

SEDIMENT PRECURSORS IN MIDDLE DISTILLATE  
FUEL INSTABILITY REACTIONS

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Keywords: Fuel Instability, Oxidation, Hydroperoxide, Oxygenates

ABSTRACT

The specific molecules that initiate the reactions that lead to fuel sediments are difficult to isolate chemically. Several diverse mechanisms could be invoked to explain experimental findings: electron transfer initiated oxidation mechanisms, free radical hydroperoxide initiated oxidation mechanisms and soluble macro-molecular oxidation mechanisms. In actual practice, these specific reactions, in addition to many other mechanisms are simultaneously occurring. Results from our experiments demonstrate that acid catalyzed condensation reactions followed by a rapid increase in polarity caused by hydroperoxide induced oxidation steps can mimic the sedimentation processes observed in many middle distillate fuels.

INTRODUCTION

Instability can be thought of as an interactive process involving the four main functional groups listed in Figure 1. The difficulty arises in isolating the chemical importance of each functional group and specific mechanisms to the overall process. It is amazing that less than 1 ppm of the fuel itself is involved in the process that has the potential to be detrimental to a whole storage tank.

Figure 1. Functional Groups Involved in Incompatibility Reactions.

R-C=C-	+	R-N-	+	R-S-	+	R-O-O-
<u>Hydrocarbon</u>		<u>Organo-Nitrogen</u>		<u>Organo-Sulfur</u>		<u>Organo-Oxygen</u>
Alkenes		Indoles		Sulfonic Acid		Hydroperoxides
Indenes		Carbazoles		Thiols		Dissolved Oxygen
Monocyclics		Pyrroles		Disulfides		Carboxylic Acids
Bicyclics		Quinolines		Sulfoxides		Peroxides
Polycyclics		Pyridines		Sulfides		Aldehydes
		Piperdines		Thiophenes		Alcohols

RESULTS AND DISCUSSION

Based on sediment analysis, it is a reasonable contention that the incompatibility of fuels can be explained by the functional groups listed in Figure 1. A myriad of chemical reaction pathways could be derived from these various functional groups in the following mechanisms; the hydroperoxide initiated polymerization oxidation reactions with olefins to produce gums; an electron-transfer-initiated-oxygenation (ETIO)<sup>2</sup>, followed by reactions that result in degradation; the hydroperoxide oxidization of organo-sulfur compounds to sulfonic acids which then subsequently catalyze condensation reactions between the other functional groups present leading both to incorporation of heteroatoms and a simultaneous increase in polarity and molecular weight and thus precipitation from the fuel; and finally, the same reaction sequence could be used to describe the soluble macromolecular oxidatively reactive species (SMORS)<sup>1</sup>. The exact chemical composition of the sediment will depend on the chemical composition of the particular fuel. Individual fuels display unique sediments. These functional groups are involved in both chemical and physical processes that leads to deleterious solids. However, certain compound classes are observed to be common to all sediments. Thus, the presence of these heteroatomic compound classes can be used as incompatibility predictors. All of these processes depend on dissolved oxygen and/or hydroperoxides to initiate the processes leading to degradation. Remove molecular oxygen and/or hydroperoxides, usually by clay filtration,

and fuel compatibility will improve dramatically<sup>5</sup>.

In the sedimentation process, a major unknown is the identity of the soluble precursor to these sediments. Figure 2 illustrates both the chemical and physical processes that lead to sediment formation. These precursors are in the early stages of research. These precursors, SMORS, could be the result of the catalytic cracking process of the petroleum crude. A classical chemistry description of SMORS is that they are derived from monomers in the fuel itself. However, this description fails because of the inability to link any SMORS precursors in the fuel to the insolubles formed in the fuel. If this intermediate could be chemically elucidated, the sedimentation process observed in practically all middle distillate fuels, incompatibility would be better understood<sup>1</sup>.

Figure 2. Chemical and Physical Processes that Lead to Insoluble Products

<u>CHEMICAL PROCESSES</u>	<u>PHYSICAL PROCESSES</u>
Fuel	Coalescence
Middle	insoluble products
Distillate	1000 - 5000 °A
Fuel	
↓	↓
<b>Soluble Macromolecular Intermediate</b>	<b>Surface Effects</b>
fuel oxidation intermediates	Collect on walls
fuel soluble	and
increasing polarity	fuel lines
N, O, and S incorporation	
↓	↓
<b>Insoluble Products</b>	<b>Temperature Effects</b>
fuel sediments	extensive oxidation
high heteroatom content	at high temperatures
Molecular weight >>500	leads to coking

It is thus easy to imagine the situation in which a blended fuel could pass the required accelerated test method, ASTM D2274, at the refinery, but then form large amounts of insolubles when it reaches the consumer<sup>6</sup>. Because of the increasing use of blended stocks, there is no "one" middle distillate fuel consequently, there is also no "one" mechanism of degradation. However, the mechanism and the functional groups involved will give a general but not specific mode of incompatibility. The key reaction in all incompatibility processes is the generation of the hydroperoxide species from dissolved oxygen. Once the molecular oxygen and/or hydroperoxide concentration starts to increase, macromolecular incompatibility precursors can form in the fuel. Acid/base catalyzed condensation reactions then rapidly increase the polarity, chemical incorporation of heteroatoms, and the molecular weight.

Three related, but separate reaction regimes can be used to explain the chemical incompatibility that is occurring during the different stages that a fuel goes through in its lifetime. At the refinery or in the early life of a fuel, SMORS, incompatibility can best be explained by acid/base catalyzed condensation reactions of the various organo-nitrogen compounds in the individual blending stock themselves. These acid/base catalyzed processes are usually very rapid reactions with practically no observed induction time period. When the fuel is transferred to a storage tank or other holding tank incompatibility can be explained by a second slow mechanism; the free-radical hydroperoxide induced polymerization of active olefins (gums). This is a relatively slow reaction, because the increase in hydroperoxide concentration is dependent on the dissolved oxygen content. These gums can be quite deleterious to combustion machinery. The third incompatibility mechanism involves; the degradation reactions observed when the fuel is stored for one or more years. Extended storage is a common practice for the military. The incompatibility process can be explained by a complicated set of reactions. It involves first the buildup of hydroperoxide moieties after the gum reactions; then a free-radical reaction with the various organo-sulfur compounds present that can be oxidized to sulfonic acids; then reactions such as condensations between organo-sulfur and nitrogen compounds and esterification reactions. This is the slowest of the reactions because of the hydroperoxide induction period and the subsequent oxidation of the

organo-sulfur compounds.

A matrix involving time, temperature, heteroatoms, hydroperoxides, and other reactive species present in fuels in the context of accelerated storage is complicated. Accelerated fuel stability tests are important to both producers and users of fuels so an understanding of these interactions is important. Model dopant studies provide a method for isolating some of these variables. Model studies to define chemical incompatibility work well with gasoline and jet fuels. With chemically more complicated diesel fuels, they are somewhat less reliable. With relatively simple fuel, model studies set the parameters for incompatibility. Thus tests performed to mimic long-term storage give results that are definitive as long as the temperature employed is low enough not to initiate homolytic hydroperoxide reactions (<100°C). Higher temperatures enable storage tests to be completed in the minimum time, a producer advantage. The significance of the accompanying uncertainty of the observed sediment-producing processes in relation to the real ambient storage conditions may be dominant, a user disadvantage. Much of the early work has concentrated on the use of organo-nitrogen and sulfur compounds, both basic and non-basic, as dopants. It was demonstrated that the solid formed from these dopants were similar to the solids obtained from shale liquids themselves. The promotion of sediment formation by these dopants has been reported to be a facile process.

In a series of papers starting in 1987, results were reported that explained some of the inconsistencies observed with deposit formation and sulfur compound interactions<sup>8</sup>. The authors show that the stability of an unstable middle distillate fuel was improved by treatment with sodium hydroxide. The subsequent addition of a sulfonic acid, 10 ppm of naphthalene sulfonic acid, restored the instability of the base washed fuel. A linear relationship between deposit formation and sulfonic acid concentration confirms that the formation of a strong acid is a limiting factor in storage instability. Further, the deposits generated by the sulfonic acid treatment were found to be identical from those formed from the fuel itself on storage. It was further reported that the chemical structures observed in the sediment precursors consisted of indoles linked to a phenalene ring system. In the particular diesel fuel studied, phenalene was detected. Oxidation products, i.e., various phenalenones, were observed to increase in concentration as the fuels were aged under ambient storage conditions. This appears to be a major step forward in the chemistry of sediment formation. However, much more study is needed to extend this observation to other middle distillates.

ETIO results are primarily from model systems. No results or sediments based on fuel system ETIO are available. For ETIO to be a viable concept in fuel degradation, two significant phenomena must be operative: a rate law based on oxygen order; lack of chemical response to both amine and phenolic free-radical inhibitors. Other model systems employing 3-methyl indole and the anthraquinone molecular ion have results that show ETIO operating in model systems.

The data in Table 1 show the results for a model system employing 3-methylindole and various acids present as co-dopants. A comparison of the sediment from the undoped to the carboxylic acid doped systems show a remarkable similarity in formula. Infra red and mass spectral results show that the carboxylic acid groups are not incorporated in the sediment. In the case of the strong acid dodecylbenzene sulfonic acid (DBSA) however, the results are quite different. The sediment generated by this acid incorporated the DBSA moiety into the sediment, this was confirmed by <sup>13</sup>C nmr and field ionization mass spectrometry.

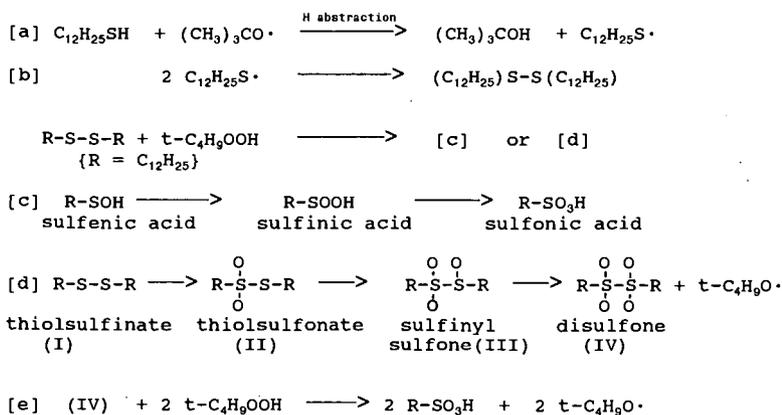
Table 1. Elemental Analysis Data for Sediments Derived from 3-Methylindole in a Middle Distillate Fuel with Added Co-Dopants

Co-Dopant*	Percent by Weight					Empirical Formula
	N	C	H	S	O	
None	5.36	72.63	5.88	16.13	-	C <sub>15.8</sub> H <sub>15.2</sub> NO <sub>2.8</sub>
Acetic acid	5.57	72.72	5.92	15.77	-	C <sub>15.2</sub> H <sub>14.8</sub> NO <sub>2.5</sub>
Hexanoic acid	5.65	72.16	5.78	16.41	-	C <sub>14.8</sub> H <sub>14.2</sub> NO <sub>2.4</sub>
Decanoic acid	5.81	72.55	5.76	15.88	-	C <sub>14.8</sub> H <sub>13.8</sub> NO <sub>2.4</sub>
Dodecylbenzene sulfonic acid	5.10	73.33	8.20	5.65	8.45	C <sub>18.4</sub> H <sub>30.3</sub> N <sub>1.3</sub> SO <sub>1.3</sub>

\* Concentration dopants =  $3.21 \times 10^{-2}$  M  
3-MI = 450 ppm N

The organo-sulfur moieties that have proved to be the most damaging are the thiols, disulfides and sulfonic acids. These results and those from other studies have indicated that some sulfur compounds might be inhibitors for controlling hydroperoxide formation in middle distillate fuels. However, they control the peroxides by undergoing oxidation to sulfonic acids as depicted in Reaction Scheme 1. Partially oxidized sulfur species, such as sulfoxides and sulfones are not generally deleterious<sup>11</sup>. Thiophene related compounds are very resistant to oxidation and are thus harmless in the stability process. Sulfonic acids are the most deleterious dopant that we have studied<sup>11,12</sup>. Thiols are excellent radical scavengers in both fuels and in model fuel systems<sup>12</sup>. The most probable mechanism for the reaction sequence for a thiol involved a hydrogen abstraction step by a t-butoxy radical that was generated from a peroxide species, such as t-butyl hydroperoxide, t-C<sub>4</sub>H<sub>9</sub>OOH. Once a disulfide is generated, steps [a and b], one or both pathways, [c and e], exists for sulfonic acid formation.

Reaction Scheme 1. Reaction Pathways of Hydroperoxides and Disulfides to Produce Sulfonic Acid



However, sulfenic acids and sulfinic acids have not been observed either in model systems or in fuels. The partially oxidized species, products I - IV in step [d], have been observed in fuels and model oxidation systems<sup>11</sup>. Product IV, a disulfone, by reaction with a mild oxidant, hydroperoxides, generates the corresponding sulfonic acid, step [e].

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# FIELD IONIZATION MASS SPECTROMETRIC ANALYSIS OF THE PHENALENONE-INDOLE COUPLING PRODUCT: THE NATURE OF INSOLUBLES FORMED IN DIESEL OILS

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**KEYWORDS:** Diesel Storage Stability, FIMS, Indoles, Phenalenones.

## ABSTRACT

There is a growing acceptance of the theory that insolubles formed during storage of diesel oils result from the acid-catalyzed coupling of phenalenone and alkyl indoles. Field ionization mass spectrometric analysis of the sediments show prominent peaks due to alkyl indoles as well as those due to coupling products of phenalenone with one, two, three or four alkylindole moieties. However, conspicuous by their absence are peaks due to alkylphenalenes and phenalenones. FIMS analysis of a coupling product of phenalenone with indole, shows a prominent peak at 182 Da, that can be assigned to dihydrophenalenone. Most peaks in the spectrum, including minor ones, lend themselves to straightforward interpretation in terms of the known chemistry of coupling. Peaks corresponding to phenalene with one and two indole units were also prominent in the spectrum. Satellite peaks corresponding to hydrogenation and oxidation products are also present. Their presence indicates a multitude of redox reactions that accompany the coupling.

## INTRODUCTION

Storage of diesel fuels often results in the formation of deposits that cause problems with filtration and pumping of the fuels. Furthermore, some soluble gum is also formed that subsequently forms deposits on the hot engine parts causing additional problems. Numerous tests have been developed to predict the tendency of a fuel to form deposits.(1) Often, these tests require stressing the fuel at elevated temperatures, and the relevancy of such tests to storage conditions is not clear. Studies have also been conducted with dopants (2, 3), but again it is unclear whether the deposits formed in the presence of the dopant are the same as those formed under storage. An improved chemical understanding of the nature and causes of deposit formation is clearly needed. Chemical characterization of the sediments is valuable, because the agents responsible for their formation may be present at extremely low concentration in the fuel, but will necessarily be concentrated in the sediments.

We have previously shown that pyrolysis-field ionization mass spectrometry (Py-FIMS) is very useful in characterizing the deposits formed during storage of fuels.(4,5) We have found that there are a few patterns that repeat in the spectra for sediments from a variety of sources and that the filtered sediments and adherent insoluble gums are very similar in chemical nature with the sediments being enriched in the benzologs of the components in the gum. Peaks due to alkyl indoles are prominent in these spectra, and clusters of peaks corresponding to dimers and higher oligomers are also evident. In accord with the mechanism proposed by Hiley and Pedley (6), most of the prominent peaks in these spectra can be ascribed to the coupling products of phenalenone with one, two, three, or four alkylindole moieties. However, the peaks due to alkylphenalenes and phenalenones themselves are not very intense. In order to better understand the coupling mechanisms, we have prepared acid-catalyzed coupling products of indole and phenalenone, and examined it by field ionization mass spectrometry. Our objective was to determine if indeed the coupling product of phenalenone and indole does not give a strong peak signal corresponding to phenalene or phenalenone.

## EXPERIMENTAL

**Coupling Reaction.** Coupling product of indole and phenalenone (perinaphthenone) was prepared by adapting the procedure of Pedley and Hiley (6) for the synthesis of 2-methylindolylphenalene. Approximately 0.66 mmol indole was stirred overnight with an equivalent amount of phenalenone in the presence of *p*-toluenesulfonic acid (also 0.66 mmol) in methanol. The product was treated with excess potassium bicarbonate and extracted with ether. The mixture of coupling products was recovered by evaporating the ether.

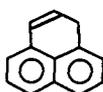
**Pyrolysis/Field Ionization Mass Spectrometry (Py/FIMS).** The technique of field ionization (FI) consists of passing vapors of the material to be analyzed through a region of intense electric field.(7) This mild technique for ionization results in the formation of only the molecular ions for most compounds, and because the ionization is generally not accompanied with any fragmentation it is particularly useful for analyzing complex mixtures. The FIMS system used in this study has been described elsewhere.(8) It consists of an activated tantalum foil field-ionizer interfaced with a 60° magnetic sector mass analyzer and a PDP 11/23 computer for data acquisition and processing. Approximately 50 µg of the sample is introduced via a heatable direct insertion probe. Mass spectral data of the evolving volatiles are collected by repeatedly scanning the magnet over a preset range while the sample is gradually heated from the initial temperature (sometimes as low as -78°C) to approximately 500°C. At the end of the run, the sample holder is retrieved and

weighed to determine the fraction that was devolatilized during the analysis. All the samples examined in this study were essentially 100% devolatilized during analysis. For a given sample, many spectra are collected, each representing a certain range of temperature. The individual spectra are added to obtain a spectrum of the total volatiles and produce a thermal evolution profile of total volatiles as well as of any given mass peak.

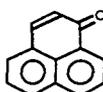
## RESULTS AND DISCUSSION

The FI-mass spectrum of the coupling product of indole (117 Da) and phenalene (180 Da) is shown in Figure 1. This spectrum represents the sum of sixteen spectra (each comprising eight scans) collected during the heat up from ambient to 500°C. Because field ionization is generally not accompanied by fragmentation, the multitude of peaks in this spectrum corresponds to either multitude of compounds in the product, or extensive fragmentation due to pyrolysis in the FIMS probe. It is therefore instructive to examine the mass spectral data as a function of the probe temperature.

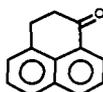
The spectrum of species that evolved almost immediately upon introduction of the probe into the inlet is shown in Figure 2a. This first set of peaks are at 117 Da (indole) and at 165, 166 (phenalenyl radical, and phenalene), and at 180 and 182 (phenalene and dihydrophenalene). The dihydrophenalene peak is substantially more intense than that due to the parent phenalene. A possible explanation is that the phenalene underwent coupling, but the dihydro analog, which cannot undergo Michael addition, survived. Surprisingly, there were also peaks at 195 and 196 Da. The peak at 196 is most likely the methyl enol ether of the dihydrophenalene, which was probably formed because the coupling was conducted in methanol as solvent. The peak at 195 Da is corresponding stable radical. The stability of the phenalenyl system is well recognized, and it is noteworthy that the radical species were seen with both phenalene and the enol ether; the latter being also capable of forming a phenalenyl radical with the loss of a hydrogen.



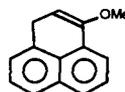
Phenalene (166)



Phenalene (180)



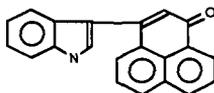
Dihydrophenalene (182)



Dihydrophenalene-enol methyl ether (196)

The fact that phenalene and dihydrophenalene evolved at almost ambient temperatures suggests that they were present in the product mixture and were not a result of some thermal cracking of coupling products. This result further reinforces the facility with which phenalene systems can undergo redox reactions (disproportionations), and lead to a multitude of products.

Upon warming the sample, the intensity of the peaks due to indole and phenalene and its analogs decreases, and a new set of peaks centered around 300 Da begins to evolve. They correspond to the coupling products of one phenalene and one indole residues. A representative spectrum is shown in Figure 2b. The simple coupling product of phenalene and indole has a molecular weight of 295 ( $180 + 117 - 2 = 295$ ). Indeed, the peak at 295 is the most intense peak in the spectra acquired between 120 and 240°C, as well as in the sum spectrum (Figure 1). This peak is also accompanied by phenalene and the dihydrophenalene analogs at 281 and 297 Da respectively. There is also a peak at 311, which is most likely due to the methyl ether of the corresponding enol. As before, strong peaks due to the phenalenyl radicals are present for the phenalene and the enol ether analogs of the coupling product. The coupling product is also accompanied by a dihydro derivative of the phenalene analog at 283 Da.



Indolenylphenalene  
(295)

A similar pattern peaks around 410 Da for the bisindolenylphenalenes emerges as the sample is further heated to above 200°C (figure 2c). For the trisindolenylphenalenes, which also evolve in the 200 to 300°C range, however the expected peak at 325 Da ( $180 + 3 \times 117 - 6$ ) is not present to any significant extent. The peaks due to other analogs are present in reasonable intensity.

In the case of fuel sediments, similar peaks have been observed in their FI mass spectra.<sup>(5)</sup> However, we were not sure whether the products were present as simple oligomers or whether the oligomers were a result of thermal fragmentation of a polymer. Results obtained here show that the vaporization of the dimers and trimers in the FIMS probe occurs around 200 to 250°C. This temperature range corresponds well with the temperature at which these species evolved from the fuel sediments. Hence, we believe that, in the fuel sediments too, the dimers and trimers are present as such.

As mentioned above, the peak due to indole evolved at almost ambient temperatures. This peak was present in the spectra collected up to about 80°C, and was due to indole trapped in the product. The indole peak again appeared above about 180°C along with the evolution of coupling products.

This result suggests that at these temperatures, some of the coupling products do fragment to liberate indole fragments.

## CONCLUSION

We have prepared an acid-catalyzed coupling product from the reaction of indole with phenalenone and analyzed it by FIMS. The mass spectrum shows the presence of the expected indolenylphenalenone, bisindolenylphenalenone, trisindolenylphenalenone, and so on. It also shows peak corresponding to redox derivatives and methyl ethers. The temperature resolved mass spectral data are consistent with simple evaporation of the oligomers and not due to thermal fragmentation.

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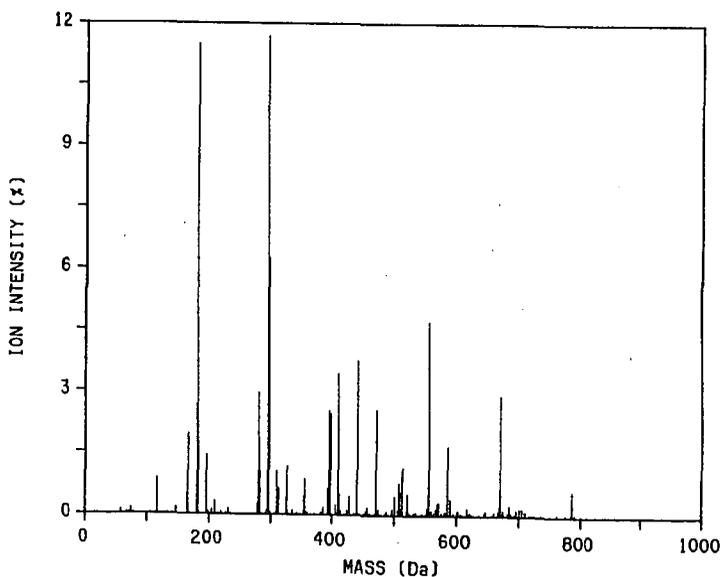


Figure 1. FI mass spectrum of the total volatiles from phenalenone-indole coupling product collected from 30 to 500°C.

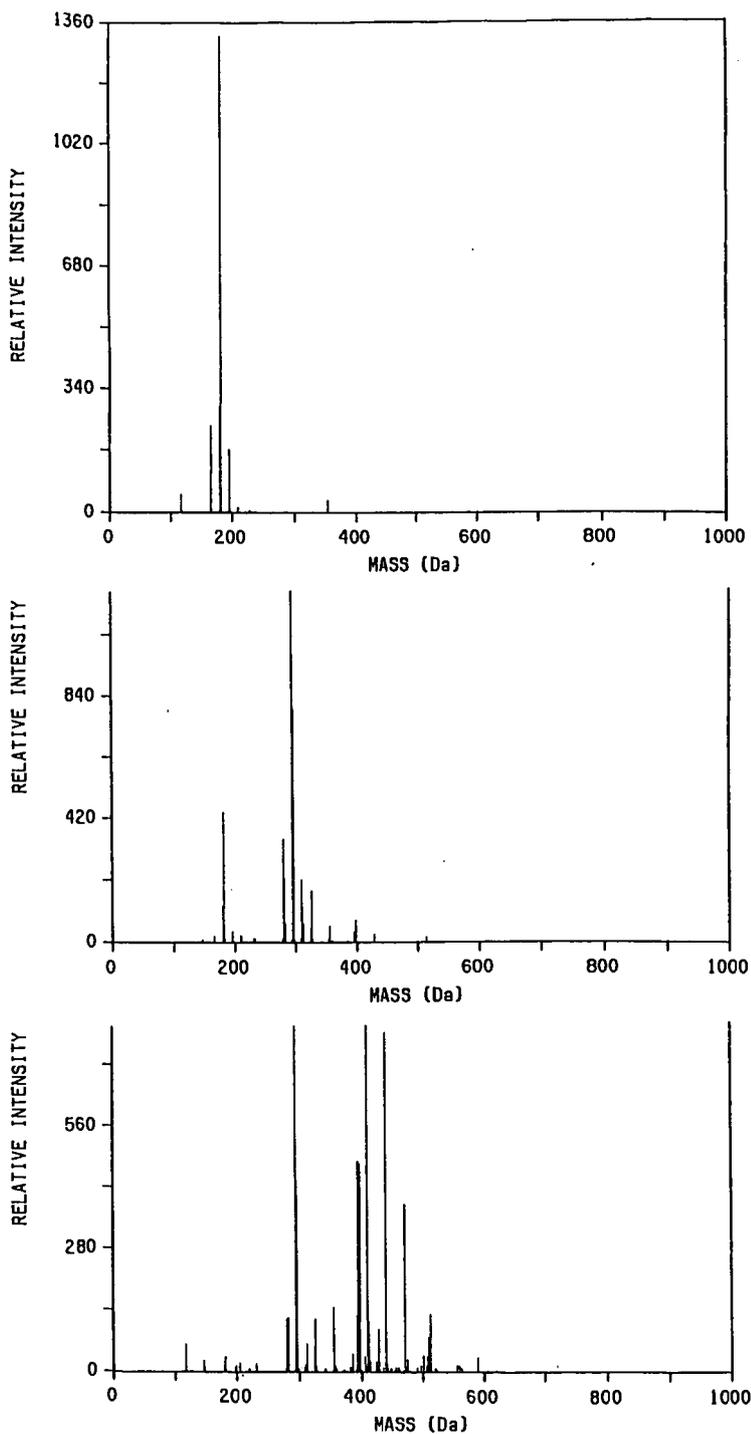


Figure 2. FI mass spectrum of the volatiles from the phenalenone-indole coupling evolving in the temperatures ranges (a) 46651°C (b) 148 to 165°C, and (c) 211 to 238°C.

**CHARACTERIZATION OF SOLUBLE MACROMOLECULAR  
OXIDATIVELY REACTIVE SPECIES (SMORS)  
FROM MIDDLE DISTILLATE DIESEL  
FUELS: THEIR ORIGIN AND ROLE IN INSTABILITY**

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**INTRODUCTION** In diesel fuels which are oxidatively unstable and at least 6 months old, it has been shown that a solid phase can be isolated from the filtered fuels by methanol extraction followed by precipitation with hexane. The weight of this material is directly proportional to the amount of sludge which forms by both accelerated storage stability tests and by continued field aging of the fuels. We have suggested that the presence of this extraction induced precipitate (EIP) or fuel Soluble, Macromolecular, Oxidatively Reactive Species (SMORS) in these fuels thus accounts for the production of thermally induced precipitate (TIP) or insoluble sediment during oxidative aging of diesel fuels.<sup>1,2,3</sup> In this paper the acronym EIP will be used in place of SMORS in most cases.

This paper describes and summarizes the characterization studies performed to date on the EIP from representative fuels which are all greater than 6 months past production. The origin and apparent role of SMORS in sediment formation in diesel fuels is discussed.

**EXPERIMENTAL** All procedures for filtering fuels, and for extraction and precipitation steps used in isolating the EIP from fuels have been described in detail elsewhere.<sup>1,2</sup>

GC analysis was performed on samples dissolved in methanol using a Hewlett-Packard Model 5890 GC equipped with flame ionization detector and HP Model 3392 integrator. A 50-m methylated silicone (nonpolar) capillary column was used for separation. Experimental conditions included an inlet temperature of 280 °C, a split ratio of 22:1 and a column temperature program between 100 °C and 280 °C. A 1-min initial hold at 100 °C was used; the temperature was then ramped at 5 °C/min to 280 °C and then held at that temperature for 10 minutes.

The field ionization mass spectral (FIMS) system used for this work has been described elsewhere.<sup>4,5</sup> At the end of each run, the sample holder is retrieved and weighed to determine the fraction that was volatilized during the pyrolysis.

Low voltage electron impact, high resolution mass spectrometry was used to determine the exact masses of several of the key fragment ions, when the EIP was introduced by pyrolysis (identical to the FIMS sample introduction).

Elemental analyses and molecular weight determinations by vapor pressure osmometry were provided by commercial laboratories. All elements including oxygen (but not sulfur) were determined by combustion and not by difference.

All blended stocks used were prepared in the laboratory as 80/20 straight run/LCO mixtures (v/v). Blends were always filtered before extraction. The straight run fuel used was a water-white, clear stock obtained from the same refinery that furnished LCO-3. All fuels and blends are described in earlier papers in this series<sup>1,2,3</sup> and a consistent fuel code has been continued.

**RESULTS AND DISCUSSION** **Elemental Analyses/Molecular Weights by Vapor Pressure Osmometry.** Table 1 summarizes the elemental analysis data (CHON) obtained for solids (EIP) extracted from 3 light cycle oils (LCOs) and 5 blends. Data are as received and not normalized to 100%. The elemental analysis results for 20% LCO/80% SR EIP from blends is shown in the bottom half of Table 1. Here it is interesting to compare the blends to the LCO's. In general the EIP from blends have somewhat higher oxygen and lower carbon content indicating that EIP from blends is more polar than from LCO's. If higher polarity equates to higher chemical reactivity, then this finding supports the long-known fact that blending reactive LCO's with non-reactive SR streams does not usually dilute the sludge forming tendencies in a direct ratio. With very reactive LCO's, dilution by as much as 70%

SR sometimes has no effect on reducing sludge formation amounts in the resulting blends.<sup>6</sup> It is noteworthy that these blends are made up immediately before the EIP is isolated for elemental analysis and thus the chemical changes in elemental analysis are due to the blending process itself and not any subsequent aging of LCO EIP in the resulting blend.

Table 2 presents a summary of the blend data from Table 1 for EIP which is normalized to 100% in order to determine an empirical formula. Data for typical average elemental analyses of TIP or sediment is given also.<sup>7</sup> The trend for blend EIP to contain more oxygen is continued in the TIP and this is reflected in the average empirical formula which contains an additional  $\text{CH}_2 + \text{H}_2\text{O}$  compared with typical EIP.

Included in Table 3 are molecular weight data obtained by vapor pressure osmometry. Note that these data are quite consistent with the molecular weight data obtained by size-exclusion chromatography (570 vs 600-900) considering errors inherent in, in particular single point VPO determinations and in size-exclusion data for molecular weights <1000 Da. for molecular shapes which are likely to be quite different from those of the standards used.

**Gas Chromatography.** When EIP samples are isolated from the methanol extract and then re-dissolved in methanol they may be subjected to analysis by GC. The dissolved EIP gave surprisingly simple chromatograms with no major peaks that would correspond with any of the moieties commonly thought to be precursors to instability. This led to the conclusion that the methanol fraction contained the presence of higher molecular weight species which were not eluted under the standard experimental GC conditions employed. This also demonstrates very clearly that the EIP does not contain any entrapped fuel species. This is an important fact in the subsequent interpretation of the PYR/FIMS data.

**Pyrolysis/Field Ionization Mass Spectrometry (PYR/FIMS).** Two representative EIP samples were chosen for PYR/FIMS analysis. These were LCO-3 and LCO-5. The EIP were isolated as a solid powder and then completely dissolved in toluene in order to introduce a homogeneous sample into the glass capillary for pyrolysis field ionization MS. Most of the toluene was removed by evaporation and then the remaining solid sample of EIP was heated at a controlled rate up to 500° C in the high vacuum source region of the MS. Subsequent weighing of the capillary tube revealed that essentially 100% by weight of the EIP had been pyrolyzed and volatilized by this procedure. Identical analyses of TIP/sludge generally show that less than 60% of the sample is consumed after pyrolysis leaving considerable char in the sample tube.

Representative data for LCO-3 are shown in Table 4. Residual toluene solvent is not shown in the figure but volatilized between approximately 30 and 125° C. Since no other ions up to 300 daltons were seen in this region it can be concluded that the original EIP samples were essentially free of entrapped fuel. In addition, as noted above, GC analysis of EIP which are re-dissolved in methanol reveal no entrapped fuel components.

The total ion mass chromatograms for the pyrolysis FIMS are quite complex. This underscores the tremendous amount of pyrolysis that the EIP samples are undergoing. At the same time it is noteworthy that the entire sample is volatilized/pyrolyzed in a fairly narrow range from 175 to 375° C. The calculated number average molecular weight of the LCO-5 EIP by this process is 582 daltons and the calculated weight average molecular weight is 687. This is in fairly good agreement for the VPO determined molecular weight of this sample (see Table 3).

Due to the complexity of presenting the data in the form of mass pyrograms for subsequent interpretation, an alternative approach has been taken. About half of the total ion current of the mass pyrogram is contained in a number of series of homologous ions separated by 14 dalton increments. These homologous ion series have been arbitrarily assigned a mass identification number, usually one of the lowest mass ions in a particular series. In the case of data for Table 4 only the most intense ion in a particular series was used to generate the temperature profile. In the case of data for Table 5 the sum of all the ions in a particularly identified ion series was determined. The mass intensity values in all cases have been taken from normalized spectra. In addition, the base peaks for all three spectra (in ion counts) were very close in intensity. For this reason the ion counts were not converted to percent relative abundance as is normally done but instead are converted to a normalized ion count. At this point it is possible to attempt a more detailed analysis of the nature of the EIP sample as revealed by the mass pyrogram in Table 4. The 9 ion series identified account

for the 9 most intense sets of masses. Most of the mass peaks in Table 4 are pyrolysis fragments of the high molecular weight EIP. This is supported by the fact that the major series below 300 daltons continue to form over the entire temperature range between 90 and 360° C. As the temperature of the pyrolysis increases the pyrolyzate fragments of higher molecular weight begin to appear (between 300 and 600 daltons) up to temperatures of 400° C.

As conjectured in an earlier paper in this series<sup>1</sup>, one of the two possible alternative origins of EIP is that a fuel soluble macromolecular species (possibly porphyrinic in nature) is carried over into the fluid catalytic cracker by the feed stock and ends up in the product blending stream. This macromolecular species could then further oxidize (making it more polar and soluble in methanol, at which point it is EIP). Finally further oxidation and condensation reactions with reactive fuel monomers precipitates the final product insoluble sediment or sludge.

Since the above conjecture rests upon a geochemical/processing origin one would then expect that the EIP from various sources would be somewhat similar at least in gross structural features. The PYR/FIMS data for the two LCOs given in Table 5 strongly indicates that this alternative origin for EIP is probably not correct. Although there are some strong similarities in the three EIP samples such as the mass series at 131 and 309, there exist major dissimilarities. In addition to this, a common geochemical origin for EIP would be porphyrinic in nature and the PYR/FIMS fragments of such an EIP moiety would result in significant amounts of pyrrolic species evolved below 300 daltons and these do not occur.

The traditional explanation for the origin of TIP/sludge or sediment postulates reactive monomeric fuel components which oxidize and condense to form larger and more polar and less fuel soluble species. The fact that the EIP species must themselves further oxidize and condense to form TIP/sludge means that we now have a probe of some intermediate stage in sludge formation from reactive fuel monomers which is itself a simpler species compositionally and is much more amenable to analysis. In fact, the EIP themselves are simply produced by reactive fuel monomeric species. This last statement suggests that the detailed chemical nature of the EIP and the sediment itself must be quite fuel dependent and the data in Table 5 support this very clearly.

This information together with the fact that the PYR/FIMS data clearly support the elemental analysis data of the EIP which implicates nitrogen and oxygen containing compounds underscores the need to continue to determine the precursors of EIP in the original fuel. The fact that EIP are formed from reactive fuel monomers implies that freshly refined LCO's will not initially have EIP present and this is the subject of our current investigations. If an LCO or LCO blend has formed as little as 20 mg/L of EIP, then the LCO itself is probably of little use in studies designed to determine the compositional precursors of either EIP or TIP/sludge. It is for this reason that many very carefully performed studies to date have not been able to pinpoint the real precursors of sludge formation. Certainly if an LCO contains high total nitrogen or indoles content it also contains the real precursors to sludge. These indicators, however, are not able to be directly or quantitatively linked to any given fuel's sludge forming tendency.

**CONCLUSIONS** All of the EIP samples analyzed for this work were from fuels which had already developed EIP, i.e., they were at least 6 months old since production. Molecular weights from VPO and PYR/FIMS were all consistent in the range of 650 to 1000 daltons. The EIP have proven to be considerably easier to analyze than the actual sludge which they apparently produce ultimately.

Since it has been shown that the EIP do not arise as a geochemical/processing artifact it can be concluded that they arise from the oxidation and condensation of reactive fuel monomers. Clues as to the nature of these fuel species are found in the elemental analysis and empirical formulas for EIP which indicates much involvement of oxygen and nitrogen. Further information from the high resolution mass spectral empirical formulas and from the PYR/FIMS indicates that nitrogen containing precursors in the fuel with a formula of  $C_nH_{2n-9}N$  and  $C_nH_{2n-15}$  are involved in the generation of EIP. The 2n-9 class includes such isoelectronic possibilities as indoles, divinyl pyridines and dihydroquinolines. The 2n-15 class includes such isoelectronic possibilities as benzoindoles, phenalidines, divinyl quinolines and carbazoles.

The EIP are more amenable to PYR/FIMS analysis as evidenced by their complete pyrolysis than the more highly oxidized and polar TIP/sludge. Even so, the PYR/FIMS technique subjects the EIP to a tremendous amount of pyrolysis. Because of this the interpretation of pyrolyzate ions to reconstruct the formation of EIP is not possible.

Only freshly refined, unhydrotreated, catalytically cracked LCO material will be suitable for future studies involving the determination of the fuel precursors of EIP and whether the formation of EIP can be inhibited by antioxidant additives. Essentially no work on the determination of fuel precursors to sludge to date has appreciated the importance of this fact. Certainly no work presented to date has verified the initial absence of EIP before beginning a detailed compositional analysis and this is essential. By the time a measurable amount of EIP has formed, it is quite possible that all of the actual precursors to sludge are already well on their way to the dimer/trimer stage and hence no longer amenable to simple GC analysis techniques to monitor their depletion from the fuel.

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Table 1. Elemental Analysis of Selected EIP. Direct determination of CHON.

Fuel Code	Fuel Type	% C	% H	% O	% N	% Total
LCO-2	100% LCO	79.4	6.1	9.9	2.5	97.9
LCO-3	100% LCO	83.2	6.5	4.6	4.8	99.1
LCO-5	100% LCO	84.2	6.7	3.1	5.6	99.6
B-2	20% LCO	75.3	6.1	10.1	4.9	96.4
B-5	20% LCO	79.4	6.3	7.5	3.0	96.2
B-5*	20% LCO	75.2	6.4	9.8	5.5	96.9
B-13	20% LCO	76.5	6.4	9.1	4.9	96.9
B-14	20% LCO	76.5	5.8	10.4	3.3	96.0

\*EIP determined after ASTM D5304 stress test.

Fuel Code is: LCO = catalytically cracked light cycle oil

B = blend of 20% LCO + 80% SR v/v

Table 2. Elemental Analysis Averages (normalized to 100%) for a wide range of 20% LCO blends for EIP and Sediment. Empirical formula also computed from these data.

Property	EIP	Sediment/TIP
% Carbon	79.4	75.4
% Hydrogen	6.4	6.9
% Oxygen	9.7	13.7
% Nitrogen	4.5	4.0
Empirical Formula	$C_{21}H_{20}O_2N$	$C_{22}H_{24}O_3N$

Table 3. Molecular Weight Analysis by Vapor Pressure Osmometry (VPO) for selected EIP samples (in Daltons).

Fuel Code	Single Point	Triple Point
LCO-3	513	525
LCO-5	486	679

Table 4. EIP of LCO-3 analyzed by pyrolysis FIMS. Mass ID referred to the major mass in that homologous mass series from the pyrolyzate. As the temperature of the sample is raised from 100 to 400 C the major ion intensities (raw data counts) are summed for that temperature range. (-) indicates a value close to zero ion counts.

Mass ID	Probe/Sample Temperature Range °C						SUM
	90-150	164-201	203-250	254-299	303-355	359-399	
131	1.2	2.8	4.5	2.2	0.6	0.1	11.4
180	4.0	6.5	1.0	-	-	-	11.5
181	1.5	1.1	1.0	0.6	0.3	-	4.5
202	0.7	1.2	0.3	-	-	-	2.2
309	0.3	0.9	3.7	1.5	0.4	-	6.8
438	-	0.4	5.2	6.1	1.5	0.1	13.3
563	-	-	0.7	9.7	12.5	2.1	25.0
580	-	-	3.5	4.2	0.5	0.5	8.9
581	-	-	2.2	3.4	1.0	0.7	7.3
SUM-->	7.7	12.9	22.1	27.7	16.8	3.5	90.9

Table 5. Pyrolysis FIMS comparative analysis of several EIP solids. The major homologous series are identified by a mass which is generally the highest in the series, but not always. Compare these values for the sum of the homologous series for the entire pyrolysis temperature range to the totals for an individual mass given in Table 4. Compound type empirical formulas for the ion series given is from independent high resolution exact mass (to 10<sup>4</sup> mass units) data.

Mass Series ID	Empirical Formula	LCO-3	LCO-5
131	C <sub>9</sub> H <sub>9</sub> N	34	21
156	---	0	20
180	C <sub>13</sub> H <sub>10</sub> N	28	51
181	C <sub>13</sub> H <sub>11</sub> N	14	57
202	---	5	24
261	---	0	0
309	C <sub>22</sub> H <sub>15</sub> NO	19	35
438	C <sub>31</sub> H <sub>22</sub> N <sub>2</sub> O	41	54
563	---	78	9
580	---	25	0
581	---	23	0

# STORAGE STABILITY OF DIESEL FUEL PRODUCED FROM BRAZILIAN CRUDE - CHEMICAL MODIFICATION DURING AGEING AND THE EFFECT OF HYDROTREATING ON FUEL STABILITY

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Keywords: diesel fuel, stability, hydrotreating

## INTRODUCTION

The growing need for diesel fuels and developments in refining processes, particularly the increased use of Fluid Catalytic Cracking (FCC), have led refiners to introduce Light Cycle Oil (LCO) in diesel formulations. Unfortunately, the cracking products, which contain chemically unstable species (1,2), induce changes in color and insolubles formation, even when diluted by blending. The insolubles are known to cause operability problems in diesel engines (3).

Degradation mechanisms are complicated and not well understood. It seems that oxidation plays a determining role (4). Acids such as carboxylic, sulfonic and phenolic, produced by oxidation of fuels have been considered to exert a catalytic effect on the quantity of sediment formed (5). It was demonstrated that aromatic compounds and non-basic nitrogen compounds are also involved in sediment formation (6). Pedley et al. (7,8) found that a major source of strongly colored sediments could be the reaction of oxidized products with alkyl indoles, yielding addition products that precipitate under the influence of sulfonic acids, produced by oxidation of thiols.

The nitrogen compounds present in LCO were largely identified (9) and included anilines, alkyl indoles and alkyl carbazoles. It seems that only the alkyl indoles are subject to changes during degradation in storage (10).

A large number of tests have been used to predict stability of middle distillates. The ASTM D 4625 has widespread acceptance for its good correlation with storage at ambient conditions (11). The new accelerated test method, ASTM D 5304, shows excellent correlation with lower temperature tests (12).

The principal processes used to improve fuel stability include hydrotreatment and the use of additives. Schrepfer et al. (13) reported that although hydrotreating is the most effective method of minimizing stability problems, it is also the most costly.

Some characteristics of Marlim crude oil such as high nitrogen content and low middle distillate yield, have led us to anticipate problems on diesel stability with the beginning of Marlim oil processing.

The purposes of this study were to estimate the impact on storage stability behaviour of diesel fuels and to evaluate: 1- the effect of the mildest Petrobrás hydrotreatment unit on fuel stability, in particular with respect to non-basic nitrogen compounds; 2- the influence of hydrotreating and the use of additive; 3- the changes in phenalenone, pyrrolic nitrogen, basic nitrogen, mercaptans, alkyl indoles, acidity during ageing at 43 °C for periods of up to 12 weeks.

## EXPERIMENTAL

Nine experimental diesel fuel samples were made up from several streams obtained in the Marlim crude processing. Their composition is shown in Table 1. The physico-chemical characteristics of selected samples are shown in Table 2. A total of 20 liters of each component was stored at low temperature under nitrogen blanket to prevent degradation before analyses.

### Effect of hydrotreating on fuel stability

Hydrotreating was performed on two feedstocks, a straight run distillate (A2) and a blend (A2/B), in the following operating conditions: LHSV: 1,5 h<sup>-1</sup>; Temperature: 320 °C; H<sub>2</sub> Partial pressure: 29 bar. The method ASTM D 5304 (Assessing Distillate Fuel Storage Stability by Oxygen Overpressure) was used to evaluate the effect of hydrotreating on improving fuels stability. The reported total insolubles values are averages of duplicate analyses. Additionally, color determinations were made before and after ageing according to ASTM D 1500.

The "pyrrolic" nitrogen compounds were separated from the samples by HPLC using basic and acidic alumina columns, based on procedures described by Boduszynski (14). The

isolated compounds were identified by GC/MS. The quantification was conducted by GC-FID using carbazole as internal standard.

#### **Kinetics of ageing at 43 °C in air**

In order to better understand the mechanisms of sediment formation in fuels produced from Marlim oil, kinetic analyses were performed in the raw LCO (B) and in the three following blends: A1/A2/B; A1/A2/AD-B; A1/HT-(A2/B). An antioxidant containing tertiary amines and metal deactivator in its formulation was added to the hot LCO. Storage stability of each fuel sample was assessed by ASTM D 4625 (Distillate Fuel Storage Stability at 43 °C for 12 weeks). The reported total insolubles values are averages of triplicate analyses. Additionally, color determinations were made before and after ageing according to ASTM D 1500.

To follow the kinetics of the blends a total of 1000 ml of each fuel was placed in amber glass bottles of the same volume and the bottles closed with vented screw caps. Six bottles of each fuel were aged concurrently in a dark room at  $43 \pm 1$  °C, in contact with atmospheric air, for periods of up to twelve weeks. After every two weeks, one bottle of each fuel was removed and allowed to cool to ambient temperature. All samples were protected from light before, during and after ageing. The filterable insolubles were determined by vacuum filtration of 300 ml of each aged fuel, through two preweighted cellulose acetate filters (0,8 µm porosity). The filters were then rinsed with isooctane to remove traces of fuel, removed from the filter support assembly, oven dried (90 °C), cooled to ambient temperature in a desiccator and reweighted. The fuel samples were also analysed for color degradation, changes in phenalenone, pyrrolic nitrogen, basic nitrogen, mercaptans, alkyl indoles and total acid number.

The concentration of phenalenone was determined by normal phase HPLC with UV detection and direct injection of the sample, based on procedure described by Marshman (15). Concentrations of phenalenone up to 0,5 mg/l could be determined by this methodology.

The changes in alkyl indoles were monitored using a capillary gas chromatograph (CG) with selective detection by isobutane chemical ionization mass spectrometry (16). The method is based on the fact that the carbazole remains relatively unaffected during ageing, as verified by some authors (10). The evolution of alkyl indoles was then determined through changes in the ratios of alkyl indoles/carbazole peak areas.

## **RESULTS AND DISCUSSION**

### **Effect of hydrotreating on fuel stability**

The effect of hydrotreating on fuel stability assessed by ASTM D 5304 is presented in Table 3. The degrees of hydrodesulfurization (HDS) and hydrodenitritification (HDN) are also indicated. The hydrotreating process improved color stability of both samples, however complete stabilization was not achieved. On the other hand, the A2/B blend was stabilized in terms of insolubles formation.

As can be seen in Table 4, the alkyl indoles were partially removed while the alkyl carbazoles remained in the original levels. Additionally, a decrease in other species such as acids and mercaptans, that are supposed to contribute to degradation, was observed. Based on these results, it is confirmed that alkyl indoles and acidity play an important role on sediment formation and that stabilization of the fuel can be achieved by hydrotreating even at mild severity, without requiring total removal of nitrogen compounds. Under low H<sub>2</sub> partial pressure, the fuel chemical composition is not deeply modified, mainly with regard to nitrogen and aromatic content.

### **Kinetics of ageing at 43 °C in air**

The results related to color changes and total insolubles formation using ASTM D 1500 and ASTM D 4625 are presented in Figures 1 and 2, respectively. The raw LCO (B) is unstable mainly with respect to color degradation. A low formation of insolubles were observed, with the majority of insolubles in the adherent form. This behaviour drastically changed when the raw LCO was added to straight run distillates (A1,A2), as can be seen through the A1/A2/B blend results. In this sample, there was extensive formation of insolubles (mostly filterable insolubles) and color degradation. The contribution of the straight run distillates components in terms of acidity seems to exert a great influence on the sediment formation. From the results of the blend with additive it can be concluded that the antioxidant was ineffective on improving fuel stability. On the other hand, the blend containing hydrotreated components exhibited satisfactory results with total insolubles content of 0,2 mg/100 ml. The color degradation was minimized but was not completely eliminated.

The results obtained from the kinetics of ageing are summarized in Table 5. As can be seen, the phenalene concentrations increased rapidly during the first two weeks of ageing, levelling off thereafter in the following samples: B, A1/A2/B and A1/A2/AD-B. It is difficult to conclude if this stabilization was a result of the balance between consumption and production of phenalene during the overall mechanism of sediment formation or was due to occurrence of degradation before the ageing at 43 °C. There appears to be a correlation between color degradation and phenalene concentration since color degradation also reached the maximum value during the first two weeks. All the samples exhibited decrease in the pyrrolic nitrogen concentration and in the ratio alkyl indoles/carbazole. The decrease agrees with the relationship between the reactivity of the alkyl indoles and the filterable insolubles formation. According to this observation it can be concluded that: 1- the degradation mechanism proposed by Pedley et al. seems to be the major source of sediment formation in samples containing LCO, 2- the additive tested was ineffective to prevent phenalene oxidation and the progressive consumption of alkyl indoles. Hydrotreating appears to remove phenalenes since phenalenes were not detected in A1/HT-(A2/B) blend. The decreases in the pyrrolic nitrogen and in the ratio alkyl indoles/carbazole were also verified in a lower extent comparing to the others samples. The mercaptans and the total acid number remained practically unaltered during the ageing. These observations suggest that exists a correlation between the insoluble formation and the alkyl indoles disappearance and that other different mechanism of degradation from the proposed by Pedley takes place. It confirms, as previously demonstrated by some authors (17), that the removal of phenalenes, indoles or acids, will result in a stable fuel.

## CONCLUSIONS

On the whole, the experimental fuels obtained from Marlim oil presented poor stability. The addition of light cycle oil in the straight run distillate, to increase the yield of diesel fuel, was not satisfactory inducing higher levels of insolubles and color degradation.

The results of ASTM D 4625 and kinetics study showed that the additive was ineffective on preventing phenalene oxidation and the progressive disappearance of alkyl indoles. Similar levels of insolubles formation and color degradation was verified in the fuel in presence and absence of the additive. In both samples it seems that the major mechanism of degradation was similar to the proposed by Pedley et al..

The hydrotreating, even at mild operating conditions, improved substantially the stability properties of the fuel. Under the tested conditions the hydrodenitritification was not complete, just only partial alkyl indoles elimination has occurred. Hydrotreating also appears to remove species that are considered to contribute to the degradation of the fuel, such as, acids, mercaptans and phenalenes. This study suggests that in this case, other mechanisms of degradation are taking place and confirms earlier findings that the major mechanism of fuel degradation depends above all on the composition of the fuel.

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**Table 1 - Composition of the samples**

Samples	Composition
A1	100 vol. % straight run distillate
A2	100 vol. % straight run distillate
HT-A2	100 vol. % hydrotreated A2
B	100 vol. % raw catalytically cracked cycle oil (LCO)
A2/B	84 vol. % A2 + 16 vol. % B
HT-(A2/B)	Hydrotreated A2/B
A1/A2/B	36 vol. % A1 + 54 vol. % A2 + 10 vol. % B
A1/A2/AD-B*	36 vol. % A1 + 54 vol. % A2 + 10 vol. % AD-B
A1/HT-(A2/B)	36 vol. % A1 + 64 vol. % HT-(A2/B)

a - hot LCO plus additive (tertiary amines and metal deactivator)

**Table 2 - Physico-chemical characteristics**

Characteristics	Method	A1	A2	HT-A2	B	A2/B	HT-(A2/B)
Specific gravity at 20/4 °C	ASTM D 1298	0,8544	0,8940	0,8918	0,8438	0,8050	0,8886
Distillation IBP/EBP, °C	ASTM D 88	217/313	110/402	132/ -	208/314	208/402	230/ -
Color	ASTM D 1500	1,0	2,5	L 1,5	4,0	3,0	1,5
Total acid number, mg KOH/g	ASTM D 674	0,54	1,80	0,02	0,04	1,10	0,04
Sulfur, wt. %	ASTM D 2822	0,33	0,88	0,21	0,70	0,59	0,18
Mercaptans, mg/kg	ASTM D 3227	10	26	7	28	30	6,2
Total nitrogen, mg/kg	ASTM D 4629	110	1100	1000	2000	1200	980
Basic nitrogen, mg/kg	UOP 269	110	616	530	446	470	430
Pyrrolic nitrogen, mg/l	UOP 278	-	18,1	16,7	989	170	99,2
% C aromatic	NMR	-	20,1	21,8	83,8	31,7	27,5

**Table 3 - Stability of hydrotreated fuels**

Heteroatoms removal	A2	HT-A2	A2/B	HT-A2/B
HDN, %	-	9	-	18
HDS, %	-	64	-	68
Stability test - ASTM D 5304				
ASTM color before test	L 2,5	L 1,5	L 3,5	L 1,5
ASTM color after test	L 8,0	L 3,5	L 8,0	L 3,5
Total insolubles, mg/100 ml	0,7	0,5	8,2	0,6
Pass/Fail criteria (max.)	IT 4,0	mg/100 ml	Color after	3,0

Table 4 - Changes in pyrrolic nitrogen compounds with hydrotreating

Compounds, µg/g	A2	HT-A2	A2/B	HT-(A2/B)
<b>Alkyl indoles</b>	<b>ND<sup>a</sup></b>	<b>ND</b>	<b>2022</b>	<b>1061</b>
C <sub>0</sub> <sup>a</sup>	ND	ND	41	7
C <sub>1</sub>	ND	ND	327	82
C <sub>2</sub>	ND	ND	722	294
C <sub>3</sub>	ND	ND	669	441
C <sub>4</sub>	ND	ND	263	237
<b>Alkyl carbazoles</b>	<b>2328</b>	<b>2074</b>	<b>2111</b>	<b>1916</b>
C <sub>0</sub>	ND	ND	55	49
C <sub>1</sub>	81	66	168	174
C <sub>2</sub>	350	313	395	355
C <sub>3</sub>	685	615	571	498
C <sub>4</sub>	832	750	644	593
C <sub>5</sub>	380	330	278	247

a - Subscript designates total number of carbons in alkyl groups.  
 b - non detected.

Table 5 - Ageing kinetics at 43 °C

Characteristics			B	A1/A2/B	A1/A2/AD-B	A1/HT-(A2/B)
ASTM color	W K M M S	0	L 5,0	L 3,0	L 3,0	L 2,0
		2	D 8,0	L 7,5	L 8,0	L 2,5
		4	D 8,0	D 8,0	D 8,0	L 3,5
		6	D 8,0	D 8,0	D 8,0	L 3,5
		8	D 8,0	D 8,0	D 8,0	L 4,0
		12	D 8,0	L 8,0	D 8,0	L 3,5
Filterable insolubles, mg/100ml	W K M M S	0	0,4	0,0	0,5	0,2
		2	0,2	3,2	3,3	0,3
		4	0,7	3,8	4,6	0,1
		6	0,9	5,2	5,8	0,5
		8	0,4	2,8	1,5	0,0
		12	1,1	5,5	2,8	0,5
Basic nitrogen, mg/kg	W K M M S	0	600	425	380	365
		2	525	350	415	330
		4	415	370	390	350
		6	460	430	425	360
		8	400	350	360	300
		12	565	360	375	330
Pyrrolic nitrogen, mg/l	W K M M S	0	737	83,4	87,1	66,8
		2	743	71,4	78,8	63,3
		4	749	65,3	70,6	65,7
		6	696	63,0	64,3	62,4
		8	744	59,2	69,1	63,4
		12	680	57,4	60,3	61,2
Mercaptans, mg/kg	W K M M S	0	13	17	23	7,5
		2	5,0	15	15	7,5
		4	5,5	14	14	7,5
		6	5,5	11	12	7,5
		8	3,0	9,0	9,0	6,0
		12	3,0	9,0	9,0	7,0
Total acid number, mg KOH/g	W K M M S	0	0,01	0,98	0,98	0,20
		2	0,02	0,94	0,93	0,18
		4	0,02	1,05	1,05	0,18
		6	0,02	0,95	0,95	0,19
		8	0,02	0,95	0,94	0,17
		12	0,02	0,93	0,92	0,20
Phenalenone, mg/l	W K M M S	0	49,9	5,1	4,3	< 0,5
		2	169,4	8,0	9,2	< 0,5
		4	269,4	7,4	8,2	< 0,5
		6	294,8	7,1	8,1	< 0,5
		8	291,7	6,9	7,6	< 0,5
		12	296,9	7,0	7,8	< 0,5
Alkyl indoles/ carbazole	W K M M S	0	98,7	48,5	50,3	26,5
		2	82,7	39,4	38,3	24,2
		4	72,8	37,5	33,5	25,1
		6	-	-	-	-
		8	77,3	35,2	28,6	22,2
		12	64,5	32,5	26,4	21,0

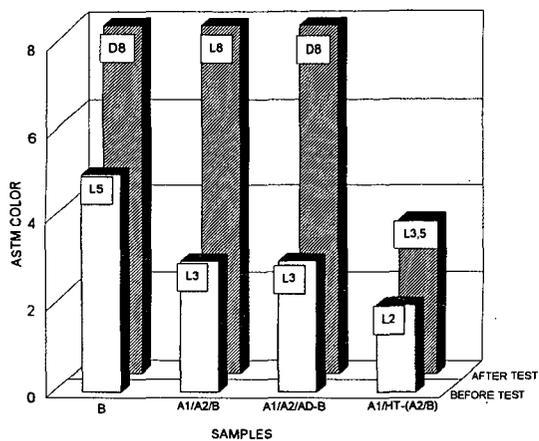


Figure 1 - Results of color changes before and after ASTM D 4625

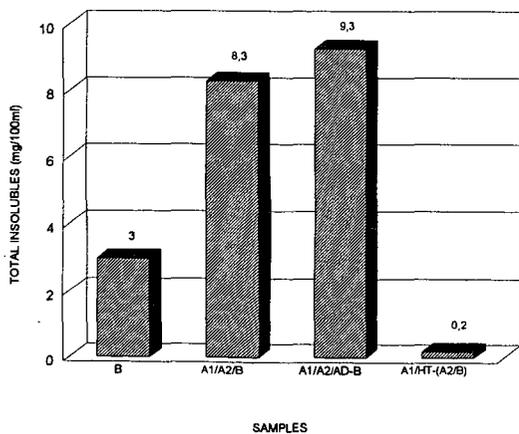


Figure 2 - Results of total insolubles of ASTM D 4625

# STUDIES ON THE STABILITY AND SEDIMENT PRECURSORS IN VISBREAKER MIDDLE DISTILLATE.

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Keywords : Middle distillate, Stability, FTIR

## ABSTRACT

Diesel fuels, particularly those incorporating secondary processed stocks, can degrade during long term storage. The degradation products can cause plugging of fuel filters and blockage of engine components. In the present paper, stability of a middle distillate cut of visbroken product from a refinery unit, before and after extraction with methanol under ambient storage conditions, has been determined. Methanol extraction has been found to reduce the tendency of the fuel to form insolubles significantly and it also separates out sediment precursors. The sediment precursors responsible for the instability of the fuel obtained under different conditions of extraction were characterized for their functional groups by FTIR. Effect of blending the sediment precursors into a typical feed stock on the stability under accelerated aging has also been studied.

## INTRODUCTION

Visbreaking is not only used for reducing the viscosity and pour point of heavy fuel oils and residues but also produces relatively cleaner feed stocks for catalytic cracking units. Middle distillates from visbreakers are blended with diesel pool, which enhances the stability problem. Recently Wechter & Hardy<sup>1</sup> and Sharma & Agrawal<sup>2-3</sup> have reported that methanol extraction removes the major portion of sediment precursors in case of light cycle oil (LCO) and total cycle oil (TCO). The present paper reports the stability behaviour of a visbreaker middle distillate from a refinery stream and the effect of methanol extraction, particularly fuel to methanol ratio on the removal of sediment precursors. These sediment precursors have also been characterized using FTIR technique and the effect of different doses of total sediment precursors on sediment formation determined.

## EXPERIMENTAL

The storage stability of the visbreaker middle distillate fuel was determined in terms of total insolubles after keeping it for 3,6, and 9 months under ambient conditions. Sediment (insoluble) precursors were separated from the fuel using methanol in sample to solvent ratio 5:1, 5:3, 5:5 and 5:10 by vol, till a neutral (stable) fuel is obtained. The fuel solvent mixture was shaken manually for 10 minutes and was kept over night for separating the fuel and solvent layer. Methanol was recovered from the upper layer by distillation to get the insolubles / sediment precursors (SP1, SP2, SP3 and SP4) as residue. Figure-1 presents the scheme employed for the above extraction.

These residues were characterized by FTIR as thin films obtained from evaporating their solutions in dichloromethane on KBr plates. Different fuels obtained after removing the sediment precursors during consequent extraction were stored under ambient conditions for 7 months and total insolubles were determined. Total sediment precursors SP (SP1+SP2+SP3+SP4) were doped in stable fuel (F4) in different concentrations and their stability was determined by modified UOP-413 accelerated test method (100 psi pressure of oxygen, 4 hours, 100 °C). Physico-chemical properties of visbreaker middle distillate and total sediment precursors were determined using standard IP/ASTM methods.

## RESULTS AND DISCUSSION

The physico-chemical properties of fuel and total sediment precursors are

reported in Table- 1 while total insolubles yield under ambient storage conditions are presented in Figure-2. Physico-chemical data of visbroken middle distillate (Table 1) reveals that the fuel is quite unstable due to presence of higher bromine number, sulphur and nitrogen content ( more than 50% of nitrogen basic in nature ).This trend is supported from the insoluble yield obtained from this fuel under ambient storage for different time intervals, which shows an increasing trend ( Figure-2 ) upto 9months (maximum storage time in the present study ).

The elemental composition of total sediment precursors indicate that nitrogen and sulphur containing aromatic structures are predominantly responsible for sediment formation.This is supported by H/C atomic ratio (1.36 as compared to 1.63 in fuel ).

Figure-1 shows that the sediment precursors yield is increasing with decreasing fuel to solvent ratio (F/S). It has been observed that with F/S 5:10 ratio ( at fourth stage ) most of the precursors are extracted out and the fuel becomes practically stable during ambient storage of seven months. This has been confirmed by keeping the fuels (F,F1,F2,F3, and F4 ) for seven months under ambient storage conditions and determining the yield of insolubles .Total insolubles obtained from different fuel (F1,F2,F3,and F4 ) under ambient storage of seven months are shown in Figure-3. It has been observed ( Figure-3 ) that total insolubles decreases slowly in F1, F2, and F3, while in F4 the decrease is quite significant and fuel becomes practically stable.

This fuel ( F4 ) has further been doped with different concentrations ( 1, 3 and 5 % wt/vol ) of total sediment precursors (SP ) and stability determined by modified UOP-413 accelerated test method. The results obtained are presented in Figure.4, which reveal that the sediment yield increases with increase of sediment precursors added. Further, it is also observed from the Figure-4 that the added precursors are more effective in sediment formation compared to those present in the original fuel.

The FTIR spectra of different precursors ( SP1, SP2, SP3 and SP4 ) are mainly of same nature. The bands at 749, 811 and 875  $\text{cm}^{-1}$ ( with decreasing relative intensity ) are observed in all the precursors, showing the same type of substitution pattern on aromatic ring . The broad OH/NH stretching bands around 3300  $\text{cm}^{-1}$  and broad carbonyl band at around 1700  $\text{cm}^{-1}$  are found to decrease in intensity from SP1 to SP4. The absence of band at 720  $\text{cm}^{-1}$  ( due to n-paraffinic  $(\text{CH}_2)_n, n \geq 4$  ) and relatively stronger band at 1456  $\text{cm}^{-1}$  due to  $-\text{CH}_2$  bending indicates the presence of significant concentrations of naphthenic structures in all the precursors.

The study thus indicated that repeated methanol extractions are required for getting the stable fuel from visbreaker middle distillate product.

#### ACKNOWLEDGEMENT :

The authors are thankful to their colleagues Dr O.S Tyagi & Mr G.M.Bahuguna for providing the IR spectra.

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TABLE- 1 Characteristics of visbreaker middle distillate and total sediment precursors

<b>Visbreaker Middle Distillates</b>		<b>Total Sediment precursors (SP)</b>	
Density, D15	0.8617	C, % Wt	85.40
Bromine number	20.7	H, % Wt	9.65
Nitrogen Total, ppm	237.3	S, % Wt	3.46
Sulfur Total, % wt	1.65	N, % Wt	0.36
Nitrogen Basic, ppm	138	O, % Wt	1.23
Carbon residue, %wt	0.04	Nitrogen Basic, ppm	932
C, % wt	83.95	Molecular Weight	274
H, % wt	11.40	Atomic H/C ratio	1.36
Atomic H/C ratio	1.63		
Molecular weight	255		
Boiling range, °C	176-393		

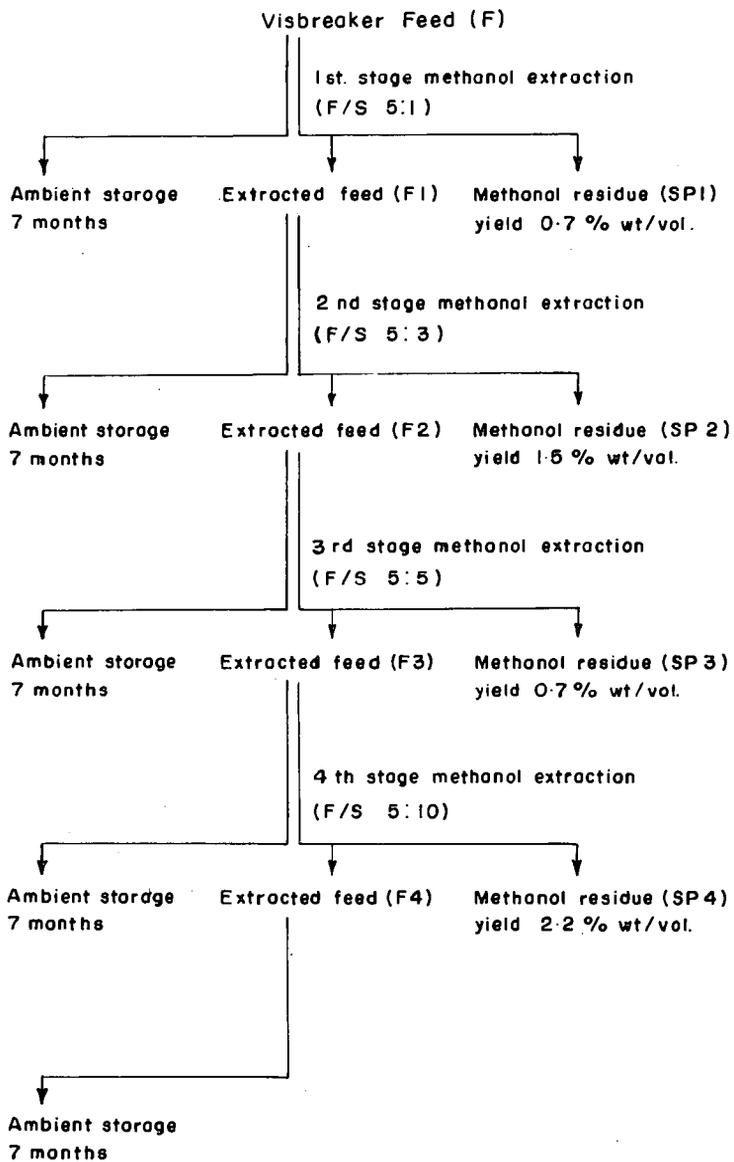


Fig. 1 - Scheme used for the extraction of insolubles / sediment precursors.

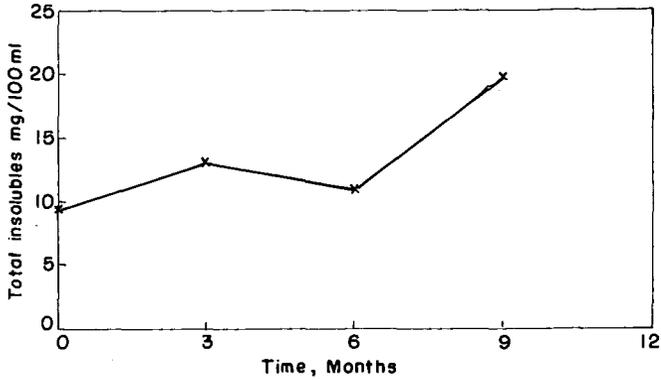
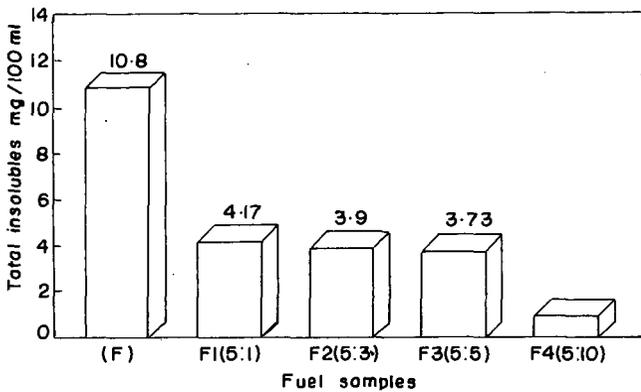


Fig. 2 - Total insolubles Vs time during ambient storage stability of visbroken middle distillate.



(Feed to Methanol ratio given in brackets)

Fig. 3 - Effect of extraction on ambient storage stability (7 months) of visbroken middle distillate.

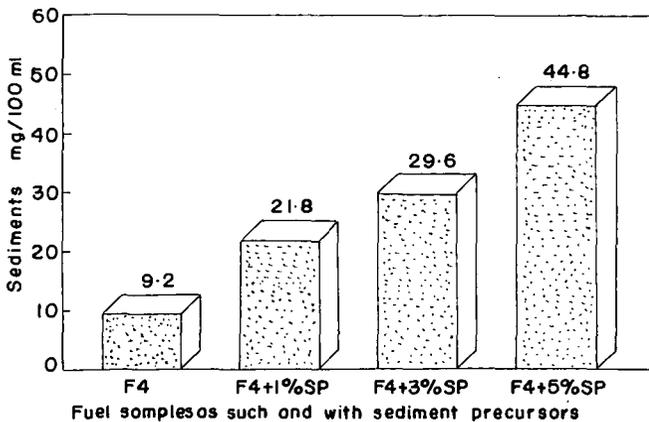


Fig. 4 - Effect of sediment precursors on extracted visbroken middle distillate (UOP-413 MODIFIED)

## INSTABILITY OF MIDDLE DISTILLATE FUELS DURING STORAGE AND CHARACTERIZATION OF INSOLUBLES BY FTIR

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Keywords : Middle distillates, Stability, FTIR

### ABSTRACT

The problem of stability of diesel fuels has become more pronounced in recent years with the increasing use of cracked stocks in the diesel pool. These cracked products induce gum and sediment formation in fuels. In the present paper, the instability of total cycle oil (TCO) derived from FCC operation of Bombay High VGO, under accelerated and ambient storage conditions has been studied with and without additive doping. During ambient storage yield of the insolubles in TCO has been found to decrease after a period of about 18 months which may be attributed to the reformation of fresh oxidised species from insolubles. However during accelerated tests trend of increasing insoluble formation with time is revealed. The qualitative composition of insolubles obtained from ambient storage of additive doped and undoped fuels has been studied by FTIR and the role of additives on the composition of insolubles is discussed.

### INTRODUCTION

Diesel fuels, particularly obtained from catalytically cracked stocks, start degradation right from production and on storage degrade to the extent that start giving application problems. The degradation mechanism and additive response depend on fuel composition, temperature, oxygen availability, static and dynamic conditions, storage time and type and size of storage vessels. In the present investigation, the instability of total cycle oil (TCO) derived from FCC stream of a refinery and doped with commercial additives has been studied under accelerated as well as ambient storage conditions. FTIR spectroscopy has been employed to explain the mechanism of additive functioning by comparing the spectra of sediments obtained under different conditions.

### EXPERIMENTAL

The total cycle oil (TCO) was doped with 100 ppm of phenol (A1) and amine (A2) types additives. Various accelerated test methods viz modified ASTM D-2274, ASTM D-4625 along with ambient storage tests for 4, 8, 12, 18 and 24 months were performed on TCO as such and doped with additives. FTIR spectra of various insolubles were recorded in absorbance mode on Perkin-Elmer 1760 FTIR spectrometer by making thin films of samples on KBr plates by evaporating their dichloro methane solution.

### RESULTS & DISCUSSION

The physico chemical properties of TCO determined by standard ASTM/IP test methods are reported in Table-1. The insoluble yields from TCO as such and doped with additives (TCO+A1, TCO+A2) under modified ASTM D-2274 test conditions are shown in Fig.1, while those obtained with ASTM D-4625 and ambient storage conditions are presented in Figs. 2 & 3 respectively. Typical FTIR spectra of sediments obtained after 18 months and 24 months storage of TCO as such and with additives (TCO + A1 and TCO + A2) are presented in Fig.4.

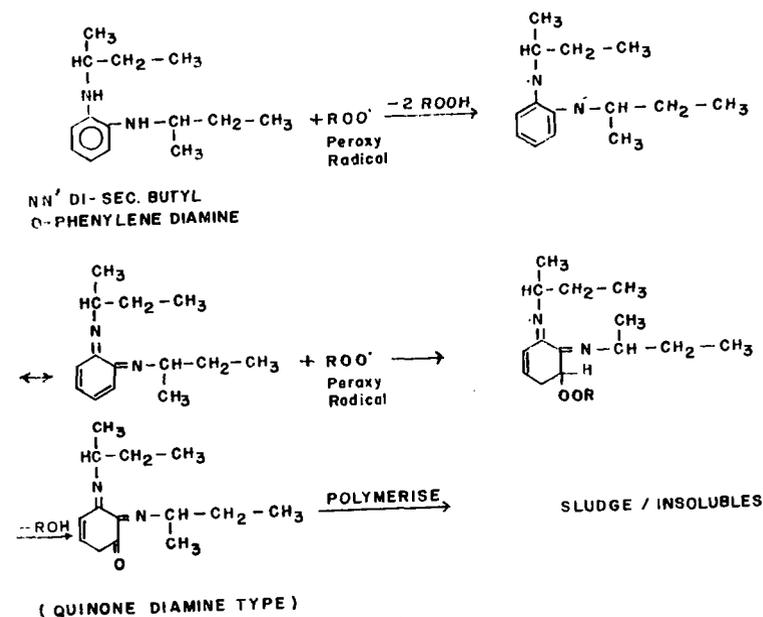
From Fig.1, it is evident that sediment yield, under accelerated test conditions (dynamic) in the presence of oxygen is reduced significantly after doping with additives due to better additive fuel interaction under these conditions. This reduction is more pronounced in case of amine type additive as compared to phenol type. But in case of

static conditions (ASTM D-4625) as the oxygen availability is limited and agitation is also not there, the overall sediment formation and reduction after doping with additives are relatively small (Fig.2). In case of ambient storage (Fig.3) sediment formation is low in the beginning which increases significantly with time up to 18 months. Here also the reduction in sediment formation after doping with additive is significant. An appreciable reduction in sediments after ambient storage of 18 months in TCO as such as well as in doped with additives is observed (Fig.3). This observed pattern may be due to the formation of fresh oxidized species after 18 months storage. This has further been confirmed from the comparison of FTIR spectra of sediments from TCO, TCO+A1 and TCO+A2 after 18 and 24 months storage (Fig.4).

The appearance of two carbonyl band around 1740 and 1710  $\text{cm}^{-1}$  (having comparable intensity) in all the sediments obtained after 24 months reveals that on longer duration, hydrolysis of ester type structures in sediments takes place forming the carboxylic and phenolic structures which are soluble in fuels. Thus the sediment yield is reduced. This is supported by the enhancement of bands at 3270 and 1600  $\text{cm}^{-1}$  due to stretching and bending vibrations of OH groups.

FTIR spectroscopy has also been employed to explain the higher effectiveness of amine type additive compared to phenol type in inhibiting the sediment formation. The comparison of FTIR spectra of sediments from TCO, TCO+A1 and TCO+A2 after ambient storage of 18 months (Figs.4 A,B,C) reveals that while there is no appreciable qualitative variation in the spectra of TCO and TCO+A1, the spectrum from TCO+A2 (Fig.4C) is quite different in nature.

The sediment from TCO as such shows an appreciable amount of ester type carbonyl 1740  $\text{cm}^{-1}$  (Fig.4A), while this is reduced considerably in sediment from TCO+A2 (Fig.4C). Further, the structures like quinone diamine type which forms during controlling the peroxy radicals also appears in the sediments due to sludge formation during storage. This may probably occur in sediment through polymerisation as per following mechanism of action of amine type additive<sup>2</sup>.



This is also supported from the FTIR spectra of sediment from TCO+A2 (748  $\text{cm}^{-1}$  band due to 3-adjacent protons on aromatic rings). The strong and broad absorptions at 3260 and 1600  $\text{cm}^{-1}$  in sediment of TCO+A2 (Fig.4C) as compared to those of TCO and TCO+A1 (Figs.4 A & B) show the dominance of structures containing OH functionalities (phenolic type). Aromatic structures are confirmed by the appearance of 3052  $\text{cm}^{-1}$  band (aromatic C-H stretching) and enhanced absorption at 1600  $\text{cm}^{-1}$ . Thus, amine type additive is more effective in inhibiting the formation of sediment containing ester type structures during ambient storage of total cycle oil.

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Table-1 Characteristics of Total Cycle Oil

Density D15	0.8821
Kinematic viscosity, at 40 °C, cSt	2.46
Pour point, °C	18
Molecular weight	177
Maleic anhydride value	5.56
Diene value	1.44
Sulphur, %wt	1.46
Nitrogen, ppm	125
Boiling range, °C (5-95% vol)	158-441

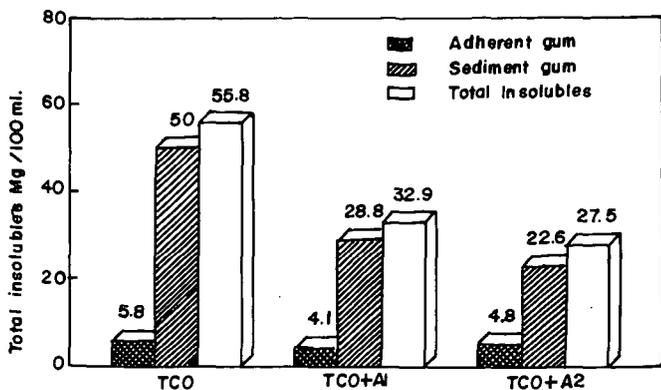


Fig. 1 : Response of Additives in TCO on stability under Modified ASTM D-2274

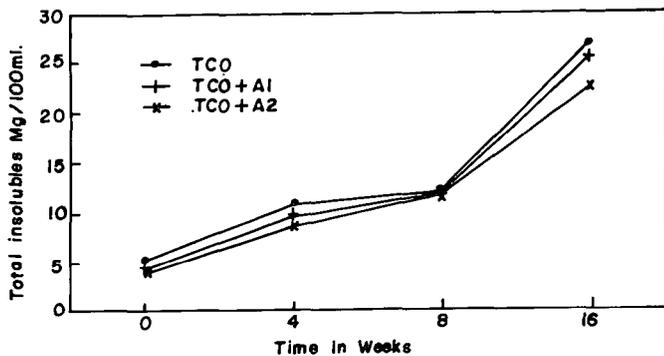


Fig. 2 : Response of Additives in TCO on long storage stability in non vented conditions at 43.3°C

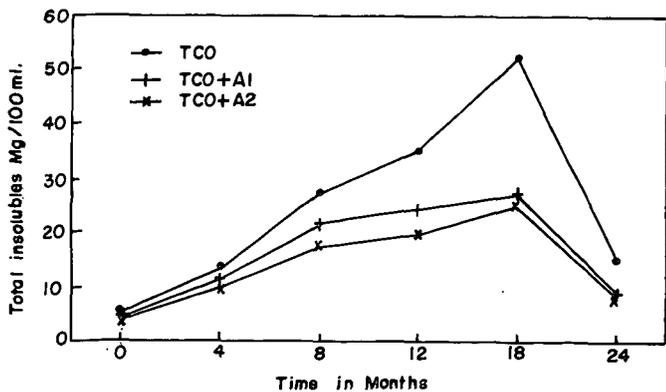


Fig. 3 : Response of Additives in TCO on Ambient storage stability.

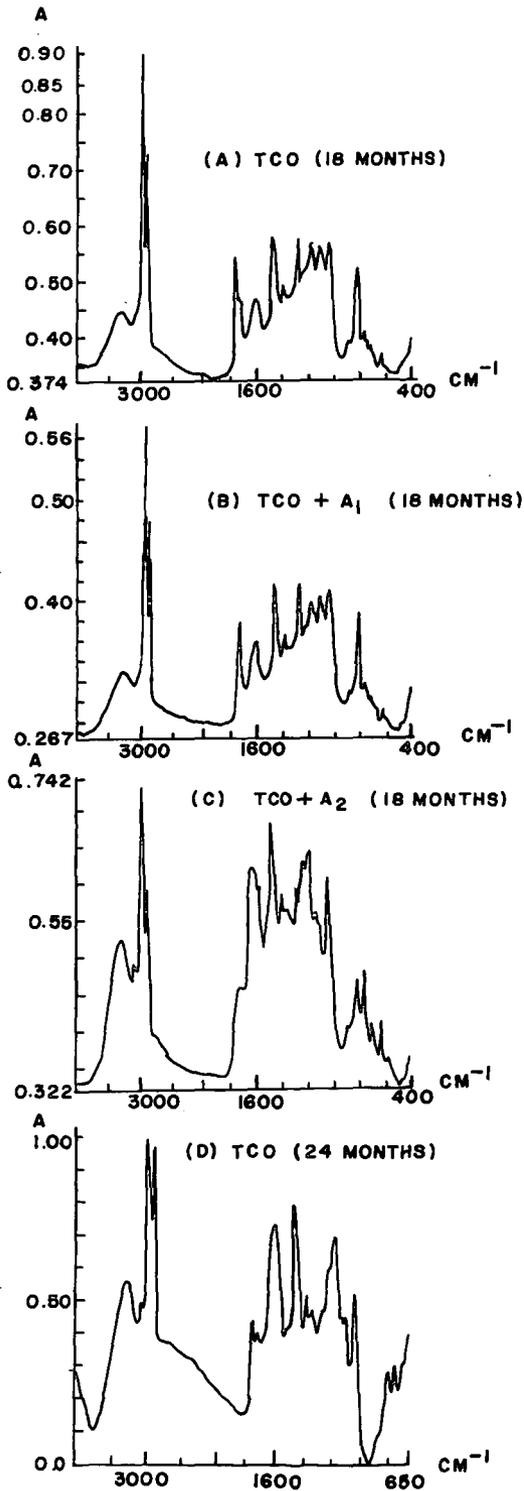


FIG. 4. FTIR SPECTRA OF SEDIMENTS

## PREDICTING STABILITY AT THE REFINERY USING SMORS

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Keywords: SMORS, diesel fuel, storage stability

### INTRODUCTION

It has been previously reported<sup>(1)</sup> that extraction with methanol will improve storage stability characteristics for mid distillate diesel fuel which is at least 6 months old. Moreover, a potential relationship between the methanol soluble, hexane insoluble extractible material and the thermally induced precipitate (TIP) which forms in some fuels under accelerated aging conditions which simulate long term ambient storage, has been suggested.<sup>(2,3)</sup> Fuel stability is currently assessed through the use of an accelerated aging procedure.<sup>(4)</sup> However, the procedure or procedures used require substantial commitments of laboratory time and resources and they are necessarily limited to predicting only the relatively short term (1 - 2 years). A predictive stability test which could serve for field use for fuels at least 6 months old, or which would require a sufficiently short turnaround time to make it attractive for procurement use is highly desirable. This is particularly true when circumstances require that the fuels may be stored for very extended periods, such as military fuel reserves.

Fuels which have been aged by six months of ambient storage in the laboratory or field show a very linear relationship between the solids produced by methanol extraction and subsequent precipitation with hexane (EIP - extraction induced precipitate), and solids, or insolubles, formed during the stress, or accelerated aging process (TIP).<sup>(2)</sup> Thus, for these fuels, the extractibles yields can be used as a predictive test for storage stability. When these aged and thermally stressed fuels are extracted with methanol after filtration for TIP, the yield of extractible solids is typically found to be no more than a few percent higher than the EIP isolated from the unstressed fuel. We propose that, for those cases where the post-stress extractibles (PEIP) yields are about equal to the pre-stress yields (EIP), there is an equilibrium concentration of distributed soluble macromolecular material (which we have previously called SMORS).<sup>(2,3,5,6)</sup> Examples of fuels which have been aged to this equilibrium condition are found in Table 1 (Code A = aged).

Fuels which are refinery fresh, or are not aged to equilibrium either because they have been stored under non-oxidative conditions (inert atmosphere, freezer conditions) or their ambient storage times are too short, will frequently show very different extractibles yields before and after accelerated aging. Until these fuels are aged to equilibrium there is no consistently useful relationship between EIP and TIP to obviate the need for a stress test. Some examples of pre (EIP) and post (PEIP) stress extractibles yields for some fresh fuels are also found in Table 1 (Code F = fresh).

Because accelerated aging tests for new fuels do not generally permit storage stability prediction beyond a year or so under ambient conditions and because they are not always reliable, we are suggesting that a stress test in combination with a post stress determination of extractibles will serve to better identify fuels which are likely to develop undesirable storage characteristics over time. This test could serve as the basis for deciding which fuels could be safely stored for additional extended periods, and which should be used promptly. We also provide additional experimental evidence to link the extractible material (SMORS) with insoluble sediment formed as a result of ambient storage.

### EXPERIMENTAL

The fuels used in this work were refinery fresh fuels which were tested for EIP and TIP (insolubles) as soon as they reached the Laboratory. They included two light cycle oil (LCO) stocks and two straight runs (SR). For experimental purposes, the fuels tested were the two LCOs and 80%/20% blends of the SR/LCO pairs. Designations for the experimental fuels are found in Table 2.

All fuels involved were tested for pre and post stress extractibles (EIP/PEIP) as soon as they were received and at later intervals, ranging between one and nine months, as well. They were tested for insolubles using the 16 hour ASTM D 5304 - 92 procedure at those same times. All fuel aliquots were prefiltered through two thicknesses of 0.8u 47mm nylon filters (MSI, Westboro,MA) using a water aspirator. Aliquots were 100 mL each; separate aliquots were used for the EIP and for the TIP/PEIP determinations. Stress conditions were 16 hrs., 90°C, 690 kPa oxygen overpressure. Post-stress samples were first filtered for TIP, then subjected to extraction for the determination of PEIP.

For the insolubles (TIP) determination: samples were filtered using glass fiber filters and the procedure described in detail elsewhere.<sup>(4)</sup> For the extractibles determinations: prefiltered aliquots were extracted (separatory funnel; shake 90 sec.) with 40 mL reagent grade methanol. The methanol phase was rotary evaporated for 30 minutes at 58-63°C. After cooling, 50 mL of reagent grade hexane was added to induce precipitation. The resulting precipitate was filtered (nylon filters) and dried at 70°C for at least 20 minutes to remove any traces of hexane before weighing.

An experimental series was performed to test possible effects of a tertiary alkyl amine stabilizer additive on insoluble sediment (TIP) formation and on post stress extractibles (PEIP) formation. The amine additive has been tested in this laboratory and elsewhere and is known to reduce insolubles formation in some fuels.<sup>(7)</sup> Light cycle oil samples (Fuels B, D) were doped with the additive in varying concentrations (6 - 890 ppm w/v) and tested, along with control samples, using the same procedures previously described for the TIP and PEIP determinations. All samples were run in duplicate and the aliquot size was 100 mL.

## RESULTS AND DISCUSSION

### Aging (Stress) and Extractibles Testing

Table 3 provides a summary of ambient storage times, pre- and post-stress extractibles levels (EIP and PEIP) and total insolubles/100 mL following the standard 16 hour LPR test (ASTM D 5304 - 92). Fuel A, tested at monthly intervals from 1-3 months passes the LPR test (current pass/fail criterion is 3 mg/100 mL). Pre- and post-stress extractibles levels indicate no tendency for the fuel to degrade over time with respect to insolubles formation and suggest this fuel could be safely stored for extended periods. Fuel B is a light cycle oil and thus might be considered a potential "worst case" fuel. During the time interval between 0 and 3 months of ambient storage the fuel passes the LPR test. The pre-stress extractibles are low, but the post-stress extractibles are increasing to the point where their level suggests that this fuel is not a candidate for long term storage. By 8.5 months of ambient storage LPR insolubles (TIP) and extractibles levels have increased to the point where they support an argument for prompt use. In particular, the post-stress insolubles yield has increased to a level which suggests the fuel is likely to deteriorate badly in the near term. Also EIP and PEIP are beginning to approach equilibrium.

Fuels C and D are an interesting pair; fuel D being a light cycle oil and C a blended fuel comprised of 20% D and 80% straight run stock. Fuel D fails the LPR test badly on initial testing. Moreover, the post-stress extractibles level (41 mg/100 mL) is high and supports the conclusion that this is an unstable fuel. As time passes and the fuel is subjected to ambient storage conditions, the condition of the fuel actually improves as noted by TIP (ASTM D 5304) and PEIP (or post-stress extractibles) levels. Note that this LCO, even at 6 months, is not aged to equilibrium and so pre-stress extractibles levels are not as effective predictors of future behavior as are the post-stress levels. By 12 months of ambient storage the fuel has improved to where it passes the LPR. The PEIP has declined as the pre-stress extractibles level has increased. If the existing extractibles (EIP) are subtracted from the PEIP one obtains a measure of the "aging tendency" during the stress test. For this LCO the trend is toward improvement. The relationship between TIP and PEIP formed during accelerated aging is striking: at 0 months of ambient storage TIP is 8.3 mg/100 mL and PEIP is 40.9 mg/100 mL; at 12 months the numbers have fallen to 1.6 and 13.8 mg respectively.

Fuel D is an unusual LCO in that its storage stability with respect to insolubles formation improves as it ages under ambient conditions. However, if criteria we have proposed for aged LCOs using a 24 hour modification of the LPR stress test (TIP  $\geq$  6 mg/100 mL; extractibles  $\geq$  32 mg/100 mL)<sup>(3)</sup> are adapted to the 16 hr test, predictions for future storage behavior can be made. Based on post-stress extractibles yields (which must be used rather

than pre-stress yields until the fuel is aged to equilibrium) we would predict that, at equilibrium, the pre- and post-stress yields would be roughly equivalent. This fuel is clearly "limited" with respect to the total insolubles it can form during its lifetime prior to use. It apparently forms insolubles rapidly, then levels out to become a rather benign fuel with respect to continued insolubles formation. While this fuel obviously improves with age, it is not a suitable candidate for procurement on the basis of its poor initial extractibles/aging tests. Moreover, even if it were to be held in storage to equilibrium, there would be so much particulate matter suspended in this fuel as to present filtration problems. Thus, this fuel is not a candidate for procurement. Fuel C, the blended stock, is a likely storage candidate on the basis of its extractibles and TIP yields. On the basis of its consistent PEIP and stress test behavior and on its fuel D LCO content, this fuel appears to be a suitable candidate for storage and makes a case for safe storage and use of cracked stock blends.

#### Effect of Additives

Tables 4 and 5 present results obtained for the two light cycle oils that were tested with the tertiary amine additive (additive #1). Fuel B was also tested using another additive, a hindered phenol (additive #2), for purposes of comparison. Table 4 summarizes additive testing for fuel B. Insolubles (TIP) formation tendency for this fuel is not reduced with either additive. Indeed, it might be argued that TIP increased somewhat on addition of the tertiary amine. PEIP yields for all samples were comparable. Thus, fuel B appears to be one of those fuels that is not affected by tertiary amine additive treatment.

Fuel D, on the other hand, is responsive to additive #1. As was the case with fuel B, additive #2 had no effect on this fuel. Table 5 shows the reduction in insolubles (TIP) that occurs when fuel D is subjected to the 16 hour LPR test after treatment with varying levels of additive #1. A corresponding decrease in PEIP levels is also observed. The fact that additive #1 reduces PEIP levels as it reduces TIP provides additional evidence for a relationship to exist between extractibles levels and the tendency toward insoluble sediment formation in diesel fuels.

#### Summary

A relationship between extractibles levels before (EIP) and after (PEIP) accelerated aging and insolubles formation tendency has been found to exist in fuels that have not been aged to EIP/PEIP equilibrium. Additional evidence for the relationship between these entities has been provided by the comparable effect of a common stability additive on post stress extractibles and insoluble sediment. Thus, we propose that a combination of the LPR (ASTM D 5304) stress test and methanol extraction of the filtered, stressed fuel with subsequent precipitation of the hexane insoluble fraction, may serve as a basis for a predictive test for storage stability. This test would enable better decisions to be made as regards the candidacy of fuels for long term storage as opposed to their candidacy for prompt usage. Moreover, for cases where storage is required, this test combination might serve as a reasonable basis for procurement.

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Table 1. Weight of Solids Isolated from the Pre- and Post-Stress Hexane-Insoluble Fraction of the Methanol Extracts of Five Aged and Three Fresh Light Cycle Oil Diesel Fuels<sup>a</sup>

fuel code	EIP: mg/100 mL	PEIP: mg/100mL	aged,A or fresh,F
LCO-1	112	116	A
LCO-2	14	17	A
LCO-3	53	63	A
LCO-4	27	40	A
LCO-5	92	114	A
LCO-12	1	14	F
LCO-13	2	101	F
LCO-14	2	58	F

<sup>a</sup>Storage stress test was for 24 h at 90°C and 690 kPa of oxygen.

Table 2. Experimental Fuel Designations.

Fuel	Type	Legend
A	Blend	80% 91-34(SR)+20% 91-35(LCO)
B	LCO	100% 91-35(LCO)
C	Blend	80% 92-1(SR) + 20% 92-2(LCO)
D	LCO	100% 92-2(LCO)

Table 3. Summary of Test Fuel Results

fuel	Months of Storage time (ambient)	TIP (mg/100mL)	EIP (mg/100mL)	PEIP (mg/100mL)
A	0	1.3	0.23	0.16
A	1	0.4	0.05	0.26
A	2	0.8	0.3	2.5
A	3	0.7	0.6	2.5
B	0	1.9	0.29	6.8
B	1	1.3	0.17	7.8
B	2	1.6	0.3	12.5
B	3	1.9	2.3	28.1
B	8.5	2.3	5.0	45.8
B	14	1.4	13	34.6
C	0	1.8	0.09	6.6
C	0.5	2.2	0.15	5.4
C	1.5	2.5	0.7	5.6
D	0	8.3	0.22	41.1
D	0.5	7.6	0.19	40.6
D	1.5	5.2	2.1	28.0
D	6	4.4	7.3	34.9
D	12	1.6	16.2	30

Table 4. Additive studies for fuel B at 8.5 months ambient storage

Sample tested	mg TIP	mg EIP	mg PEIP
Fuel	2.3	5.0	48.8
Fuel + 24ppm #1	3.3	-	39.3
Fuel + 24ppm #2	2.5	-	42.6
Fuel + 24ppm # 1,2	3.2	-	47.2

Table 5. Studies for fuel D at 6 months ambient storage using additive #1.

Sample tested	TIP	EIP	PEIP
Fuel	4.4	7.3	34.6
Fuel + 6ppm	1.3	-	17.5
Fuel + 24ppm	1.1	-	16
Fuel + 890ppm	1.7	-	22.6

**A FUEL STABILITY STUDY  
FILTERABLE AND ADHERENT INSOLUBLES AS FUNCTIONS OF TIME**

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Keywords: Insolubles; Adherents; Filterables

**INTRODUCTION**

It is generally accepted that the insoluble substances that form in middle distillate fuels in storage are the result of an oxidative coupling of reactive molecules which may be of the same or of different species. It is also generally accepted that the reactive species are to be found among those containing a heteroatom such as nitrogen, sulfur, or oxygen and among unsaturated hydrocarbons. However, the number of reactive compounds is large and the chemical mechanism by which they are converted into insoluble products has not been established despite years of study.

In 1958, Sauer and coworkers<sup>(1)</sup> postulated the formation of hydroperoxides which then split out water to form aldehydes. The aldehydes then reacted with other peroxides to form peroxyhemiacetals which, in turn, decomposed to form monomeric oxidation products and condensed, esterified products of higher molecular weight. Another hypothesis noted by Taylor and Frankenfeld<sup>(2)</sup> and by Por<sup>(3)</sup> is based on a free radical chain mechanism.

From a study of U.K. stocks, Pedley and Hiley<sup>(4)</sup> have suggested that phenalenes and indoles are the precursors of some fuel sediments. The phenalenes are known to oxidize to form phenalenones which can react by acid catalyzed condensation with indoles to form indolylphenalenes. These then form insoluble products by reaction with acids.

Pedley et al<sup>(5)</sup> investigated Australian stocks and found that all fuels which proved to be unstable during storage contained both alkylindole and phenalene species. Marshman<sup>(6)</sup> from a study of research blends made from fresh components obtained from U.K. and European refineries concluded that the stability of a fuel is related to the concentrations of phenalenes and indoles, but the relationship is not straightforward.

**ACCELERATED TESTS OF STORAGE STABILITY**

Such studies are useful in providing an understanding of the complex chemical mechanism by which sediment is formed. However, the person storing middle distillate fuels is more interested in the rate at which sediments will form. For example, the military and the Strategic Petroleum Reserve, both of which have to store large quantities of fuel, cannot tolerate unstable fuels.

For that reason, a number of test methods have been developed and standardized to provide an indication of the stability of a fuel. ASTM Test Methods D 2274, the accelerated stability procedure, and D5304, oxygen overpressure procedure, are two of the methods. The former has long been a required test in the Navy's distillate fuel specification; the latter is being considered as an alternate or replacement.

In Test Method D2274, which was used in obtaining the data to be presented in this paper, a 350 mL volume of filtered fuel is aged at 95°C for 16 hours while oxygen is bubbled through the fuel at 3 L/h. The fuel is then cooled and insolubles are recovered. Particulates (FI) are recovered by filtration and gums adhering (AI) to the glassware are recovered by solvent washing. The insolubles are weighed and their sum is reported in mg/100 mL as a measure of the fuel's oxidative storage stability.

## PROCESS ANALYSIS

The reactions which lead to insolubles formation start as soon as the middle distillate fuel is produced and comes in contact with an oxygen-containing atmosphere. The rate of reaction depends upon the specific fuel system and the materials with which it comes into contact. Copper and some other metals are oxidation catalysts. Rust also has some catalytic properties. Acidic materials can catalyze some of the potential reactions. Consequently, some of the instability reactions may have already occurred prior to laboratory testing of a fuel sample. An early step in the Test Method D2274 procedure is the filtering of the fuel sample to remove any solids that may have formed or that may have entered from other sources.

Let us examine what we think occurs during a D2274 type of testing. First of all, some of the reaction products is bound to be soluble in the fuel, so it is only after the saturation limit is reached that particulates begin to appear in the fuel as filterable insolubles .

Second, during the period required to reach saturation, another rate process is already removing instability products from the fuel. It is an adsorption process, and Fick's law of diffusion defines the rate of diffusion of the instability products to the glassware surface:

$$Q = D(A)(c/t) \quad (1)$$

Q is the quantity diffusing to the adsorption surface per unit time, D is the diffusion coefficient, A is the area of the glassware wetted by fuel, and c/t is the concentration gradient between the bulk fuel and the surface of the glassware. Thus, while the instability reactions are placing reaction products in solution, the diffusion and adsorption process is removing material from solution and depositing it on the glassware.

Presuming that the reaction process is faster than the rate at which reaction products are removed as adherent insolubles, the solubility limits of the reaction products in the fuel will eventually be reached and the filterable insolubles will begin to precipitate from solution. As long as reaction products are produced at a rate faster than they can be removed by adsorption, excess material will precipitate to add to the quantity of filterable insolubles.

If the concentrations of the reactants is rate controlling, there will be a gradual decrease in the rate of formation of filterable insolubles. However, if reactant concentrations are high, other rate processes may be limiting. For example, the rate at which dissolved oxygen can be replenished from the oxygen which is bubbled through the fuel in Test Method D2274 may be the controlling process. In such cases, the rate of formation of FI would be constant, and a plot of cumulative FI as a function of stress time would be linear, until the concentrations of the reactive fuel components decreases to the point where their concentrations are controlling the rate.

Because the instability reaction products (IRP) in solution will remain constant at the saturation concentration, the rate of formation of adherent insolubles will be constant, i.e. a plot of cumulative AI versus time will be linear. However, once the formation of reaction products drops below the rate just sufficient to maintain saturation, the rate of adherent insolubles formation will begin to decrease, i.e. the slope will decrease and the cumulative AI will approach an asymptotic value.

If both the filterable insolubles and the adherent insolubles approach asymptotic values, the ratio of the two must also approach an asymptotic value.

## EXPERIMENTAL PROCEDURE AND RESULTS

The author has previously reported some results obtained when twenty-one fuel stocks were individually stressed in a D2274 procedure using a range of stress times.<sup>(7)</sup> The time response curves of total insolubles vs. stress time have an S-shape if the period is sufficiently long and the total insolubles level approaches an asymptotic value. The study showed that tests using a single stress time are incapable of fully defining the stability characteristics of a fuel. It was also found that pre-aging a fuel prior to determining its time response curve appeared to affect only the duration of the induction period.

The same twenty-one stocks and the same tests form the basis of this paper, in which we examine the manner in which stress time affects the individual components of total insolubles, i.e. the filterable insolubles (FI) and the adherent insolubles (AI). Properties of the stocks were presented in the earlier paper.

The experimental data tend to support the postulated mechanism. Figures 1 to 4 show the filterable insolubles, the adherent insolubles, and the ratio of filterables to adherents as functions of the time the four fuels were left in the 95°C bath. These illustrations were selected as representative of the twenty one stocks mentioned earlier. Similar curves were obtained with the other fuels.

Although fuels which had data points at five or more times and which had one or more data points representing times of sixty or more hours were preferred, the need to show representative fuels did not always permit such preferences to be honored. In general, the shapes of the curves were not as certain with fewer points or with a smaller range of times.

Figure 1 shows the time response curves for a light cycle oil (LCO). Note the initial linear responses of both the AI and the FI. A rate limiting phenomenon controlling the formation of filterable insolubles below 40 hours of stress is postulated. Above the 40 hour stress point, it appears the concentration of the active components of the fuel are controlling. The AI also exhibit a linear rate response below the 40 hour point, which is consistent with the postulated mechanism. The ratio of FI to AI seems to be approaching an asymptotic value of about 2.

Figure 2 shows the time response curves for a 40/60 volume percent blend of an LCO in a straight run (SR) fraction. The range of times ran only to 46.2 hours but, within that time range, we did obtain six data points. The curves indicate that saturation is not reached until 20 hours have elapsed. The standard 16-hour test would have shown this to be a very stable fuel with very low insolubles whereas, in another 20 hours, it approached its asymptotic level of roughly 3.5 mg/100 mL.

The FI curve shows that the concentrations of active components is controlling, and the AI curve supports the adsorption hypothesis because it is linear. The FI/AI ratio curve seems to be reaching an asymptotic value of about 2.

Figure 3 shows the time response curves for a 30/70 blend of an LCO with an SR fraction. The FI time response curve shows a decreasing rate of FI formation, so the concentrations of active ingredients is postulated as controlling. The AI response curve is again linear, and the ratio curve seems to be approaching an asymptotic value of about 1.

Figure 4 shows the time response curve for a blend of a high sulfur heavy diesel fuel in a CAT 1H fuel. The maximum stress time is 40 hours, but we do have five data points. Linear fits are obtained for both the FI and the AI, and the ratio of the two seems to be reaching an asymptotic value of about 3.5.

## FINDINGS AND CONCLUSIONS

1. Formation of FI remains essentially zero until the fuel is saturated with instability reaction products (IRP's). Thereafter, the rate of FI formation may be linear if there is a limiting rate factor such as oxygen supply, or it may decrease as reactive components are depleted.

2. Once a fuel is saturated with IRP's, AI formation is constant until reaction rates are too slow to keep the fuel saturated.

3. After the fuel becomes saturated with IRP's, the FI/AI ratio starts to approach a constant value. Experience indicates this is often about 1 or 2. We have seen no value above 6.

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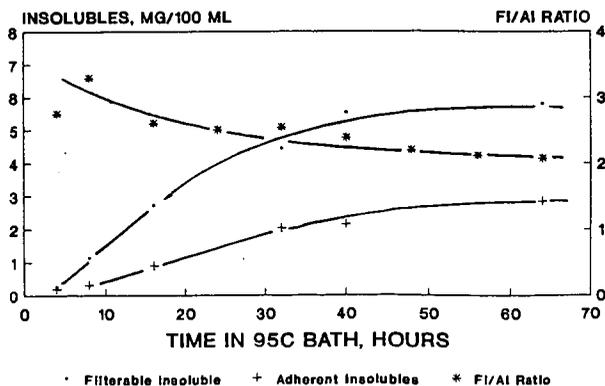


Fig. 1 - Time response curves for a light cycle oil, showing FI, AI, and the FI/AI ratio as functions of time.

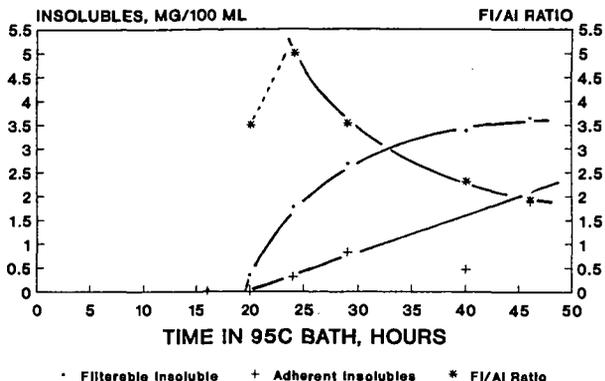


Fig. 2 - Time response curves for a 40/60 volumetric blend of LCO in an SR stock, showing the FI, AI, and FI/AI ratio as functions of stress time.

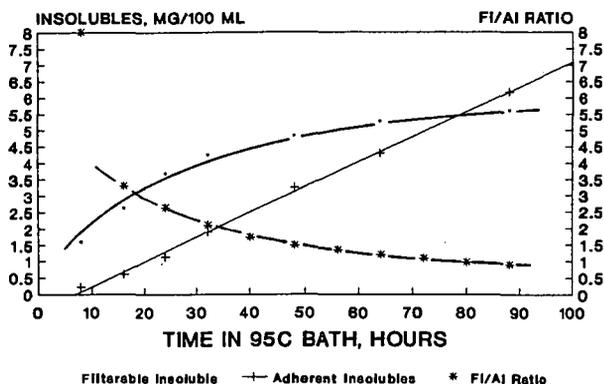


Fig. 3 - Time response curves for a 30/70 blend of a blend of an LCO in an SR stock, showing the FI, AI, and FI/AI ratio as functions of stress time.

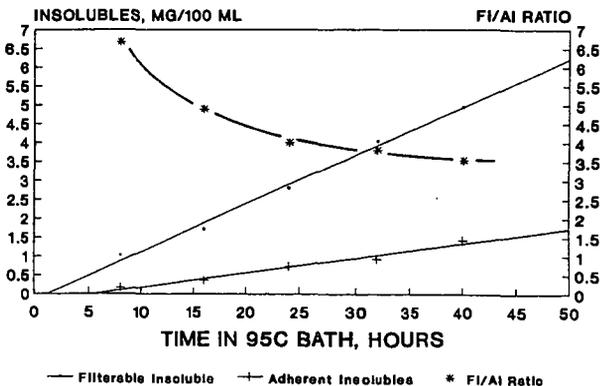


Fig. 4 - Time response curves for a blend of high sulfur, heavy diesel fuel in a CAT 1H fuel, showing the FI, AI, and FI/AI ratio as functions of time.

## EFFECTS OF SULFUR COMPOUNDS ON A JP-8 SURROGATE FUEL

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Keywords: Jet fuel stability, deposit formation-effects of sulfur compounds, thermal desorption/pyrolysis-GC-MS

### INTRODUCTION

The thermal stability of military jet fuels is of increasing concern as the fuels must withstand ever increasing loads as the coolant/heat sink for the system of advanced aircraft<sup>(1)</sup>. Fuels exposed to elevated temperatures and oxygen form soluble and insoluble oxidation products. The formation of insoluble deposits in fuel systems and the resulting possibility of system failure is of particular concern.

Hazlett pointed out the role of phenols and oxidative phenolic coupling in the formation of insoluble deposits under accelerated storage conditions in 1986<sup>(2)</sup>. We have observed phenols as the only reactive species in engine augments fuel tube and spray ring deposits from a military engine<sup>(3)</sup>. From the real engine deposits we postulate deposit initiation by oxidative phenolic coupling, followed by condensation to three dimensional aromatic networks as the initial phenolic dimers and oligomers are exposed to more heat energy. In experiments with fuel samples, solid phase extraction of polar compounds were predominately phenolic for non-hydrated fuels but not with hydrated fuels<sup>(4)</sup>. The hydrated fuels oxidized rapidly and extensively to give alcohols and carbonyl products, including the homologous series of 5-alkylidihydrofuranones. Hydrated fuels did not form significant amounts of insoluble solid deposit. Non-hydrated fuels oxidized slowly and formed large amounts of insoluble deposits. Heneghan has observed this inverse relationship of deposit formation and "oxidizability" for 20 different fuels as measured by eight separate techniques<sup>(5)</sup>.

Non-hydrated fuels are generally high in sulfur relative to hydrated fuels. The catalytic effect of sulfuric and sulfonic acids in the decomposition of  $\alpha$ -arylhydroperoxides to phenols is well known<sup>(6)</sup>. Hardy, et. al., observed the effect of several sulfur compounds as anti-peroxidants<sup>(7)</sup> in fuels and in model systems<sup>(8)</sup>.

If oxidative phenolic coupling is a major mechanism for deposit formation, the effect of sulfur compounds in the production of phenols by decomposition of arylhydroperoxide precursors should significantly increase deposit formation. The relative effects of different classes of sulfur compounds is probably predictable, but the effect of these compounds on phenolic coupling is not known. A previously prepared, 12 component, surrogate fuel<sup>(9)</sup> presents a test media for doping experiments with representative sulfur compounds from which reaction products of fuel components and sulfur compounds should be easy to follow, compared to complex real fuels.

Aliphatic thiols, thiophenols, thiophenes, benzothiophenes and disulfides are represented by dopant compounds. Gravimetric results of deposit formation, extraction and analysis of polar products by GC-MS and analysis of insoluble solids by step wise thermal desorption/pyrolysis-GC-MS gives a fairly complete picture of the oxidation and deposit processes. The information should establish a relationship of structure to deposit tendency for these classes of sulfur compounds. To investigate possible effects of the sulfur compounds in phenolic coupling, 2-propylphenol was added to all samples.

### EXPERIMENTAL

Surrogate fuel: Isooctane, 5.0 %, wt./wt., methylcyclohexane, 5.0 %, m-xylene, 5.0 %, cyclooctane, 5.0 %, tetramethylbenzene, 5.0 %, tetralin, 5.0 %, dodecane, 20.0 %, methylnaphthalene, 5.0 %, tetradecane, 15.0 % and hexadecane, 10.0 %, were 99% grade purchased from Aldrich.

Dopant compounds: 2-propylphenol, 3,4-dimethylthiophenol, phenylethylmercaptan, dibenzothiophene, phenylsulfide, 2-ethylthiophenol, 2-ethylthiophene and hexanethiol were Aldrich reagent grade. Solvents: acetone, methanol, methylene chloride and toluene were Aldrich reagent or HPLC grade. High purity helium, nitrogen and oxygen gases were used as supplied by Central Kentucky Welding Supply.

Fuel stressing: The flask test apparatus and operation have been described previously<sup>(9)</sup>. 30.0 mL of surrogate fuel and dopants were stressed in a 50 mL round bottom flask, equipped with a Friedrichs condenser with coolant at 0-5 °C and heated with mantles controlled to 175 +/- 2 °C. The fuel was nitrogen purged until temperature equilibrated and oxygen was then sparged into the fuel at 100 mL/min. via 0.53 mm fused quartz capillary. Samples were stressed for 24 hours, filtered and washed upon reaching room temperature. Stressed fuel was vacuum filtered with Osmonics<sup>®</sup> 0.45 silver membrane 47 mm filter. Glassware and filters were washed with heptane. Filtered deposits were washed with acetone. Filters, with acetone insoluble material were dried in vacuum (20-30 torr, 80 °C) 36-48 hours and reweighed. Acetone soluble gums were collected as filtrate, the solvent evaporated with dry nitrogen and weighed.

Solid phase extraction: 1.0 g J & W silica gel SPE cartridges were conditioned with 2 x 5 mL portions of methanol, methanol/acetone, acetone, acetone/heptane and heptane. A 5.0 mL portion of filtered, stressed fuel was extracted and the cartridge washed with 3 x 3 mL of heptane, lightly air dried (2 x 10 mL) and the extract eluted with 3.0 mL methanol. Methanol was evaporated with dry nitrogen, the extract weighed and immediately rediluted to 1.0 mL with methanol.

Analysis: Hewlett Packard 5890 series II GC/5890 MS with 7673A autosampler. MS scanned 35-550 m/z, six minute solvent delay. 1.0  $\mu$ L splitless injection, 280 °C injection port and transfer line. 50 meter x 0.25 mm x 0.5  $\mu$ m J & W DB-5 MS column at 30 psi head pressure. Purge line 0.5 min., 2 min. at 60 °C, 2 °C/min. to 250 °C,

10 °C/min. to 280 and 10 min. final hold. Sample samples by thermal desorption/pyrolysis with CDS model 1000 Pyroprobe®. Coil probe, 2 x 16 min quartz tube. Approximately 10 mg of dry sample for sequential thermal desorption and pyrolysis at 200, 280, 450, 750 and 1100 °C. Interface at 200 and 280 °C for first two samples, probe fired immediately upon attaining interface temperature. Interface at 325-330 °C for final three pyrolysis runs. Probe fired 99.9 seconds in all cases and GC run started immediately after probe firing. MS scanned 15-550 m/z. GC purge time four minutes. Initial temperature @ -50 °C for six minutes, 10 °C/min. to 50 °C, then three °C/min. to 280 °C and 17.33 min. hold for 110 min. Total run time with the same column as soluble sample runs.

## RESULTS & DISCUSSION

The conditions of the flask test in this work (175 °C, 24 hr., 100 mL/min. O<sub>2</sub>) represent extremes, short of pyrolytic conditions, for the thermal-oxidative stress of fuel and must be understood to represent no possible real case. If anything, it is a hyper-accelerated storage model. The advantage of the conditions is the production of oxidation products and deposits in quantities amenable to the analytical methods used in a relatively short time.

We have subjected nine samples to thermal oxidative stress under identical conditions: The surrogate fuel, undoped; surrogate + 1.0 % 2-propylphenol; and surrogate + 1.0 % 2-propylphenol with 0.5 % sulfur compound (3,4-dimethylthiophenol, 2-ethylthiophenol, phenylethylmercaptan, hexanethiol, 2-ethylthiophene, dibenzothiophene and phenylsulfide). Soluble oxidation products are represented as silica gel extracts. Fuel insoluble, but acetone soluble and acetone insoluble material is called solids. Table 3 is a compilation of the gravimetric data obtained. Relative comparison of these data to that obtained from real fuels (4) suggest that solid formation is the most valid indicator of thermal stability.

Fuels stable to deposit formation and thermally stable by JFTOT, etc., such as JP-7, JPTS, POSF 2747 and the surrogate fuel form substantial amounts of gum but insignificant solids in the flask test. Less stable fuels form less gum but dramatically more solids. The fuels with high gum and extract concentrations can be characterized as "oxidizable" fuels and those with high solids but low gums and extracts as "non-oxidizable". Table 3 shows dibenzothiophene, phenylsulfide and 2-ethylthiophene as dopants that produce "oxidizable" fuels relative to undoped surrogate (JP-8S) or surrogate doped only with 2-propylphenol. The thiophenols and alkyl thiols, 3,4-dimethylthiophenol, 2-ethylthiophenol, phenylethylmercaptan and hexanethiol doped fuels are "non-oxidizable" and form larger amounts of solid deposit. 2-ethylthiophene is somewhat anomalous by gravimetric data as well as chromatographic analysis. This is probably due to extreme oxidative conditions, cleaving the ring to form a sulfonic acid.

Space permits only representative chromatograms and product identification for polar extracts and thermal desorption/pyrolysis of solids. The more extreme cases are used. Chromatograms of polar extracts of "oxidizable" fuels are Figure 1a, surrogate, no dopant, 1b, phenylsulfide dopant and Figure 1c, dibenzothiophene dopant. Tables 1a, 1b and 1c are product identification for the corresponding chromatograms. Figures 2a and 2b are chromatograms of "non-oxidizable" fuels, doped with phenylethylmercaptan and 3,4-dimethylthiophenol. Tables 2a and 2b are product identification for these chromatograms.

Comparison of the chromatograms shows a dearth of oxidation products from the fuels doped with the thiol and thiophenol and a proliferation of oxidized species in undoped and fuels doped with phenylsulfide and dibenzothiophene. 2-propylphenol and 2,4,5-trimethylphenol are the most abundant compounds in the extracts of phenylethylmercaptan and 3,4-dimethylthiophenol doped surrogate. The trimethylphenol has to be the product of hydroperoxide decomposition from the 1,2,4,5-tetramethylbenzene (durene), present in the surrogate fuel. The phenols are minor components in the chromatograms of the "oxidizable" fuel extracts. The sulfones of dibenzothiophene and phenylsulfide are found in the respective chromatograms (at about 94 and 88 min. R.T.). The most reasonable interpretation of these observations is that the alkyl and aryl thiols both quickly oxidize to sulfonic acids that catalyze phenol production from  $\alpha$ -arylhydroperoxides. Oxidation of aliphatic fuel components is inhibited. The sulfide and thiophene are oxidized to sulfones but essentially do not affect oxidation of fuel components.

Sequential thermal desorption/pyrolysis with GC-MS analysis has proven a valuable technique for characterization of insoluble solids, but care must be exercised in interpretation of data. Pyrolysis onset temperature and the result of thermo-synthesis degradation and rearrangements can not be exactly known. Total ion chromatograms for the technique applied to solids formed by the surrogate fuel doped with 2-propylphenol and 3,4-dimethylthiophenol are presented in Figure 3. The temperature sequence the sample is subjected to for separate chromatograms is 200, 280, 450, 750 and 1100 °C. Experience has shown that solid deposits from jet fuels contain high concentrations of absorbed fuel components. These are essentially all desorbed at 200 °C. 280 and 450 °C provide the most useful information for characterizing the solid matrix. At 280 °C, it is assumed that strongly absorbed compounds are desorbed and weak chemical bonds are broken. At 450 °C, we assume pyrolytic decomposition of the polymeric matrix without extensive rearrangement or pyrosynthesis. This is supported by model studies with "Noryl" (poly-2,6-dimethylphenol) polymer (3). Pyrolysis at 450 °C produced monomeric C<sub>1</sub>-C<sub>3</sub> phenols in high abundance and several -O- and -CH<sub>2</sub>- linked dimers. The major product was 2,6-dimethylphenol. We assume that this step condenses remaining solid sample and subsequent chromatograms are essentially all from aromatic hydrocarbons.

Figures 4a and 4b through 7a and 7b, are the respective total ion chromatograms obtained from solids of fuels doped with phenylsulfide, dibenzothiophene, phenylethylmercaptan and 3,4-dimethylthiophenol at 280 and 450 °C. These chromatograms support the oxidative phenolic coupling as the mechanism for formation of extensive solid deposits. The chromatograms from the "non-oxidizing" thiophenol and mercaptan doped surrogate are essentially all phenolic and aromatic while the chromatograms of solids from sulfide and thiophene doped fuel show predominately alkenes, alcohols and ketones. The sulfonic acids of phenylethylmercaptan and 3,4-dimethylthiophenol are present in the respective chromatograms, as are the dibenzosulfone and phenylsulfoxide.

The data from this work is consistent with sulfonic acid formation and catalysis of phenol production to result in insoluble solid deposits formed by oxidative phenolic coupling. A consequence of these observations is that it should be relatively simple to devise a method to predict fuel stability (to solid deposit formation) that would be

based on caustic extraction followed by further separation and analysis. Such a method would need to include removal of extractable interferences such as deicer.

The dilemma of stability to peroxidation versus deposition remains. Hydrotreated fuels would seem to solve the deposition problems if engines and fuel transfer systems were "peroxide proof". At present, it seems the solution requires antioxidants that are themselves not deposit promoters.

#### ACKNOWLEDGMENTS

This work was supported under USAF contract F49620-90-C-09076 and subcontract RI-84470X, contract F33615-92-C-2207 (University of Dayton Research Institute). We especially thank Dr. Mel Roquemore, Bill Harrison, Ellen Stewart, of WL/POSF, and Dr. Dilip Ballal and Dr. Shawn Heneghan of UDRI for contributions and assistance.

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Figure 1a. Total Ion Chromatogram of Solid Phase Extract of JP-8S + 1.0 % 2-propylphenol. 24 Hour Flask Test at 175 °C With Flowing Oxygen.

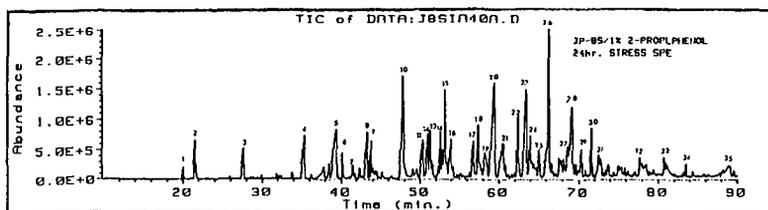


Figure 1b. Total Ion Chromatogram of Solid Phase Extract of JP-8S + 1.0 % 2-propylphenol and 0.5 % Phenylsulfide. 24 Hour Flask Test at 175 °C With Flowing Oxygen.

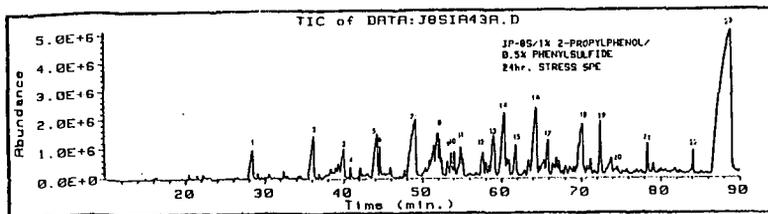


Figure 1c. Total Ion Chromatogram of Solid Phase Extract of JP-8S + 1.0 % 2-propylphenol and 0.5 % Dibenzothiophene. 24 Hour Flask Test at 175 °C With Flowing Oxygen.

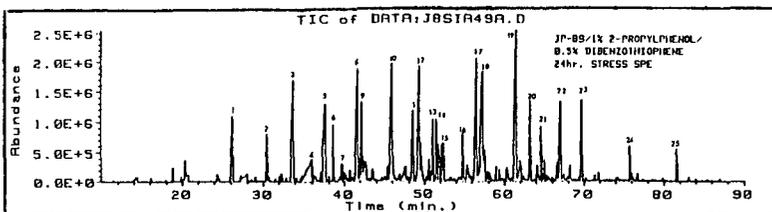


Figure 2a. Total Ion Chromatogram of Solid Phase Extract of JP-8S + 1.0 % 2-propylphenol and 0.5 % Phenylethylmercaptan. 24 Hour Flask Test at 175 °C with Flowing Oxygen.

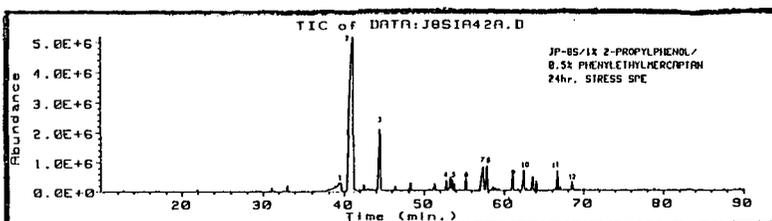


Figure 2b. Total Ion chromatogram of Solid Phase Extract of JP-8S + 1.0 % 2-propylphenol and 0.5 % 3,4-dimethylthiophenol. 24 Hour Flask Test at 175 °C With Flowing Oxygen.

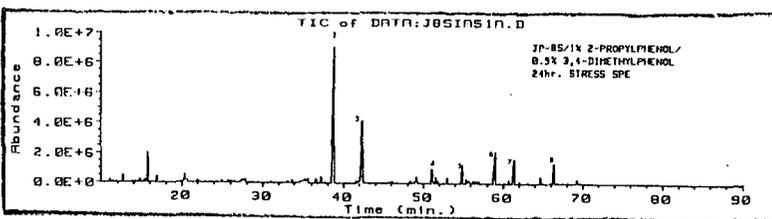


Table 1a. Peak Identification for Figure 1a.

Peak #	Rt (min.)	Compound
1.	20.06	Methyldihydrofuran
2.	21.60	Mixed phenol/furanmethanol
3.	27.65	Ethyldihydrofuran
4.	35.37	Propyldihydrofuran
5.	39.43	Mixed acid
6.	40.20	2-propylphenol
7.	41.56	Aliphatic alcohol
8.	43.36	Butyldihydrofuran
9.	43.87	2,4,5-trimethylphenol
10.	47.62	Mixed isobenzofurandione/methyl naphthalene
11.	50.37	Isobenzofuranone
12.	51.02	Pentyldihydrofuran
13.	51.29	Substituted benzene
14.	52.60	C <sub>6</sub> phenol
15.	53.21	Tetradecane
16.	53.99	Methylisobenzofurandione
17.	56.80	Benzopyranone
18.	57.40	Substituted benzopyran
19.	58.29	Hexyldihydrofuran
20.	59.47	Naphthalenone
21.	60.45	Indole-diol
22.	64.02	C <sub>6</sub> phenol?
23.	63.53	Propenylbenzodioxole
24.	64.02	C <sub>6</sub> phenol
25.	65.15	Heptyldihydrofuran
26.	66.43	Hexadecano/C <sub>7</sub> dihydrofuran.mix
27.	68.66	Methylnaphthalenol
28.	69.19	Phenylketone
29.	70.39	Substituted cycloketone
30.	71.62	C <sub>8</sub> dihydrofuran
31.	72.64	Substituted naphthalene
32.	77.64	C <sub>9</sub> dihydrofuran
33.	80.78	Substituted aromatic
34.	83.47	C <sub>10</sub> dihydrofuran
35.	89.03	Substituted aromatic

Figure 1c. Total Ion Chromatogram of Solid Phase Extract of JP-8S + 1.0 % 2-propylphenol and 0.5 % Dibenzothiophene. 24 Hour Flask Test at 175 °C With Flowing Oxygen.

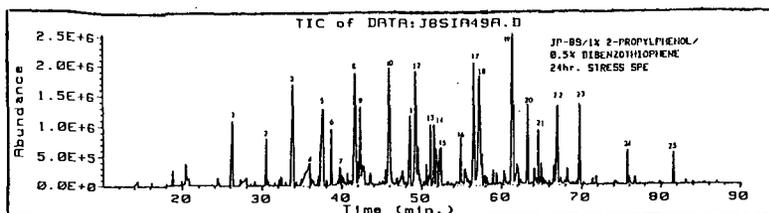


Figure 2a. Total Ion Chromatogram of Solid Phase Extract of JP-8S + 1.0 % 2-propylphenol and 0.5 % Phenylethylmercaptan. 24 Hour Flask Test at 175 °C with Flowing Oxygen.

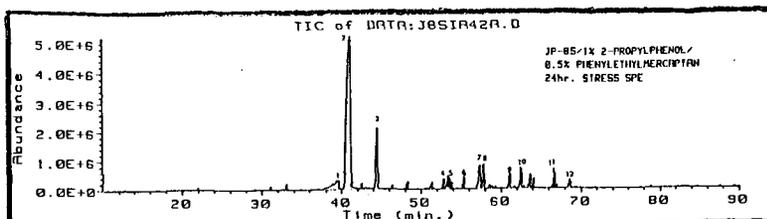


Figure 2b. Total Ion chromatogram of Solid Phase Extract of JP-8S + 1.0 % 2-propylphenol and 0.5 % 3,4-dimethylthiophenol. 24 Hour Flask Test at 175 °C With Flowing Oxygen.

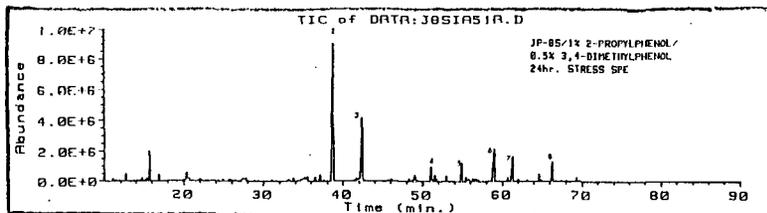


Table 1a. Peak Identification for Figure 1a.

Peak #	Rt (min.)	Compound
1.	20.06	Methyldihydrofuran
2.	21.60	Mixed phenol/furanmethanol
3.	27.65	Ethyldihydrofuran
4.	35.37	Propyldihydrofuran
5.	39.43	Mixed acid
6.	40.20	2-propylphenol
7.	41.56	Aliphatic alcohol
8.	43.36	Butyldihydrofuran
9.	43.87	2,4,5-trimethylphenol
10.	47.62	Mixed isobenzofurandione/methyl naphthalene
11.	50.37	Isobenzofurawone
12.	51.02	Pentyldihydrofuran
13.	51.29	Substituted benzene
14.	52.60	C <sub>6</sub> phenol
15.	53.21	Tetradecane
16.	53.99	Methylisobenzofurandione
17.	56.80	Benzopyranone
18.	57.40	Substituted benzopyran
19.	58.29	Hexyldihydrofuran
20.	59.47	Naphthalenone
21.	60.45	Indole-diole
22.	64.02	C <sub>6</sub> phenol?
23.	63.53	Propenylbenzodioxole
24.	64.02	C <sub>6</sub> phenol
25.	65.15	Heptyldihydrofuran
26.	66.43	Hexadecane/C <sub>7</sub> dihydrofuran mix
27.	68.66	Methylnaphthalenol
28.	69.19	Phenylketone
29.	70.39	Substituted cycloketone
30.	71.62	C <sub>8</sub> dihydrofuran
31.	72.64	Substituted naphthalene
32.	77.64	C <sub>9</sub> dihydrofuran
33.	80.78	Substituted aromatic
34.	83.47	C <sub>10</sub> dihydrofuran
35.	89.03	Substituted aromatic

Table 1b. Peak Identification for Figure 1b.

Peak #	Rt (min.)	Compound
1.	28.52	Ethylidihydrofuran
2.	36.34	Propylidihydrofuran
3.	40.12	Hexanoic acid
4.	40.97	2-propylphenol
5.	44.37	Butylidihydrofuran
6.	44.72	C <sub>6</sub> dihydrofuran
7.	49.27	Isobenzofurandione
8.	52.13	C <sub>5</sub> dihydrofuran
9.	53.83	Methylbenzofurandione
10.	54.23	Alkanol
11.	54.99	Methylisobenzofurandione
12.	57.78	Benzopyranone
13.	59.12	Hexylidihydrofuran
14.	60.53	Dihydronaphthalenone
15.	61.94	Phthalate
16.	64.56	Phenylpropenal
17.	66.07	C <sub>7</sub> dihydrofuran
18.	70.27	Substituted cycloketone
19.	72.52	C <sub>8</sub> dihydrofuran
20.	73.91	Naphthoic acid
21.	78.50	C <sub>9</sub> dihydrofuran
22.	84.25	C <sub>10</sub> dihydrofuran
23.	88.94	Phenylsulfone

Table 1c. Peak Identification for Figure 1c.

Peak #	Rt (min.)	Compound
1.	26.22	Ethylidihydrofuran
2.	30.49	Dione ?
3.	33.82	Propylidihydrofuran
4.	35.95	Phenylethylethanone
5.	37.55	Carboxylic acid
6.	38.50	2-propylphenol
7.	39.69	Substituted cyclohexanone
8.	41.72	Butylidihydrofuran
9.	42.25	2,4,5-trimethylphenol
10.	46.03	Isobenzofurandione
11.	48.52	Isobenzofurandione
12.	49.29	Butylidihydrofuranone
13.	51.11	Substituted benzofuran
14.	51.52	Substituted alkane
15.	52.42	Pentylidihydrofuran
16.	54.86	Benzopyranone
17.	56.62	Hexylidihydrofuran
18.	57.34	Substituted benzoic acid
19.	61.45	Substituted benzene
20.	63.27	Heptylidihydrofuran
21.	64.57	Alkane
22.	67.02	Substituted ketone
23.	69.73	Octylidihydrofuran
24.	75.77	Nonylidihydrofuran
25.	81.54	Decylidihydrofuran

Table 3. Gravimetric Analysis of Thermally Stressed Fuels

Stress Sample	Gums	Solids	Total	SiOH Extract*
				mg/5mL Fuel
Surrogate + Dopant	Mass % of Fuel			
1 % 2-propylphenol/0.5 % dibenzothiophene	4.70	0.46	5.00	110.20
1 % 2-propylphenol/0.5 % 2-ethylthiophene	4.13	0.58	4.71	210.20
JP-8S (No dopant)	3.32	0.06	3.38	122.70
1 % 2-propylphenol/0.5 % phenylsulfide	2.43	0.29	2.72	191.50
1 % 2-propylphenol	1.71	0.16	1.87	155.80
1 % 2-propylphenol/0.5 % 2-ethylthiophenol	0.57	0.91	1.48	29.00
1 % 2-propylphenol/0.5 % 3,4-dimethylthiophenol	0.38	1.30	1.68	32.00
1 % 2-propylphenol/0.5 % phenylethylmercaptan	0.35	0.46	0.81	34.10
1 % 2-propylphenol/0.5 % hexanethiol	0.29	0.43	0.72	21.60

\*SiOH extract: Represents values for "soluble gums".

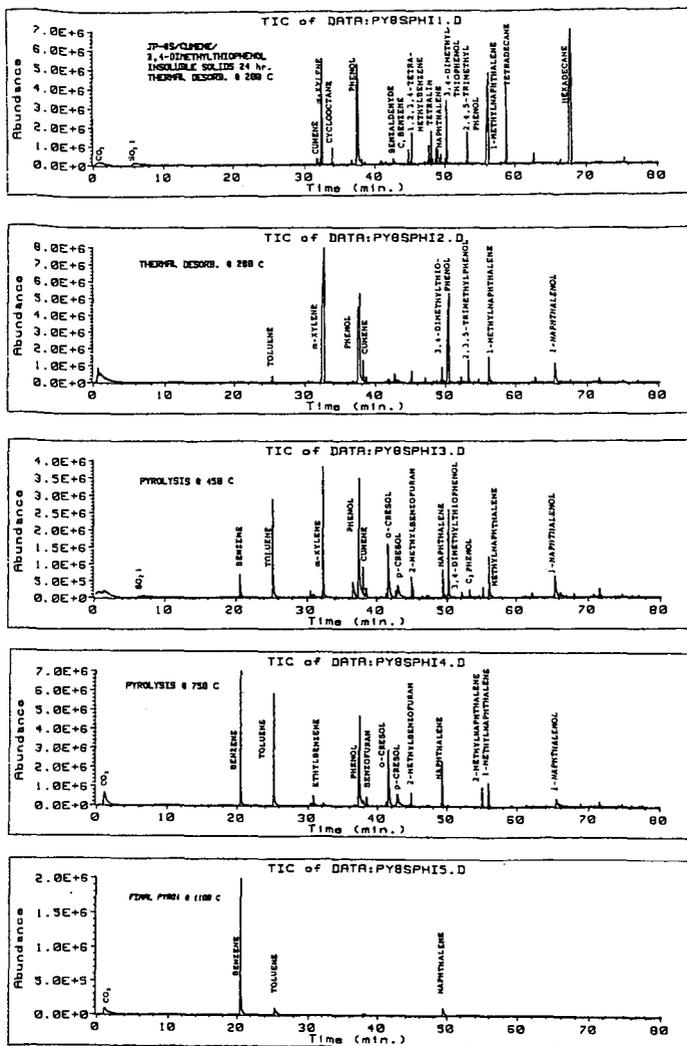
Table 2a. Peak Identification for Figure 2a.

Peak #	Rt (min.)	Compound
1.	39.42	Substituted benzoic acid
2.	41.18	2-propylphenol
3.	44.50	2,4,5-trimethylphenol
4.	52.75	Dihydronaphthalenone
5.	53.28	3,4-dihydrobenzopyran-2-one
6.	55.22	1,2-dihydroxypropylbenzene
7.	57.37	Benzopyran-2-one
8.	57.84	Substituted benzopyran
9.	61.04	Sub. dihydrobenzopyranone
10.	62.50	C <sub>5</sub> phenol
11.	66.65	Pentadecane
12.	68.60	Methylnaphthalenol

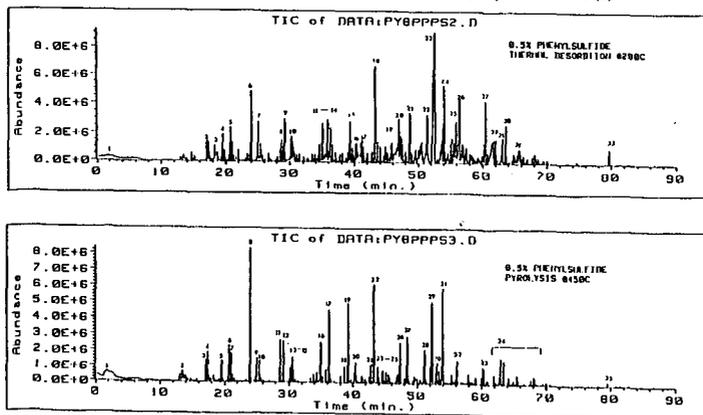
Table 2b. Peak Identification for Figure 2b

Peak #	Rt (min.)	Compound
1.	15.72	Ketone
2.	38.77	2-propylphenol
3.	42.35	2,4,5-trimethylphenol
4.	51.06	Methylbenzofuranone
5.	54.90	Benzopyran-2-one
6.	58.96	Substituted dimethylphenol
7.	61.29	Dimethyl-2,3-dihydroindene-1-one
8.	66.29	Substituted phenol

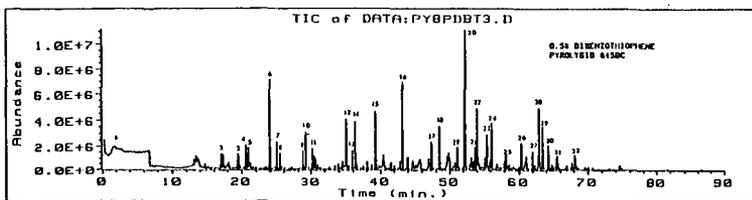
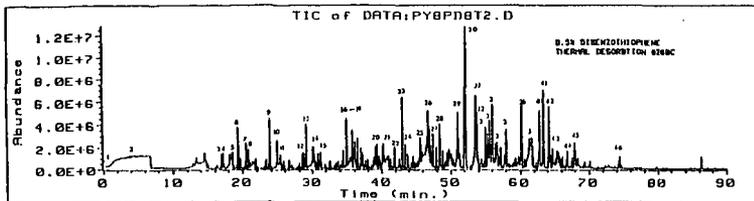
Figure 3. Sequential Thermal Desorption/Pyrolysis Total Ion Chromatograms of Insoluble Solids From JP-8S Doped With Cumene and 3,4-dimethylthiophenol.



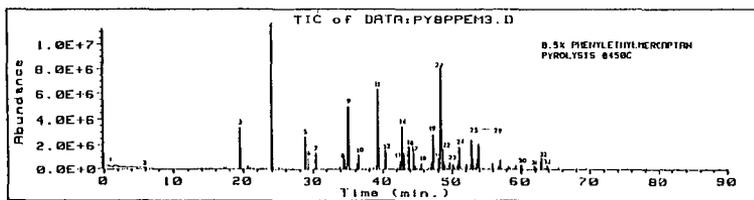
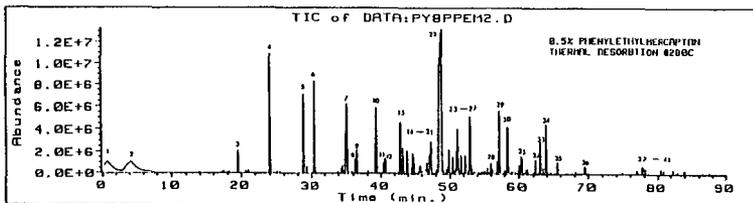
Figures 4a & b. Total Ion Chromatograms of Insoluble Solids From JP-8S + 1.0 % 2-propylphenol and 0.5 % Phenylsulfide. Thermal Desorption at 280 °C (a) and Pyrolysis at 450 °C (b).



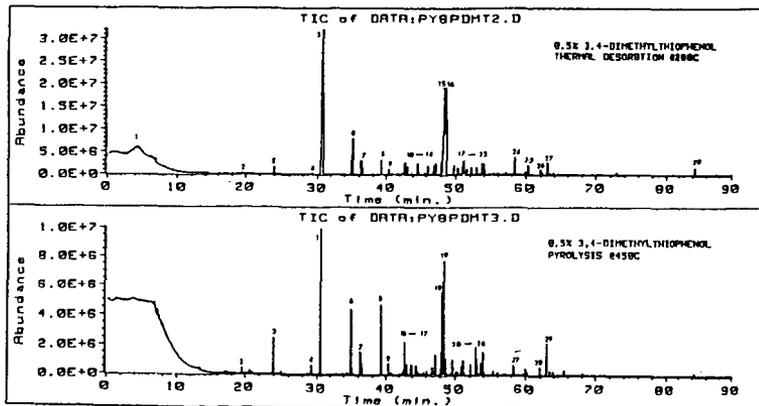
Figures 5a & b. Total Ion Chromatograms of Insoluble Solids From JP-8S + 1.0 % 2-propylphenol and 0.5 % Dibenzothiophene



Figures 6a & b. Thermal Desorption @ 280 °C and Pyrolysis @ 450 °C of Solids Formed From JP-8S Doped With 1.0 % 2-propylphenol & 0.5 % Phenylethylmercaptan.



Figures 7a & b Thermal Desorption @ 280 °C and Pyrolysis @ 450 °C of Solids Formed From JP-8S Doped With 1.0 % 2-propylphenol & 0.5 % 3,4-dimethylthiophenol.





## SURFACE FOULING: SHORT- VS. LONG -TERM TESTS

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Keywords: Autoxidation, Autocatalysis, Surface Fouling

### INTRODUCTION

Problems associated with surface fouling of fuel lines, nozzles, and heat exchangers caused by thermo-oxidative stressing of aviation fuel have been documented.<sup>1</sup> With enhanced aircraft performance, heat loads from both the airframe and the engine that must be dissipated via the fuel become greater. The resultant additional fuel degradation exacerbates aircraft system failures. Since the extent of surface fouling depends strongly upon the particular aviation fuel, it is important to be able to assess each fuel in a simple accelerated laboratory test for simulating the thermo-oxidative stress experienced in aircraft fuel lines.

In the present study a simple dynamic test is employed, whereby the fuel is stressed under well-defined chemical-oxidation conditions that are near-isothermal. Quantification of surface and filtered insolubles provides an objective evaluation of fuel behavior at each temperature. In addition, the dependence of deposition rate upon stress duration provides a temporal profile of the reaction. The general laboratory goal is to evaluate fuel at several temperatures in an attempt to simulate thermo-oxidative stress but not the fluid-dynamic conditions in aircraft. These results can then be used to calibrate Computational-Fluid-Dynamics (CFD) models<sup>2</sup> for calculating fouling under the diverse temperature and fuel-flow conditions that are found within aircraft but are difficult to achieve experimentally with small-scale rigs.

The present investigation has involved fouling of heated stainless-steel surfaces caused by a particular Jet-A aviation fuel designated POSF-2827. Although this is a representative fuel that meets USAF specifications, it has a propensity for fouling heated surfaces at low temperatures, making it an ideal candidate for experimental study.<sup>3</sup> Recent results were reported from this laboratory on surface deposition on stainless-steel surfaces as a function of stress duration for fuel flowing through a heat exchanger at 185°C under near-isothermal conditions.<sup>4,5</sup> These results indicated that deposition arises from a bulk-formed species designated a surface-deposition precursor, P, and that deposition is complete within 10 min of stressing inside 0.125-in-o.d. stainless-steel tubing. Deposition over the temperature range 155-225°C was found to occur during a time interval that correlates with the measured time for oxygen consumption.<sup>6,7</sup> The experimental test time in these prior experiments was set at 6 hr to ensure measurable deposits yet maintain surface fouling predominantly on the steel rather than on previously deposited surfaces.

The goal of the current study was to compare deposition in short-term (6-hr) tests with that in long-term tests where most of the deposition occurs on previously deposited surfaces. Results reported here show that the average surface fouling rates measured during extended test times differ from those measured during a 6-hr test. Since the bulk-fuel/wall temperature is held constant during the course of these experiments as a result of the low flow rate, deposits serve only to change the surface layer without influencing the bulk temperature of the fuel.

As the test time is extended, the deposition-rate-versus-stress-duration profile broadens, the maximum is reduced, and its location shifts to longer stress duration. These observations made at 155 and 185°C are shown to arise from a transition in the rate of oxygen loss as a result of surface fouling and a reduction in adherence to a fouled surface. The implications of these findings with respect to inherent surface fouling within aviation fuel systems are discussed.

### EXPERIMENTAL

POSF-2827 fuel has a JFTOT breakpoint of 266°C and a sulfur level of 0.079% (w/w). This fuel falls into a category described by Kendall and Mills<sup>8</sup> where the presence of sulfur compounds tends to inhibit oxidation but at the expense of increased insoluble formation.<sup>3</sup>

Data were collected using the Near-Isothermal Flowing Test Rig (NIFTR) which has been described previously.<sup>4,5</sup> The advantage of the NIFTR experiment is the ability to measure deposition rates and dissolved oxygen as a function of reaction time at a fixed temperature. For each selected fuel-flow rate, the reaction time or stress duration is determined by tube dimensions and location along the tube axis. In the present experiment deposits were collected on 0.125-in.-o.d., 0.085-in.-i.d. commercial stainless-steel (304) tubing. The standard heated section was 32 in.; however, for test times longer than 6 hr, the spatial distribution of the deposition broadened and the complete profile could not be collected on a single pass through the heat exchanger. Three approaches were taken: 1) only the limited profile was collected on a single pass, 2) the fuel was passed back through a second tube within the NIFTR to double the path length, and 3) the fuel-flow rate was reduced to extend the stress duration accordingly within a single pass. It is important to distinguish stress duration from experimental test time in dynamic isothermal experiments. Stress duration is the reaction time at temperature, and the experimental test time (along with the fuel-flow rate) determines the total quantity of fuel passed through the system. The total fuel ranged from 25 to 1035 mL. Dissolved oxygen was measured in separate experiments using the entire tube as a reaction region, with stress time being varied by changing the fuel-flow rate.

Deposition rates at 185 and 155°C are based on the quantity of carbon in the deposits determined from surface-carbon burnoff (LECO RC-412) of 2-in. sections cut from the 32-in. heated tube. Rate is expressed in units of micrograms of carbon per unit volume of tube section per unit test time which is equivalent to micrograms of carbon per unit stress time within a tube section per unit volume of fuel passed through the system.<sup>5</sup> In each case the fuel is saturated with respect to air, with oxygen being measured as 64 ppm (w/w).<sup>9</sup>

## RESULTS AND DISCUSSION

**Deposition.** The measured deposition rate averaged for 6, 24, 30, 32, 48, and 69 hr is shown in Figure 1 as a function of stress duration at 185°C for a fixed fuel-flow rate of 0.25 mL/min. The following observations describe the changes in surface deposition with extension of integration time: 1) the profile broadens with significant tailing; 2) the maximum in the deposition rate is reduced; and 3) the center of the deposition peak shifts to slightly longer stress times. Also, the profiles appear to approach a common shape at the longest experimental times. Extended reaction time in the 30- and 69-hr experiments was afforded by a second pass through the heat exchanger. Results of similar experiments at 155°C are presented in Figure 2. The same trends are observed; however, the reaction time frame is extended to permit completion of the deposition processes at lower temperature.

Note that when comparing rates averaged over different experimental times, the baseline drops as the experimental time is increased. Background carbon which is independent of experimental test time has not been subtracted, and its impact is reduced in the longer-term averages.

The major difference between 6-hr tests and those of much longer duration is the nature of the surface. Initially the deposition occurs on cleaned stainless-steel tube surfaces. As the experimental time is extended, the surface gradually makes a transition to a completely carbonaceous-coated one. Deposition should be constant after complete coverage of the stainless-steel surfaces; for example, after the 48-hr test at 185°C, the surface density at the maximum is 90  $\mu\text{g cm}^{-2}$ . The maximum deposition rate per unit area is 1.1  $\mu\text{g cm}^{-2}$  per hour of experiment. The observed variation in deposition is related to surface changes, and the major factor will be shown to be the rate of oxygen consumption.

**Oxygen Loss.** The residual dissolved oxygen for this fuel has been reported as a function of reaction time in stainless-steel tubes.<sup>5</sup> Accelerated oxygen consumption observed at higher conversion was attributed to autocatalysis. Figure 3 shows the oxygen loss at 185°C measured using 1) a 32-in. cleaned stainless-steel tube,<sup>5</sup> 2) a tube that previously had been coated with carbonaceous deposits containing 0.27 mg of carbon, and 3) a tube coated with the same deposits containing 1.5 mg of carbon. The initial rates are similar. Autocatalysis causes the rapid increase in rate at higher conversion in the cleaned tube; however, this appears to be a surface-related phenomenon that is no longer observed when the surface becomes coated with deposits. Rates measured with the coated tubes remain constant, indicating a predominantly zeroth-order or oxygen-non-limited reaction.<sup>4</sup> After 8-9 min all of the oxygen is converted, and the source of the deposits (namely, P) can no longer be maintained. This

time corresponds to the location of the maximum in the shifted deposition profile at 185°C. Similarly, oxygen loss measured at 155°C (Figure 4) shows the same trend.

If the stainless-steel tubing is viewed as the norm, then deposits perturb the oxygen consumption by eliminating autocatalysis. If the coated (passivated) tubing is viewed as the norm--an alternative and preferable view--then the stainless steel perturbs the oxygen consumption by providing active catalytic sites which, at higher conversion, lead to an increased oxygen reaction rate. Deposition in short-term (6-hr) tests over the temperature range 155-225°C correlates with oxygen loss measured in cleaned stainless-steel tubes;<sup>6</sup> similarly, deposition in long-term tests is expected to correlate with oxygen loss measured using tubes that have been passivated by deposits. The higher deposition rate observed in 6-hr experiments results from the oxygen loss that occurs during surface-induced autocatalysis. The reduction in surface deposition rate, the broadening of the deposition profile, and the shift in the maximum in the long-term experiments are manifestations of the slower, constant rate of oxygen loss.

The deposition profiles in long-term tests have tails that extend well beyond the region of 100% oxygen conversion. For example, at 185°C, despite complete oxygen depletion at 9 min, the deposition continues beyond 17 min. This is interpreted as reduced surface adherence of P.

**Implications.** Autocatalysis has been attributed to thermal dissociation of an oxidation product such as hydroperoxide.<sup>5</sup> The present results indicate that autocatalytic effects in POSF-2827 fuel are caused by a surface-induced reaction of an oxidation product involving active sites on stainless steel. Carbonaceous deposits remove active sites, thereby eliminating autocatalysis.

Carbon-burnoff techniques generally require the use of cleaned surfaces for minimizing background. Based upon the current findings, when surface-induced autocatalysis occurs, the maximum deposition and the oxygen reaction rates will be faster in short-term experiments that are carried to high conversion. Fuel evaluation in this laboratory is predicated on accelerated short-term tests that stress the fuel to complete oxygen conversion. In rating fuels, a deposition-rate criterion has not been applied; instead a total integrated quantity of deposit, i.e. the area under the deposition profile in units of micrograms/milliliter, has been used.

Catalytic effects of metals dissolved in fuels, in particular, copper from copper tubing as in Naval applications, can reduce fuel thermal stability, even at low concentrations.<sup>1</sup> Kendall and Mills<sup>8</sup> observed this effect in flask tests, and Morris and Turner<sup>10</sup> observed it in expanded JFTOT experiments. Conceivably, the role of dissolved copper in catalyzing oxygen loss is analogous to the role of stainless-steel walls in what has been termed surface-induced autocatalysis.

Fuel-evaluation techniques such as the JFTOT and Hot Liquid Process Simulator (HLPS) which make use of clean aluminum and stainless-steel surfaces, respectively, would be expected to be sensitive to the nature of the surface and also the manner in which oxygen is consumed. For example, Clark et al.<sup>11</sup> have reported that a metal deactivator (MDA) functions optimally on clean metal surfaces; however, once a lacquer layer has formed, MDA does not reduce deposition. The vulnerability of JFTOT results in short-term tests has been discussed by Clark and Bishop.<sup>12</sup> The initial surface-passivation effects of MDA may mask problems detectable only during extended time periods. In view of the current results, the short-term benefit of MDA may be surface passivation which prevents autocatalysis. The reduced deposition would then be explained in terms of MDA slowing oxygen consumption rather than hindering adherence to the surface. In recent studies the DuPont fuel additive JFA-5 which contains the MDA, N,N'-disalicylidene-1,2-propanediamine, has been found to eliminate autocatalytic oxygen loss in POSF-2827 fuel.<sup>13</sup>

## CONCLUSIONS

The dependence of the surface deposition rate of POSF-2827 fuel on isothermal stress duration at 155 and 185°C has been found to be a function of the experimental test time. In short-term (6-hr) tests, initial deposition is governed by the autocatalytic consumption of oxygen. For long-term (~ 70-hr) tests during which the initial stainless-steel surface becomes covered with deposits, the deposition profile changes to one governed by a slower loss of oxygen.

Oxygen loss in cleaned stainless-steel tubes is enhanced at high conversion as a result of surface-induced autocatalysis. After deposits have completely covered the stainless-steel surfaces, active sites necessary for autocatalysis are removed.

#### ACKNOWLEDGMENTS

This work was supported by Wright Laboratory, Aero Propulsion and Power Directorate, Wright-Patterson Air Force Base, Ohio, under USAF Contract No. F33615-90-C-2033. The authors would like to thank Mr. Tim Gootee for conducting the surface-carbon analyses, Mrs. Marian Whitaker for editorial assistance, and Dr. James M. Pickard for valuable discussions.

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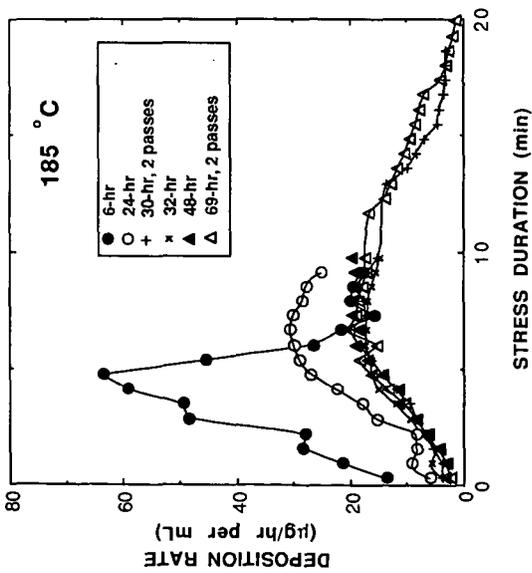


Fig 1. Deposition Rate vs. Stress Duration for POSF-2827 Fuel at 185°C for a Series of Experimental Test Times Measured with a Fuel-Flow Rate of 0.25 mL/min.

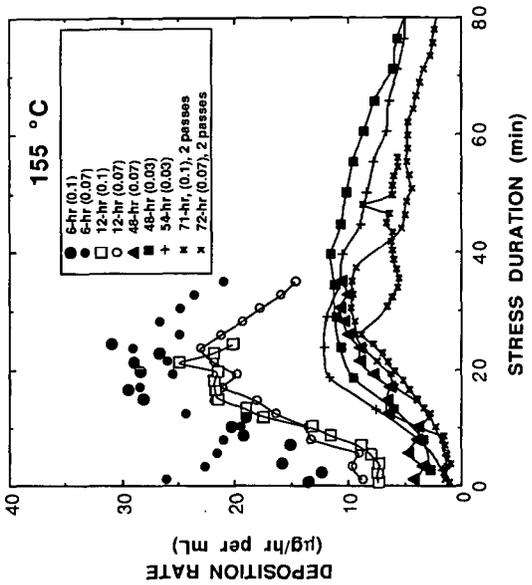


Fig 2. Deposition Rate vs. Stress Duration for POSF-2827 Fuel at 155°C for a Series of Experimental Test Times.

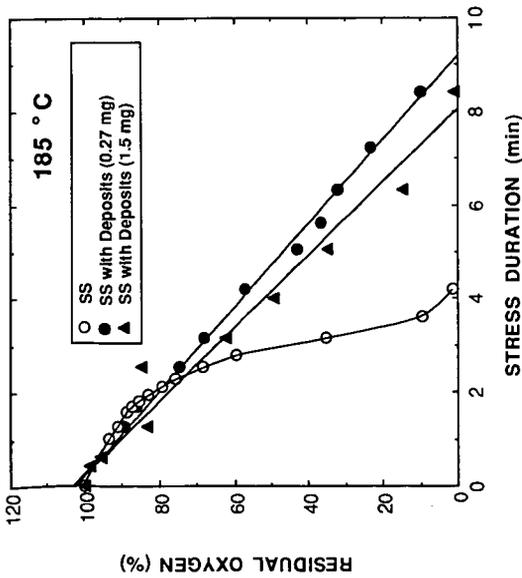


Fig 3. Residual Dissolved Oxygen vs. Stress Duration for POSF-2827 Fuel at 185°C. Measurements Made in 1) Cleaned Stainless-Steel Tubing, 2) Tubing Pre-deposited with 0.27 mg of Insolubles, and 3) Tubing Pre-deposited with 1.5 mg of Insolubles.

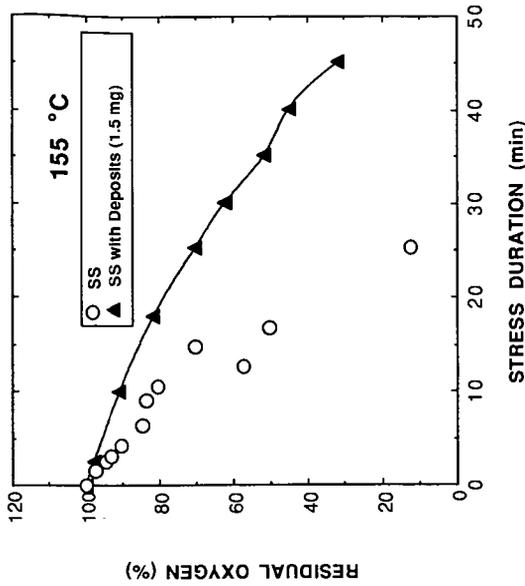


Fig 4. Residual Dissolved Oxygen vs. Stress Duration for POSF-2827 Fuel at 155°C. Measurements Made in 1) Cleaned Stainless-Steel Tubing and 2) Tubing Pre-deposited with 1.5 mg of Insolubles.

## THERMAL STABILITY OF DIESEL FUELS BY QUANTITATIVE GRAVIMETRIC JFTOT

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Keywords: Thermal stability; diesel fuel; gravimetry

### INTRODUCTION

The current worldwide standard test method for assessing thermal stability of jet turbine aviation fuels is the ASTM D3241 method. This method generates a visual tube deposit rating which is not quantitative, but assumes that very dark colors equate to unstable fuels. The tube rating is coded against color standards and the darkest color is usually said to fail a fuel for use in jet turbine engines/fuel systems. The method also generates a semi-quantitative filter pressure drop. The pressure drop is so semi-quantitative that it also is afforded a pass/fail criterion for fuel acceptance in jet aircraft.

In 1991, we described the construction of a test device which duplicated all of the experimentally important parameters of the D3241 method but which substituted a weighable 302 stainless steel (s/s) foil strip for the bulky tube, so that direct weighing of thermal surface deposits could be made.<sup>1</sup> In addition, the nominal 17 micron (dutch weave) s/s filter of the D3241 was substituted with a nylon membrane 0.8 micron filter which was also capable of direct weighing of the fuel entrained solids generated by the test.

In subsequent papers, the use of this device for generating a large data base of results based on aviation fuels from many different refinery processes and many different geographic/crude sources was described.<sup>2,3</sup> In addition this new device, dubbed the gravimetric jet fuel total oxidation tester (JFTOT) after the original ASTM D3241 device, was also used to assess quantitatively the effects of temperature, pressure, and fuel flow in addition to the effects of dissolved metals and various fuel additives.

Now that a reasonable data base for jet turbine fuels has been established regarding the deposit yields for s/s strip deposit weight and filterable deposit weight it was of interest to see how the gravimetric JFTOT would respond to mid distillate diesel type fuels. A suite of 7 fuels which were similar to number 2 diesel fuels and met all the additional criteria of NATO F-76 (US Navy) diesel fuel were selected for the test matrix. These fuels had originally been selected for a separate study involving long term ambient storage stability and thus were chosen in an attempt to span as wide a range of fuel properties as possible and still meet the specification requirements for military use.

### EXPERIMENTAL

The precision flow device consists of a reciprocating single piston HPLC pump which is connected to the fuel reservoir at atmospheric pressure on the suction side and to a high pressure filter holder containing a 0.8 micron Nylon 66 pre-filter on the high pressure side. The fuel then flows through a heated section which is maintained at the chosen test temperature by the thermostated block heater. This heated section contains the pre-weighed s/s strip (weighed to the nearest 0.001 mg on a microbalance) which is held in position by the strip holder which is assembled into the s/s tube. The fuel flows through this heated section which has a surface to volume ratio of  $17 \text{ cm}^{-1}$  at 3.0 ml/min and a residence time of 6 seconds. The fuel is cooled to room temperature and exits through a back pressure valve maintained at 3.4 MPa (500 psi) into a clean glass container.

The effluent fuel is immediately vacuum filtered through a pre-weighed 0.8 micron Nylon 66 filter (weighed to the nearest 0.01 mg for the 47mm filters and to the nearest 0.001mg for the 13mm filters). At the end of the timed test, the strip assembly is removed from the block heater and allowed to cool, while maintaining fuel flow, for about 10 minutes. The foil strip is then removed, rinsed with hexane and allowed to dry, along with the rinsed fuel filter, for approximately 1 hour at 70°C. After equilibration to room temperature the strip and filter are weighed. The increases in weights are reported in mg/L. Exact details of the weighing technique and examples are given in previously published papers.<sup>1,2,3</sup>

## RESULTS

Seven recent production diesel fuels were tested with the Gravimetric JFTOT using the standard conditions of 260°C for 2.5 hours at a fuel flow of 3.0 mL/min at a pressure of 500 psi. The results are shown in Table I.

Figure 1 gives the ranking for the filterable deposit weights with a range from 0.9 mgs/L to 23.8 mg/L. For comparison the weight of filterable solids for n-tetradecane is indicated in this figure by a solid line and the maximum and minimum filterable solids weight for jet fuels tested to date is indicated by dashed lines.

The ranking of the s/s foil strip surface deposit weights are given in Figure 2. In this figure the solid line indicates the strip surface deposit weight for n-tetradecane and the dashed lines indicate the maximum and minimum strip surface weights for jet fuels tested to date.

## DISCUSSION AND CONCLUSIONS

The dashed lines in Figures 1 and 2 show the maximum and minimum values of the jet turbine fuels used to generate the data base in the last 4 years. Jet fuel average strip weights (in Figure 2) range between 0.02 and 0.20 mg/L with a number average of about 0.08 mg/L and a worldwide volume weighted average of about 0.04 mg/L. These fuels represent a very high percentage of the huge volume of jet fuels currently used worldwide and thus form a significant set of values against which to compare any and all future jet fuel batches.

The jet fuel average filterable solids weights (dashed lines in Figure 1) range between 0.5 and 5.0 mg/L with a number average of about 1.5 mg/L and a worldwide volume weighted average of about 0.8 mg/L.

Table 1 shows the data generated by the gravimetric JFTOT device for 7 representative diesel fuels from the US. The yield of the two types of solid deposit measured are given in mg/L of fuel for both the strip weight and the filterable solids weight. It is interesting to note that even with this very small number of fuels the gravimetric JFTOT is capable of easily distinguishing between fuels as to their tendency to form solids under the conditions of this particular test. Strip weights range between 0.00 and 0.32 mg/L with an average weight of about 0.12 mg/L. Filterable deposit weights range between 1.0 and 24.0 mg/L with an average weight of about 12 mg/L.

For the large jet fuel data base it has been pointed out already that the filterable deposit weight is always about 10 to 20 times the strip deposit weight for any given fuel. This effect appears to be even more pronounced with the diesel fuels where the filterable deposit weights appear to be about 100 times heavier than the strip deposit weights for any given fuel.

In order to compare the 7 diesel fuels with the jet fuel data base for thermal stability the data in Table 1 are arranged into strip weights in Figure 2 and filter deposit weights in Figure 1. In Figure 2 it can be readily seen that most of the diesel fuels exhibit very good thermal stability with respect to the strip deposit weights for the jet fuel data base. Only fuel B exceeds the heaviest jet deposit weights. If this part of the test can be interpreted as the tendency of a fuel to form insulating lacquer deposits on aircraft heat exchangers, then clearly many diesel fuels are as "stable" as jet fuels in this regard.

The filterable data are shown in Figure 1, where a somewhat different picture can be seen. In this case, two of the fuels (D and E) are very good with respect to the jet fuel data base. On the other hand, two of the diesels are very "thermally unstable" (B and C) when compared to the jet fuel data base, and 3 of the diesels are "marginal" (A, F and G) being somewhat higher than the highest weights obtained for jet fuel in the past 4 years.

If the filterable weight data (or strip plus filter weight data) are used to assess the overall thermal stability performance in any given fuel, then only about a third of the diesel fuels could be deemed thermally stable when compared to typical thermally stable jet fuels. It should be noted that although it is tempting to use the data in this way and call the filterable deposit the material when might cause filter blockage, flow control valve sticking and nozzle fouling/clogging, no attempt has yet been made to validate this kind of correlation.

One should also note in Figures 1 and 2 the solid line which is given for the pure component n-tetradecane in the gravimetric JFTOT. This data can be used in two ways. First, it can serve as a "solvent blank" for both filterable and strip deposit weights for jet fuels. If used in this way it is apparent that most production jet fuels worldwide are very thermally stable indeed to the JFTOT test conditions. Secondly, it can serve as a solvent blank for the diesel fuels, in which case some of the current production diesel fuels are also very thermally stable.

These results indicate that the gravimetric JFTOT is a useful concept for ranking diesel fuels for their thermal stability. The diesels ranged from quite low (better than jet) to quite high (an order of magnitude greater than jet fuel) in their overall deposit forming tendencies. This type of information can be used in two possible ways. First, if gravimetric JFTOT data can be correlated to such phenomena as diesel engine injector fouling, it could be used to assess any given diesel fuels thermal stability for the intended diesel engine application.

Second, and more provocative, this type of information on diesel fuels could be used by commercial or in some cases by military aircraft operators to assess the thermal stability application for aircraft use. This would be subject to a given diesel fuel's suitability in all other aspects in addition to thermal stability. Various additional areas where diesel fuel might be limited would be the higher viscosity and higher freeze point/cloud point of diesel fuel which would then preclude its use as aircraft fuel. The obvious advantage especially to long distance aircraft would be the extended range possible with the usually higher density diesel fuel in volume limited aircraft.

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Table I. Insolubles Formed From Diesel Fuels After Gravimetric Testing. All weights in mg/L of fuel. Test conditions of 260°C, 3.0 mL/min for 2.5 hours			
Fuel	s/s Strip Weight	Filter Weight	Total Weight
A	0.23	13.6	13.83
B	0.32	23.8	24.12
C	0.16	21.1	21.26
D	0.01	0.9	0.91
E	0.02	1.8	1.82
F	0.00	8.2	8.20
G	0.08	14.8	14.88

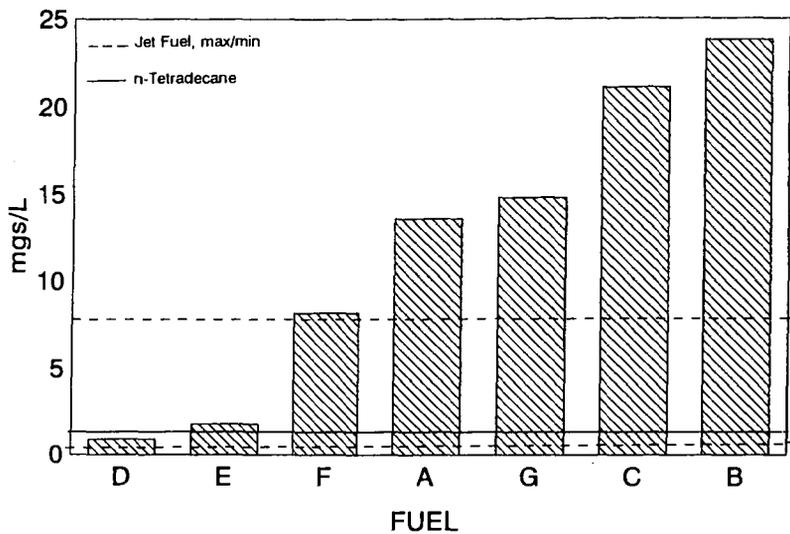


Figure 1 - Gravimetric JFTOT Filter Weights  
Seven Diesel Fuels

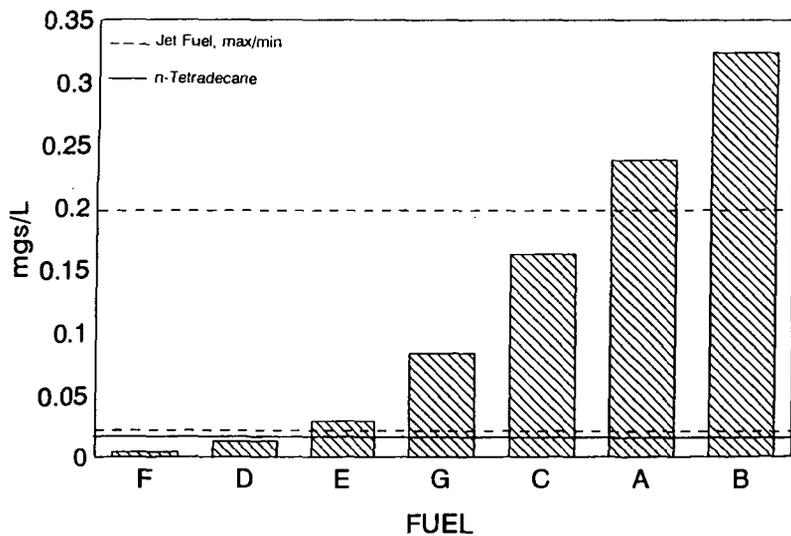


Figure 2 - Gravimetric JFTOT S/S Strip Weights  
Seven Diesel Fuels