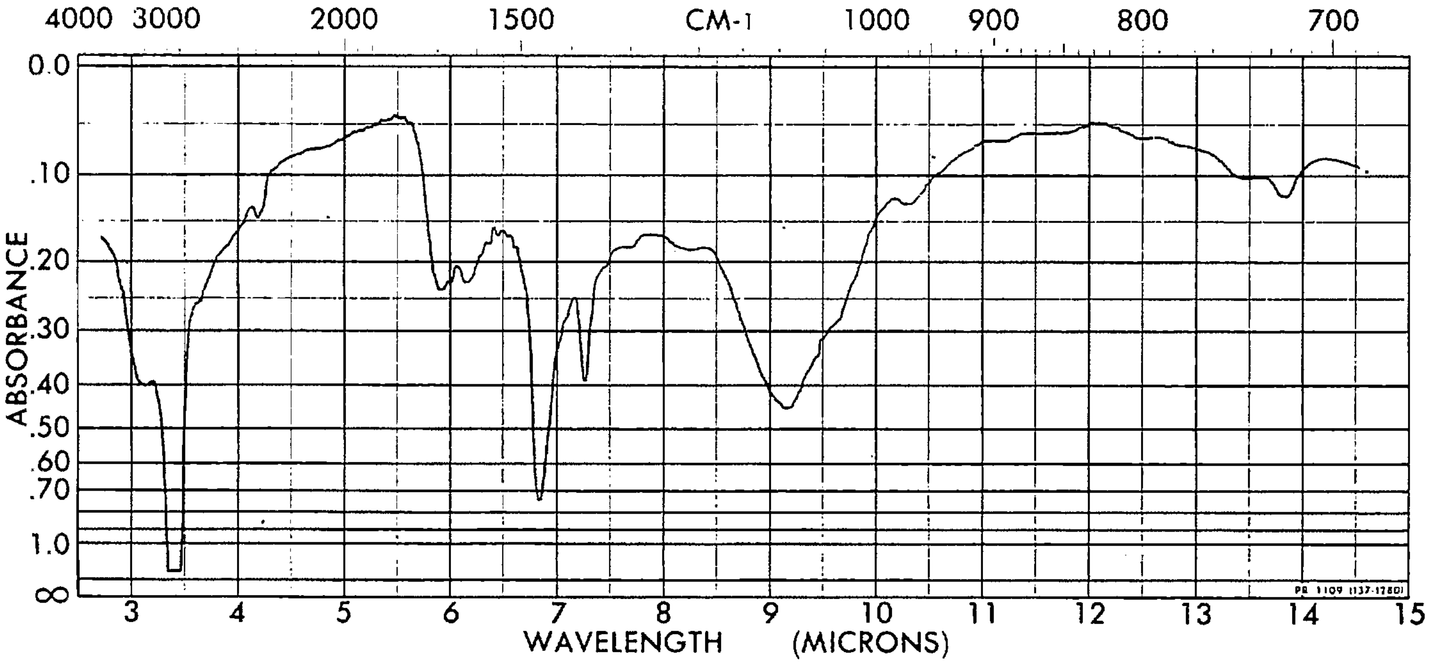


TABLE 29

ELEMENTAL ANALYSES ON SHALE SEDIMENTS(a)

	Fuels		Sediments					
Shale Liquid(b)	N Content (ppm)	S Content (ppm)	% C	% H	% N	% O(c)	% S	C/N Mole Ratio
"A"(d)	11 800	6200	74.82	7.98	5.78	10.54	0.88	15.1
"C"(d)	12 200	6200	79.32	8.42	5.60	6.66	0.82	16.5
A-4	3 600	2300	65.59	8.22	7.21	12.08	6.90	11.0
A-6(e)	12 000	>5600	75.93	7.99	6.84	8.26	0.98	12.6
A-6(e)	12 000	>5600	76.28	8.14	6.35	8.28	0.95	13.3
C-3	4 100	103	63.59	7.99	8.08	13.5	6.84	10.0
C-3							6.63(f)	
JP-5(g)	<100	<10	48.55	5.98	1.0	30.55	13.92	50
Alkyl Indoles (C_3-C_{10} Side Chains)								11-18

(a) Storage at 110°F in dark except where noted.
(b) See Appendix A.
(c) By difference.
(d) Distilled but not hydrotreated.
(e) Different samples from separate experiments.
(f) Repeat determination
(g) Heavily hydroprocessed (see Appendix Table A-6) stored at room temperature in light.

3. CONCLUSIONS

Based upon the results described above, the following conclusions can be drawn:

1. Nitrogen-containing compounds are the principal source of sediment formation. Organic sulfur- and oxygen-containing compounds by themselves, in general, do not cause sediment formation.

2. There are large differences in the reactivity of nitrogen compounds toward sediment formation. Removal of all nitrogen compounds from alternate sources may, therefore, not be necessary to produce stable fuels. (NOx emissions may still be a problem.)

    - Alkylated nitrogen heterocycles, especially with more than one alkyl group, are most deleterious; other N compounds are much less harmful.

    - The location of the alkyl group is important in determining reactivity; the most active positions are those adjacent to the N atom. Alkylation <u>on</u> the N atom reduces activity.

3. Interactions between nitrogen trace impurities can exert a significant effect on sediment formation.

    - "Non-deleterious" nitrogen-containing species such as amines can interact with other nitrogen compounds to either promote or inhibit sediment formation.

4. The nature of the hydrocarbon diluent has a lesser but still significant effect on storage stability.

    - Sediment formation increases as the diluent becomes more complex in the order, n-decane < jet fuel < No. 2 diesel fuel.

    - The nature of the diluent also influences interactive effects.

    - These effects are apparently not due to differences in gross hydrocarbon composition or differences in solvency but are, most likely, caused by trace impurities present in less highly refined fuels.

5. Most oxygen- and sulfur-containing compounds do not produce sediment by themselves but may influence the sediment forming reactions of nitrogen compounds.

   - Organic acids can be deleterious to storage stability by promoting nitrogenous sediment formation; the magnitude of the effect depends on the nature of the diluent.

   - Sulfonic acids can produce sediment by themselves and may catalyze sludge formation with nitrogen compounds.

   - Some compounds, especially aromatic thiols, tend to inhibit nitrogenous sediment formation to a significant extent.

6. Storage conditions can strongly affect the rate of sediment formation.

   - Increased temperature accelerates the reaction.

   - Exposure to light accelerates sediment formation and changes its reaction pathway.

   - Dissolved oxygen appears necessary for sediment to form at an appreciable rate.

   - Water may promote the reaction but the magnitude of the effect depends on the nature of the diluent and the water level.

7. The sediment forming reaction appears to be an oxidative condensation of the nitrogen compound to give low molecular weight oligomers.

   - The activation energy for the reaction is low, ranging from 10-15 Kcal/mole.

   - The reaction with model compounds shows a linear response to increasing concentration of nitrogen compound and appears to be a first-order reaction.

   - The sediment is apparently made up of several different compound types depending on the nature of the nitrogen compound and storage conditions.

8. Shale-derived middle distillates afford sediment resembling that from model compound studies.

   - Sediments obtained are similar to those from model compound tests but are more complex.

   - The neutral heterocyclic fraction of the shale liquid (which contains alkylated indoles and pyrroles) is most reactive toward sediment formation.

   - Interactive effects are similar to those in model compound studies.

9. Sediment formation in shale-derived middle distillates is only roughly correlated with total nitrogen content.

   - Samples with 3000 ppm N or greater show poor storage stability.

   - Fuels with <500 ppm total nitrogen have fair to good storage stability.

   - Predictions of storage stabilities in intermediate nitrogen ranges are difficult to make.

10. An accurate prediction of the storage stability of a shale-derived fuel cannot be made solely on the basis of the total nitrogen content.

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APPENDIX A

SOURCES AND INSPECTIONS ON TEST FUELS AND SHALE LIQUIDS

TABLE A-1

INSPECTIONS ON TEST FUELS FOR MODEL COMPOUND STUDIES

	No. 2 Diesel[a]	JP-8 [b]
API Gravity 60/60	35.8	41.3
Specific Gravity	0.8458	0.8189
Color (ASTM D1500)	0.5	0.0
Viscosity (cSt @ 100°F)	3.02	1.62
Acid No. (ASTM D664)	.03	0[c]
Existent Gum (Steam Jet)		1.0 mg/100 ml
Wt.% S	0.19	703 ppm
Wt.% N	40 ± 10 ppm	5 ± 1 ppm
Hydrocarbon Type		
Saturates, %	76.0	82.6
Aromatics, %	23.0	17.2
ASTM Distillation		
IBP	281	251
10%	397	342
20%	433	375
30	464	394
40	492	415
50	520	430
60	547	448
70	573	465
80	602	483
90	632	504
FBP	684	548

(a) Blended from components; additive-free.

(b) Sample was a commercial Jet A which is equivalent to an additive-free JP-8.

(c) No titer obtained.

TABLE A-2

INSPECTIONS ON UNTREATED SHALE DISTILLATES[a]

	Distillation Range	
Designation:	A.	C.
Property	325-640°F	325-700°F
Yield[b]	31.4%	45.4%
API Gravity (60/60°F)	31.5	29.7
Specific Gravity	.9100	.8773
Color[c]	Black	Black
Pour Point (°F)	+10	+25
Viscosity (cSt @ 100°F)	4.51	5.47
Ash	.01%	.01%
Elemental		
% C	84.84	82.53
% H	11.61	12.36
% N	1.18	1.22
% S	0.62	0.62
Fe (ppm)	16	250
V (ppm)	<1	2
Compound Type		
% Saturates	45.4	43.6
% Aromatics	30.8	31.1
% Polars	21.9	24.1
ASTM Distillation (760 mm)	°F	
IBP	326.1	356.5
10 pct recovered	431.9	446.8
20	466.5	484.3
30	492.3	513.8
40	515.5	545.1
50	541.4	573.4
60	565.0	598.6
70	583.4	624.0
80	609.0	651.2
90	645.4	683.3
FBP	787.2	736.9

(a) From Occidental Oil Shale Co. In Situ. Shale Oil (Ref. 4).

(b) Based on crude shale liquid charged to still.

(c) Too dark for ASTM Color test.

TABLE A-3

INSPECTIONS ON HYDROTREATED SHALE DISTILLATES[a]

	Hydrotreated Samples[b]								
Boiling Range	A. 325-640°F			B. 325-670°F			C. 325-700°F		
	A-1	A-2	A-3	B-1	B-2	B-3	C-1	C-2	C-3
Total Pressure (psi)[c]	1500	1200	800	1500	1200	800	1500	1200	800
API Gravity	43.0	43.0	42.1	41.9	41.9	40.6	40.8	37.1	36.8
Color (ASTM)	1.5	1.0	1.0	1.0	0.5	0.5	1.5	5.5	3.5
Cloud Point (°F)	+6	+6	+4	+18	+14	+18	+26	+28	+26
Pour Point (°F)	0	0	0	+10	+10	+10	+20	+20	+20
Cetane Index[d]	60.0	59.5	57.0	60.5	60.2	57.5	60.0	55.5	54.8
Viscosity (cSt, 100°F)	2.24	1.95	1.90	2.39	2.39	2.35	2.80	3.12	3.06
Elemental Analysis									
% C	81.94	85.47	85.81	85.55	85.58	84.66	86.47	86.65	86.50
% H	12.92	14.00	13.73	13.85	13.48	13.99	13.96	13.42	13.1
S (ppm)	49	--	44	67	68	46	56	122	103
N (ppm)[e]	480	--	240	340	300	360	420	3900	4100
Pyrrole N (ppm)			10.7	8.8		5.2	7.3		58.1
Compound Type									
% Sats	84.9	84.0	76.0	83.1	82.3	80.4	84.4	71.5	70.8
% Arom	15.1	13.8	21.8	14.7	16.6	19.2	15.2	27.7	29.0
% Polars	0.5	0.3	0.5	0.7	0.7	0.3	0.3	0.3	0.3
% Ash	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

TABLE A-3 (Continued)

INSPECTIONS ON HYDROTREATED SHALE DISTILLATES[a]

Boiling Range	Hydrotreated Samples[b]								
	A. 325-640°F			B. 325-670°F			C. 325-700°F		
	A-1	A-2	A-3	B-1	B-2	B-3	C-1	C-2	C-3
Total Pressure (psi)[c]	1500	1200	800	1500	1200	800	1500	1200	800
ASTM Distillation									
IBP (°F)	233	233	234	237	236	237	238	239	241
10%	320	310	317	352	350	356	362	383	385
50%	482	480	486	502	498	506	515	530	529
90%	605	604	607	629	623	629	651	654	652
FBP	702	715	718	752	724	737	770	756	753

(a) Prepared by hydrotreating crude *in situ* shale liquids (Table A-2) - See Ref. 4.

(b) Samples are designated according to boiling range (A = 325-640°F; B = 325-670°F; C = 325-700°F) and hydrotreating severity; details in Ref. 4.

(c) Catalyst: Shell 325; one LHSV; Temp: 710°F.

(d) Estimated using ASTM D976; this method is in common use for petroleum diesels but may not be strictly applicable to fuels from alternate sources.

(e) Antek method.

TABLE A-4

INSPECTIONS ON "OFF SPEC" HYDROTREATED SHALE LIQUIDS[a]

Designation[b]	Boiling Range (°F)	% C	% H	% N	% S	Pyrrole N (ppm)
A-4	325 - 640	85.85	13.60	0.36	0.23	181.4
A-5	325 - 640	85.65	13.51	238 ppm	27.4 ppm	11.7
A-6	325 - 640			1.2	5.6	988
B-4	325 - 670	85.18	13.60	329 ppm	0.18	8.1
C-4	325 - 700	85.82	12.72	1.0	0.3	537.5

(a) Prepared from in situ shale liquids (Table A-2) by incomplete hydrotreating.

(b) Samples are designated according to boiling range (A = 325-640°F; B = 325-670°F; C = 325-700°F) and hydrotreating severity (A-1 = liquid A at 1500 psi, etc.); see Ref. (4) for more details on preparation of these samples.

TABLE A-5

PHYSICAL PROPERTIES OF SHALE OIL AND SHALE OIL MATERIALS(a)

	JP-5 Precursor 4604	JP-8 Precursor 4605	DFM Precursor 4606	Hydrotreated Residue 4607	JP-5 Product 4608	JP-8 Product 4609	DFM Product 4610
Bottom Sediment and Water (ASTM D-96), vol %	<0.05	<0.05	<0.05	0.05	0.05	<0.05	<0.05
Density (ASTM D-1481) @ 60°F, gm/ml	0.8063	0.8101	0.8409	0.8880	0.8068	0.8036	0.8342
Molecular Weight (Cryoscopic)	160	160	204	300	167	156	201
Pour Point (ASTM D-97), °F	<-60	-60	-5	+95	-60	-60	-5
Refractive Index (Abbe) @ 67°C	1.4293	1.4313	1.4448	1.4749	1.4299	1.4283	1.4471
Viscosity (ASTM D-445), cSt @ 40°C	1.271	1.336	2.678	9.068 @ 140°F too waxy	1.352	1.299	2.599
Viscosity (ASTM D-445), cSt @ 100°C	0.679	0.694	1.113	3.727	0.706	0.687	1.101
Carbon, Wt %	85.8	85.3	86.5		86.2	86.2	86.6
Hydrogen, Wt %	13.6	13.6	13.2		13.8	13.8	13.4
Nitrogen, ppm	3000 (M-H)	3600 (M-H)	3600 (M-H)		0.5 (MC)	22 (MC)	15 (MC)
Oxygen, ppm	200	270	310		1100	90	80
Sulfur, ppm	.4 (HA)	1 (HA)	.6 (HA)		15 (HA)	.6 (HA)	7 (HA)

HA = Houston Atlas

MC = Microcoulometric

M-H = Mettler-Heraeus

(a) Samples of Sohio-refined Paraho Shale Oil. See Ref. 6 for details.

TABLE A-6

PARAHO JP-5 SHALE OIL - SAMPLE CHARACTERISTICS(a)

Inspections	
S, ppm (wt)	698
N, ppm (wt)	10.0
Gum, exist (mg/100 cc)	2.0
FIA, Vol. %	
Aromatics	12.4
Olefins	1.5
Saturates	85.1
PM Closed Cup Flash Pt., °F	120.0
Freeze Pt., °F	-52.6
Smoke Pt., mm	25.0
Kin. Viscosity cSt @ 30°F	7.63
ASTM D-86, °F	
IBP/5%	305/336
10/20	345/365
30/40	376/388
50/60	398/408
70/80	416/426
90/95	436/453
FBP	491
% Recovery	99.0
% Loss	0
% Residue	1.0
API Gravity, 60/60	46.8

(a) Composite No. R-6536 (Ref. 5).

TABLE B-1

Reproducibility of Sediment Data Using Old Technique$^{(a)}$

Fuel	Replicate	DMP$^{(b)}$ (ppm)	Storage$^{(c)}$ Days	Total$^{(d)}$	Deposits (mg/100 cc) Mean $\bar{x}$	Deposits (mg/100 cc) Standard Deviation δ	Deposits (mg/100 cc) Standard Error $\delta/\bar{x}$ x 100
Diesel	1	1500	14	96.6	217.3	170.7	79%
	2			338.0			
	1	750	14	38.8	74.5	50.5	68%
	2			110.2			
	1	1500	28	452.1	572.9	170.8	30%
	2			693.6			
	1	750	28	358.1	431.8	104.2	24%
	2			505.5			
Average: $\delta/\bar{x}$							50%
JP-8	1	1500	14	123.1	114.8	11.7	10%
	2			106.5			
	1	750	14	36.3	60.2	33.8	56%
	2			84.1			
	1	1500	28	341.5	343.0	2.1	0.60%
	2			344.4			
	1	750	28	133.0	133.5	.64	0.47%
	2			133.9			
	1	1500	56	566.5	575.9	13.3	2.3%
	2			585.3			
	1	750	56	259.1	254.2	6.91	2.7%
	2			249.3			
Average: $\delta/\bar{x}$							12%

(a) 120°C 1-1/2 hour -- cool in disiccator.
(b) All at 43.3°C (110°F)
(c) No adjusted for fuel blank.
(d) DMP = 2,5-dimethylpyrrole; ppm level given as nitrogen basis.

TABLE B-2

Reproducibility in Diesel Fuel Using New Techniques[a]

Replicate	N-Cpd (ppm N)[b]	Storage (Days)	(°F)	Total	Deposits (mg/100 cc) Mean, $\bar{x}$	Standard Deviation δ	Standard Error $\delta/\bar{x} \times 100$
1 2	DMP (1500)	14	72	33.9 22.3	28.1	8.20	29%
1 2	DMP (1500)	14	110	189.0 188.1	188.6	0.64	0.34%
1 2	DMP (1500)	14	150	342.7 344.6	343.7	1.34	0.39%
1 2	DMP (750)	28	72	42.1 45.5	43.8	2.40	5.5%
1 2	DMP (750)	24	110	126.3 77.2	101.8	34.7	34%
1 2	DMP (1500)	28	72	110.0 107.0	108.5	2.12	2.0%
1 2	DMP (1500)	28	150	647.2 608.4	627.8	27.4	4.4%
1 2	DMP (150) 3-MeI (1350)	28	110	41.5 58.5	50.0	12.0	24%
1 2	DMP	28	110	239.9 252.6	246.3	8.98	3.6%
1 2	DMP (150) Isoq (1350)	28	110	57.9 57.4	57.7	0.35	0.61%
Average: $\delta/\bar{x}$							10%

(a) Careful rinsing with isooctane followed by drying at 120°C for 1-1/2 hours followed by vacuum pump overnight.
(b) DMP = 2,5-dimethylpyrrole, 3 - MeI = 3-methylindole, isoq = isoquinoline.

TABLE B-3

Color Tests for Pyrroles and Indoles Stored in Jet Fuel and No. 2-Diesel at 110°F

			ASTM D1500 Color							
			No. 2 Diesel				JP-8			
Replicate	Nitrogen Compounds	PPM Added(a)	Start	14 Days	28 Days	56 Days	Start	14 Days	28 Days	56 Days
1	None	---	0.5	0.5	0.5	0.5	0.0	0.0	0.5	0.5
2	None	---	0.5	0.5	0.5	0.5	0.0	0.0	0.0	0.5
1	DMP(b)	1500	0.5	3.5	4.0	(5)	0.0	3.0	3.5	2.5
2	DMP(b)	1500	0.5	4.0	4.0		0.0	3.0	3.5	2.5
1	DMP(b)	750	0.5	3.0	3.5		0.0	2.0	2.0	2.0
2	DMP(b)	750	0.5	3.0	3.0		0.0	2.0	2.5	2.0
1	DMP(b)	150	0.5	2.0	2.0		0.0	1.5	1.5	1.5
2	DMP(b)	150	0.5	1.5	1.5		0.0	1.0	2.0	1.5
1	2-Methylindole	1500	0.5	0.5	1.0		0.0	0.5	1.5	1.0
2	2-Methylindole	1500	0.5	0.5	1.0		0.0	0.5	1.5	1.0
1	2-Methylindole	750	0.5	0.5	1.0		0.0	0.5	1.5	0.5
2	2-Methylindole	750	0.5	0.5	1.0		0.0	0.5	1.0	1.5
1	2-Methylindole	150	0.5	0.5	0.5		0.0	0.5	1.0	1.0
2	2-Methylindole	150	0.5	0.5	0.5		0.0	0.5	1.0	2.0
1	3-Methylindole	1500	0.5	0.5	1.0		0.0	1.0	3.0	3.0
2	3-Methylindole	1500	0.5	0.5	1.0		0.0	1.0	2.5	3.0
1	3-Methylindole	750	0.5	0.5	0.5		0.0	0.5	2.0	2.5
2	3-Methylindole	750	0.5	0.5	1.0		0.0	0.5	2.0	2.0
1	3-Methylindole	150	0.5	0.5	0.5		0.0	0.5	0.5	1.5
2	3-Methylindole	150	0.5	0.5	0.5		0.0	0.5	0.5	1.0
1	Indole	1500	0.5	0.5	0.5	0.5	NT(3)			
2	Indole	1500	0.5	0.5	0.5	0.5				

TABLE B-3 (Contd.)

			ASTM D-1500 Color							
			No. 2 Diesel				JP-8			
Replicate	Nitrogen Compounds	PPM Added(a)	Start	14 Days	28 Days	56 Days	Start	14 Days	28 Days	56 Days
1	Pyrrole	1500	0.5	0.5	0.5	0.5	NT(3)			
2	Pyrrole	1500	0.5	0.5	0.5	0.5				
1	1,2,5-trimethylpyrrole	1500	0.5	2.0	---	---	NT(3)			
2	1,2,5-trimethylpyrrole	1500	0.5	2.0	---	---				
1	1,2,5-trimethylpyrrole	150	0.5	2.0	---	---	NT(3)			
2	1,2,5-trimethylpyrrole	150	0.5	2.0	---	---				
1	1,2,5-trimethylpyrrole	1500	0.5	2.5	2.5	---	NT(3)			
2	1,2,5-trimethylpyrrole	1500	0.5	2.5	2.5	---				
1	1-methylpyrrole	1500	0.5	0.5	0.5	0.5	NT(3)			
2	1-methylpyrrole	1500	0.5	0.5	0.5	0.5				
1	1-phenylpyrrole	1500	0.5	0.5	0.5	0.5	NT(3)			
2	1-phenylpyrrole	1500	0.5	0.5	0.5	0.5				
1	2,4-dimethyl-3-ethyl pyrrole	1500	0.5	(4)	(4)	(4)				
2	2,4-dimethyl-3-ethyl pyrrole	1500	0.5	(4)	(4)	(4)				

---

(1) Nitrogen basis.
(2) DMP = 2,5-dimethypyrrole
(3) NT = not tested in JP-8
(4) Too dark to measure
(5) Colors with DMP are generally too dark to measure by 56 days.

TABLE B-4

Studies with 2,5-Dimethylpyrrole (DMP) in No. 2 Diesel Fuel[a] at Various Times and Temperatures

Level Added (ppm)[b]	Storage Temp (°F)	Averaged Sediment Values (mg/100 cc)							
		7 Days				14 Days			
		Replicates	Insol.	Adherent	Total	Replicates	Insol.	Adherent	Total[c]
1500	110	--	--	--	--	5	51.6	141.2	192.8
750		8	24.1	0.6	24.7	15	57.2	28.4	85.6
150		--	--	--	--	--	18.1	5.8	23.9
		28 Days				56 Days			
1500	110	7	115.1	254.9	370.0	4	559.6	236.1	795.8
750		6	65.3	180.5	245.8	4	205.7	156.3	362.0
150		12	31.9	9.0	40.9	7	24.1	50.4	74.5
		80 Days							
	110								
750		4	359.4	63.2	422.6				
150		4	82.4	7.1	89.5				
		14 Days							
1500	74	3	35.9	7.0	42.9				
750		2	26.1	0.8	26.9				
		14 Days							
	155								
1500		2	215.0	160.4	375.4				

TABLE B-5

Insoluble, Adherent and Total Sediments from Fuels Containing Pyrroles and Indoles After Storage at 110°F

Nitrogen Compounds	Level (ppm)[a]	Sediment (mg/100cc)[b]								
		14 Days			28 Days			56 Days		
		Insol	Adherent	Total	Insol	Adherent	Total	Insol	Inherent	Total
					Normal Decane[c]					
2,5-Dimethylpyrrole	750	35.0	9.1	44.1	28.3	73.7	102.0	---	---	---
					JP-8					
2,5-Dimethylpyrrole	1500	19.6	88.9	108.5	11.1	302.6	313.7	138.1	448.2	586.3
	750	7.3	54.0	61.3	6.6	133.9	140.5	5.4	248.3	253.7
	150	0	0.8	0.8	.5	17.8	18.3	3.6	37.6	41.2
2-Methylindole	1500	trace	trace	trace	1.9	12.7	14.6	0.5	25.4	25.9
	750	0.4	0	0.4	3.6	7.8	11.4	2.5	12.4	14.9
	150	trace	trace	trace	trace	trace	trace	trace	0.5	0.5
3-Methylindole	1500	1.0	3.0	4.0	0.9	.10	1.0	0.3	trace	0.3
	750	1.1	trace	1.1	0.8	.10	0.9	0.2	0.7	0.9
	150	0	0	0	.09	.10	1.0	0.5	0.1	0.6
					No. 2 Diesel					
2,5-Dimethylpyrrole	1500	51.6	141.2	192.8	115.1	254.9	370.0	559.6	236.1	795.8
	750	57.2	28.4	85.6	65.3	180.5	245.8	205.7	156.3	362.0
	150	18.1	5.8	23.9	31.9	9.0	40.9	24.1	50.4	74.5
2-Methylindole	1500	trace	trace	trace	1.1	11.9	13.0	1.0	25.4	26.4
	750	0	0.4	0.4	2.8	7.0	9.8	2.5	12.5	15.0
	150	4.5	15.5	20.0	5.0	trace	5.0	0.2	3.0	3.2
3-Methylindole	1500	0.7	0	0.7	0.1	0.5	0.5	0.5	4.0	4.5
	750	0.2	0	0.2	0.1	0.1	0.2	0.9	0.8	1.7
	150	0	0	0	0.1	0.1	0.2	0.4	0.7	1.1

TABLE B-5 (Contd.)

No. 2 Diesel (Cont'd.)

Nitrogen Compounds	Level (ppm)[a]	Sediment (mg/100cc)[b] 14 Days Insol	14 Days Adherent	14 Days Total	28 Days Insol	28 Days Adherent	28 Days Total	56 Days Insol	56 Days Adherent	56 Days Total
Pyrrole	1500	0	0.7	0.7	3.0	trace	3.0	0.5	trace	0.5
Indole	1500	0	trace	trace	0.4	1.0	1.4	trace	1.0	1.0
1-Methyl pyrrole	1500	0	0	0	0	0	0	0	0	0
1-Phenyl pyrrole	1500	0	0	0	0	0	0	0	0	0
2,4-Dimethyl-3-ethyl pyrrole	1500	14.5	5.3	19.8	10.3	16.0	26.3	---	---	---
1,2,5-trimethylpyrrole	1500	67.8	19.8	82.6	---	---	---	474.0	352.0	826.0
	750				92.3	24.8	117.1			
	150	10.2	5.8	16.0	24.0	4.4	28.4	9.1	25.1	34.6

(a) Nitrogen basis; ppm = mg/100 cc.
(b) Average of 2-10 replicates, diesels corrected for blank, blank corrections: 14-day 0; 28-day 0.5, 56-day 0.5.
(c) Purified over silica gel and activated alumina.

TABLE B-6

ASTM Color Test Results for Various Nitrogen Compounds Stored in No. 2 Diesel Fuel at 110°F

Replicate	Nitrogen Compound[a]	ASTM D1500 Color			
		Start	14 Days	28 Days	56 Days
1	None	0.5	0.5	0.5	0.5
2	None	0.5	0.5	0.5	0.5
1	Benzimidazole[b]	---	---	---	---
2	Benzimidazole[b]	---	---	---	---
1	7-Azaindole	0.5	0.5	0.5	1.5
2	7-Azaindole	0.5	0.5	0.5	1.5
1	3-Methylpyrazole	0.5	0.5	0.5	0.5
2	3-Methylpyrazole	0.5	0.5	0.5	1.0
1	2-Methylpiperazine	0.5	0.5	0.5	0.5
2	2-Methylpiperazine	0.5	0.5	1.0	0.5
1	3-Methylpyridazine	0.5	1.0	1.0	1.0
2	3-Methylpyridazine	0.5	1.0	1.0	1.0
1	2-Methylpyrazine	0.5	0.5	0.5	0.5
2	2-Methylpyrazine	0.5	0.5	0.5	0.5
1	Quinaldine[c]	0.5	0.5	1.0	2.5
2	Quinaldine[c]	0.5	0.5	1.0	2.0
1	*m*-Tolylnitrile	0.5	0.5	0.5	0.5
2	*m*-Tolylnitrile	0.5	0.5	0.5	0.5
1	*n*-Undecylcyanide	0.5	0.5	0.5	0.5
2	*n*-Undecylcyanide	0.5	0.5	0.5	0.5
1	2-Methylbenzoxazole	0.5	0.5	1.0	0.5
2	2-Methylbenzoxazole	0.5	0.5	1.0	0.5
1	2-Methylbenzothiazole	0.5	0.5	1.0	0.5
2	2-Methylbenzothiazole	0.5	1.0	1.0	0.5

(a) All added at 1500 ppm N.
(b) Insoluble in No. 2 diesel.
(c) Quinaldine = 2-methylquinoline.

TABLE B-7

Insoluble, Adherent and Total Sediments(a) For Various Nitrogen Compounds Stored in No. 2 Diesel at 110°F

Nitrogen Compound(b)	28 Days			56 Days			112 Days		
	Insol.	Adherent	Total	Insol.	Adherent	Total	Insol.	Adherent	Total
3-Methylpyrazole(d)	0	0	0	0	0.7	0.7	0	1.0	1.0
4-Methylpyrazole(d)	0	0	0	0	0	0	0	0.2	0.2
3,5-Dimethylpyrazole(c)	0	0	0	Trace	Trace	Trace	4.8	120.5	125.3
Pyrazine	0	0	0	0	0	0	0	0	0
2-Methylpyrazine(d)	0	1.4	1.4	0	1.1	1.1	--	--	--
2,3-Dimethylpyrazine	0	0	0	Trace	Trace	Trace	0	0.7	0.7
2,5-Dimethylpyrazine	0	0	0	Trace	Trace	Trace	0	2.0	2.0
2,6-Dimethylpyrazine	0	0	0	0	0	0	0	0.6	0.6
2-Methylpiperazine	0.2	4.3	4.5	1.9	5.0	6.9	--	--	--
1-Methylpiperazine	0	0	0	Trace	Trace	Trace	2.1	3.0	5.1
N,N-Dimethylpiperazine	0	0	0	0	0	0	0.4	0.8	1.2
2,5-Dimethylpiperazine	0	0	0	0	Trace	Trace	0.3	17.6	17.9
2,6-Dimethylpiperazine	0	0	0	0	Trace	Trace	0.2	24.1	24.3
2-Methylpiperidine	0	0	0	0	0	0	2.8	10.4	13.2
3-Methylpiperidine	0	0	0	0	0	0	6.2	9.5	15.7
2,6-Dimethylpiperidine	0	0	0	0	0	0	1.0	2.8	3.8
3,5-Dimethylpiperidine	0	0	0	0	0	0	0	2.1	2.1
Pyrrolidine	0	0	0	0	0	0	0	0	0
1-Methylpyrrolidine	0	0	0	0	Trace	Trace	2.9	20.9	23.8
2,5-Dimethylpyrrolidine	0	0	0	0	Trace	Trace	1.0	10.5	11.5
Quinoline	0	0	0	0	0	0	0	0	0
Isoquinoline	0	0	0	0	0	0	0	0	0
3-Methylquinoline(d)	0.3	1.5	1.8	0	4.7	4.7	--	--	--
1,2-Dihydro-2,2,4-trimethylquinoline	--	--	--	14.5	2.1	16.6	--	--	--
7-Azaindole(c)	0.3	0.7	1.0	0	8.7	8.7	--	--	--
2-Methylbenzoxazole	0	0	0	0	0	0	0	Trace	Trace
2-Methylbenzothiazole	0	0	0	0	0	0	0	Trace	Trace
3-Methylpyridazine	0	4.2	4.2	0	4.0	4.0	--	--	--
<u>n</u>-Undecylcyanide	0	0	0	0	Trace	Trace	0	Trace	Trace
Trioctylamine	0	0	0	0	0	0	0	0	0
<u>m</u>-Tolylnitrile	0	0	0	0	0	0	0	Trace	Trace

(a) Compounds added at 1500 ppm N level (wt/vol); sediments average of 3 replicates unless otherwise noted.

(b) For structures, see Figure 1.

(c) Average of 6 replicates.

(d) Average of 2 replicates.

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