

EFFECTS OF NITROGEN COMPOUNDS ON
DEPOSIT FORMATION DURING SYNFUEL STORAGE*

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INTRODUCTION

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

One of the substances most difficult to remove is nitrogen. In addition, it is known that nitrogen content can adversely effect fuel stability. This is illustrated by Figure 1, where three jet fuels, prepared by catalytic hydrotreating shale liquids, were subjected to the standard JFTOT thermal stability test (2). Clearly, the higher the nitrogen content of a fuel, the poorer its thermal stability. Some of the samples were severely hydrotreated yet still retained significant amounts of nitrogen and exhibited poor thermal stability (2).

Recent work at Exxon has shown that nitrogen compounds, especially of the pyrrole type, promote sediment or sludge formation in JP-5 jet fuel stored under ambient conditions. The reaction is first noted by an almost immediate darkening of the fuel. This is followed by the appearance of sludge which continues to increase on standing. The reactions to form sediments were strongly influenced by light, acids and oxygen present in the fuel.

As a result of these preliminary observations, the present study was undertaken to investigate this phenomenon further. The major objectives of this program are: (1) to determine whether other nitrogen containing species, likely to occur in synfuels, will have effects similar to pyrroles, (2) to test for interactions between nitrogen compounds and other impurities, (3) to determine the effects of storage parameters such as light, temperature and oxygen content of the fuel on sediment formation and (4) to elucidate the chemical structure and mechanism of formation of the sediments produced.

EXPERIMENTAL

The test compounds were the highest quality commercially available. They were purified by distillation when necessary. High quality n-decane was employed

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Table 3. Components in Gas Samples Collected at Various Time Intervals and Reaction Conditions Listed in Table 1

Number	Time (min)	H ₂	CO ₂	C ₂ H ₆	CH ₄	CO	C ₃ H ₈	C ₃ H ₆	i-C ₄ H ₁₀	H ₂ S	n-C ₄ H ₁₀
53-1	40	76.8	10.8	0.3	0.8	0.3	0.2	0.05	0.04	0.1	0.07
53-2	70	75.3	16.5	0.7	1.8	0.5	0.4	0.06	0.06	0.2	0.10
53-3	98	66.2	22.9	1.5	3.5	0.7	0.9	0.06	0.10	0.2	0.18
53-4	120	68.3	21.5	1.6	3.7	0.6	0.9	0.04	0.10	0.2	0.19
53-5	235	67.9	18.6	1.7	4.1	0.5	1.0	0.04	0.12	0.2	0.28
54-1	40	0.2	15.0	0.4	1.1	0.3	0.3	0.06	0.03	0.7	0.07
54-2	80	0.3	12.4	0.4	1.5	0.4	0.3	0.04	0.04	0.5	
54-3	110	0.5	14.8	0.8	2.2	0.4			0.06	0.6	
54-4	130	0.7	14.1	0.9	2.4	0.5	0.5	0.04	0.03	0.3	0.13
56-1	120	63.6	24.3	1.9	5.2	0.8	1.0	0.07	0.09	1.2	0.22
56-2	240	53.6	31.2	4.6	10.7	0.7	2.5	0.07	0.22	1.6	0.59
56-3	420	57.6	27.7	4.2	12.6	0.6	1.4	0.02	0.08	0.6	0.17

TABLE 1
Effects of Nitrogen Compounds on Sediment Formation in Purified n-Decane

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

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

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

(3) Trace of liquid appeared after 30 days.

as the diluent. This was further purified by percolation through columns of activated alumina to remove traces of reactive, polar materials. The nitrogen compounds were tested at the 2,000 ppm level (nitrogen basis) which is within the limits expected from fuels derived from shale or coal (1). The compound 2,5-dimethylpyrrole was employed as a standard. The oxygenated compounds were added in amounts equivalent to 500 ppm O.

Duplicate sets of samples were set up using glass bottles. One set was stored in darkness at ambient temperature (24°C). The second set was irradiated with long wave (366 nm) UV light with an intensity of 1100 $\mu\text{W}/\text{cm}^2$ (3). A separate sample of *n*-decane with 4,000 ppm N as 2,5-dimethylpyrrole was exposed to normal sunlight to serve as a control. The bottles were removed from storage at intervals, the precipitate filtered and dried under vacuum at 110°C for 1-1/2 hours before weighing and subsequent analysis.

RESULTS AND DISCUSSION

Effects of Various Nitrogen Compounds

Compound type analyses of various light distillates of shale liquids have been reported (4). They show that pyrroles, quinolines, and pyridines are the dominant species present along with lesser amounts of amides, anilides and alkyl amines. Compounds of these types were, therefore, chosen for this study. The effects of various representative nitrogen-containing compounds on sediment formation in purified *n*-decane are given in Table 1. It is clear from this data that sediment formation is not unique to 2,5-dimethylpyrrole (DMP) although of those compounds tested, DMP easily produced the greatest amount. It is interesting that the three compounds giving the most sediment were all of the pyrrole type, DMP, indole and carbazole. Of the other compounds studied, only 2,6-dimethylaniline and 2-methylpiperidine afforded any measurable sediment. However, several of the primary amines produced colored solutions which intensified with time. Their effects on long term storage stability is unknown.

Importance of Light as a Promoter

The importance of light as a catalyst for sediment formation is illustrated by the plots in Figure 2. The difference between the irradiated and dark-stored samples is quite large early in the period and tends to get much smaller later. Thus, with DMP, sediment in the irradiated sample exceeded that for the dark sample by a factor of ten after one day but was only about 38% greater after 60 days. This suggests that exclusion of light will retard but not prevent sediment formation.

The sample stored in sunlight formed sediment slightly more rapidly than the UV irradiated material (Figure 2). This effect is not of practical significance but may have a bearing on the mechanism of sediment formation.

It should be noted that the build up of sediment in the dark follows a straight time relationship while the light catalyzed reaction does not. The dark reaction appears to be at least "pseudo" zero order while the catalyzed reaction is of a higher order. It should also be emphasized that the shape and general magnitude of the curves obtained in *n*-decane is in excellent agreement with those from actual JP-5 fuel.

Influence of Organic Acids and Phenols

Pyrroles are oxidized more rapidly in acidic than neutral media (5). As a result, it was of interest to determine whether organic acids, likely to be present in synfuels, would catalyze the formation of sediments in hydrocarbon media.

FIGURE 1

VARIATION OF JFTOT BREAKPOINT TEMPERATURE WITH NITROGEN LEVEL AFTER HYDROTREATMENT

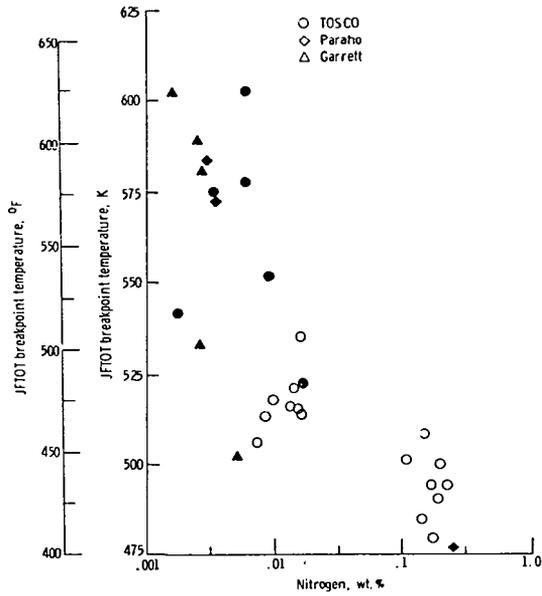
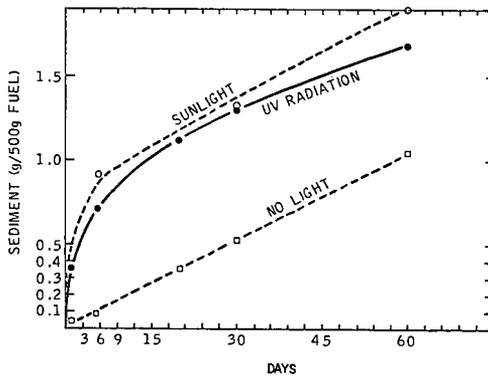


FIGURE 2

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



Preliminary experiments in JP-5 indicated a significant effect. This was confirmed in experiments using n-decane as the diluent. The results are summarized in Table 2.

TABLE 2

SEDIMENT FORMATION WITH 2,5-DIMETHYLPYRROLE (DMP)
UNDER THE INFLUENCE OF ORGANIC ACIDS

Acid (1)	Storage Conditions (2)	Cumulative Sediment (g/500 g Decane)					Appearance
		1 Day	5 Days	15 Days	30 Days	60 Days	
None	Light	.213	.524	.869	1.12	1.52	Dark Red
	Dark	---	.060	.197	.394	.840	Dark Red
<u>n</u> -Decanoic	Light	.390	.821	1.25	1.49	1.84	Dark Red
	Dark	.057	.147	.497	.990	1.50	Dark Red
Cyclohexane Carboxylic	Light	.391	.821	1.26	1.56	1.83	Dark Red
	Dark	.083	.216	.621	1.08	1.84	Dark Red
Benzoic	Light	.259	.476	.858	---	---	Clear,
	Dark	.057	.165	.414	---	---	Colorless
<u>n</u> -Decanoic Alone (3)	Light	---	---	---	---	---	Clear,
	Dark	---	---	---	---	---	Colorless

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

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

(3) No DMP in these samples.

Both n-decanoic acid and cyclohexanecarboxylic acid significantly increased the rate of sedimentation. This was evident in both light and dark. The acids promoted a 20% increase in sediment in 60 days in the light and by 100% or more in the dark over samples containing DMP alone. Control samples containing the acidic compounds but no DMP gave no sediment nor was any darkening of the fuel observed. Benzoic, a typical aromatic acid, showed no effect under light storage, but did tend to increase deposit formation in the dark.

It would appear that the acid and light catalysts operate independently rather than in any sort of synergistic or antagonistic fashion. This was apparent from a 3x3 factorial analysis of the data from Table 2. In the case of DMP and decanoic acid, the "light effect" accounted for 0.674 g of sediment in 15 days and 0.683 g in 60 days. The corresponding values for the "acid effect" are .303 g and .663 g. The sums of the two acting independently would be .977 g for 15 days and 1.34 g for 60 days. These values are fairly close to the 1.06 g and 1.00 g obtained in the same time periods from the experiment when both light and acid were present. It would appear that the two catalysts do not interact. An analysis was made for cyclohexanecarboxylic acid with similar results.

A number of phenols were examined with respect to promoting sediment formation with DMP in n-decane. All had an inhibitory effect, although considerable variation was observed. Results of these studies are given in Table 3. One of the most effective inhibitors was 2,6-di-t-butylphenol. Plots of sediment formation with DMP both with and without added 2,6-di-t-butylphenol are shown in Figure 3. A 58% reduction in sediment formation was obtained under light storage at 60 days and 80% reduction after 15 days as compared to controls. Under dark storage conditions, the corresponding reductions were 45% and 82%. A 3x3 factorial analysis for these experiments was performed. The "light effect" in this case is .683 g

TABLE 3

EFFECTS OF PHENOLS ON DEPOSIT FORMATION⁽¹⁾ WITH 2,5-DIMETHYLPYRROLE

Phenol Added ⁽²⁾	Cumulative Sediment (g/500 g/Decane)			
	15 Days		60 Days	
	Light	Dark	Light	Dark
None	.869	.197	1.52	.840
2,4,6-Trimethyl-	.681	.123	1.33	1.01
2,6-Di- <u>t</u> -Butyl-	.173	.035	.640	.496
2,4-Dimethyl-	.569	.213		
2,6-Di- <u>t</u> -Butyl-4-Methyl-	.270	.138		
2-Hydroxy-3-Isopropyl- (3-Isopropylpyrocatechol)	.154	.058		

(1) All samples contained 4,000 ppm N as 2,5 dimethylpyrrole.

(2) At levels of 500 ppm O.

(1.52 g - .837 for DMP alone) and the "phenol effect" is -.344 g. The net additive effect would be .339 g (.683 g - .344 g). However, the actual sediment obtained in the presence of both the phenol and light is .640 g, .20 g less than that observed under dark storage alone (60 day results). Apparently, this phenol is effective in combatting the effects of the light catalyzed reaction as well as the sedimentation under dark storage conditions.

The influence of other phenols on sediment formation varied considerably (Table 3). Those with t-butyl or isopropyl groups were most effective in retarding sedimentation. Substitution in position 4 with methyl groups tended to reduce effectiveness although the effect was not large. Work is continuing in this area to elucidate structural effects further.

Similar effects of acids and phenols were observed with indole as the nitrogen compound (Figure 4). Decanoic acid significantly increased sediment formation in the case of indole. A 6-fold increase in sediment was observed in the sample stored under UV light. Insufficient data is available for a factorial design analysis, but, in this case, light and acids may interact in some way to promote especially heavy sediment formation. Di-t-butylphenol appears to have a slight inhibitory effect on sediment formation with indole (Figure 4). The 2,4,6-trimethylphenol showed no detectable influence. These findings suggest that certain phenols may prove useful as sludge-preventing additives for future synfuels of the JP-5 type.

Characteristics and Chemical Structure of the Sediments

Determining the structure of the nitrogenous sediment is useful for elucidating the mechanism of formation and thereby finding methods of preventing it. Although storage conditions and the presence of acid may effect the rate of formation and quantity of sediment, they do not seem to alter the characteristics of the sediment. Elemental analyses of the sediments suggest that the deposits are made up largely of repeating units of the 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, obtained under various storage conditions, was:

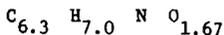


FIGURE 3

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

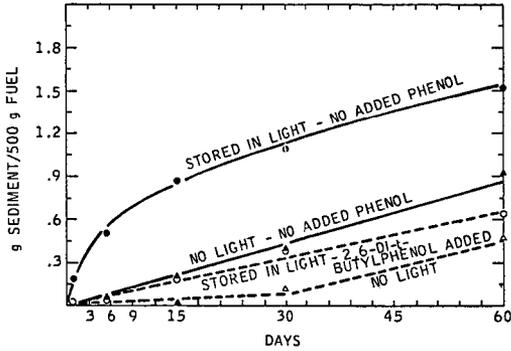
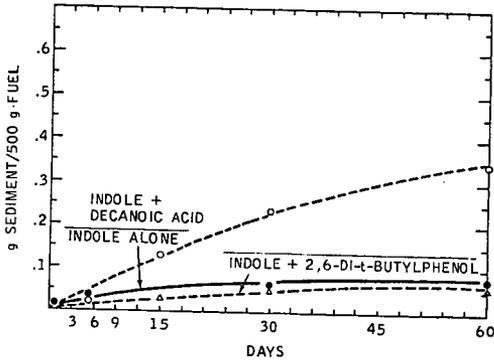
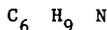


FIGURE 4

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



while that of dimethylpyrrole is:



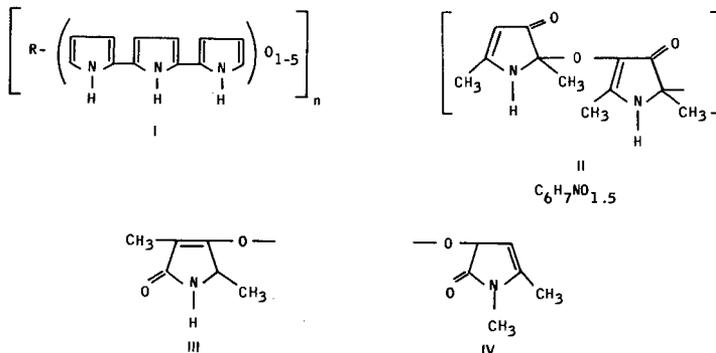
The major infrared bands from the sediments are shown in Table 4. The spectra were obtained as smears or mulls between salt plates since the extreme insolubility of the sediment precludes the measurement of solution spectra. The analysis confirms that the pyrrole ring is intact and suggests that oxygen has been introduced in the form of a carbonyl group. The strong $-CH_3$ absorption relative to $-CH_2$ indicates the methyl groups remain intact and that no long chain $-CH_2-$ units (from other components of the media) have been introduced. Previous reports (5) have proposed structure I, the so-called "pyrrole black" for the sediment obtained from pyrrole added to various fuels. The present results do not support this structure since no "R" group is present and a carbonyl group clearly is. Instead, a structure such as II (7) is more likely. The partial structures, III and IV, cannot be ruled out although an unlikely methyl group migration is required (8).

TABLE 4

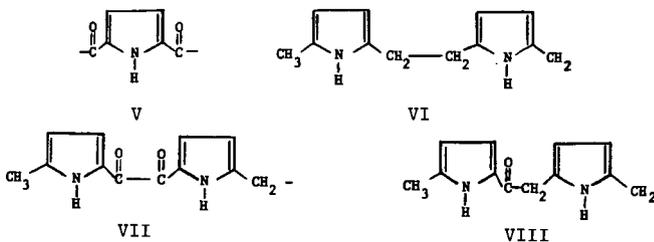
MAJOR IR BANDS IN SEDIMENT FROM 2,5-DIMETHYLPYRROLE (1)

Cm^{-1}	Significance
3300-3500 (s)	-NH or -OH
2970 (s) 1375 (s)	-CH ₃
2925 (w) 1450 (w)	Lack of -CH ₂
1640-1670 (vs)	Conj C=O or Amide

- (1) Smear or mull between salt plates.
 (2) s = strong; vs = very strong; w = weak.



The mass spectra of sediment samples are complicated because of the sediment's polymeric nature. However, some generalizations are possible. If a single structure is present, the representation best fitting all data is II, although partial structures III and IV cannot be ruled out. In addition, the mass spectra of some samples suggests the sediment may consist of several compound types of which four (V-VIII) 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.



Surprisingly, the highest parent peaks observed (~400 mass units) correspond to no more than 3-4 pyrrolic units. This is consistent with reports on the autoxidation of 1-methylpyrrole (8). These workers found no more than five repeating pyrrole units in a short chain. Additional work is scheduled in this area to determine the character and mechanism of sediment formation.

CONCLUSIONS

- Nitrogen compounds can be seriously deleterious to the storage stability of synfuels.
 - (a) Pyrrolic types and some amines are deleterious; many other nitrogen containing compounds are not.
 - (b) The pyrrolic compounds vary in the magnitude of their influence on sediment formation. The rate is very high with 2,5-dimethylpyrrole.
- Storage conditions may play an important role; the effect of light is particularly noteworthy.
- Certain trace impurities are also important in their effects on promoting sediment formation.
 - (a) Carboxylic acids accelerate the formation rate; the effect is most pronounced in the dark.
 - (b) Some phenols inhibit sediment formation; structural effects are important.
- The sediments appear to have a definitive structure which may be amenable to analysis. With DMP this appears to be low to medium molecular weight oligomers consisting of partially oxidized repeating units of the nitrogen compound.

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4. See, for example, Paulson, R. E., Jensen, H. B., and Cook, G. L., Amer. Chem. Soc., Division of Petroleum Chem. Preprints 16 (1):A49 (1971); Dinneen, G. U. *et al.*, "Composition of Shale-Oil Naphtha", U.S. Bureau of Mines Bulletin 593 (1961).
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