TANK CLEANING STRATEGIES AND TECHNIQUES

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Abstract

Recent increases in contamination levels at retail outlets in the United States have prompted the need for improved contaminant removal techniques. These have involved both diesel and gasoline. This paper will discuss several techniques employed to remove both contaminants and additive separations. The utilization of chemicals, tank design modifications and housekeeping all play an important role in fuel storage. Tank cleaning becomes necessary when contaminant levels reach a point where problems are being experienced. Contaminants usually enter the system through various means. The most prevalent of all contaminants is water. Water promotes biological growth, attracts particulate matter, and can pull various additives from the fuel.
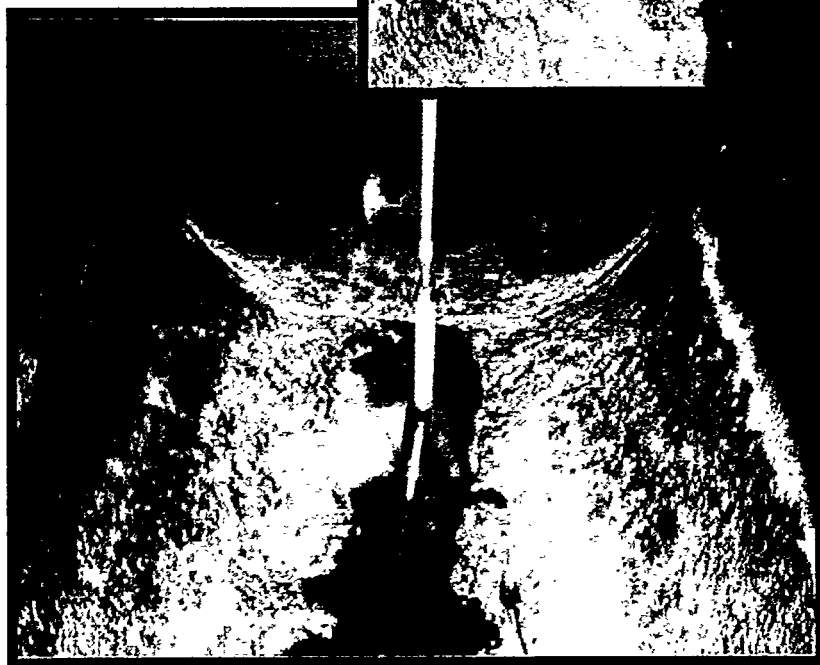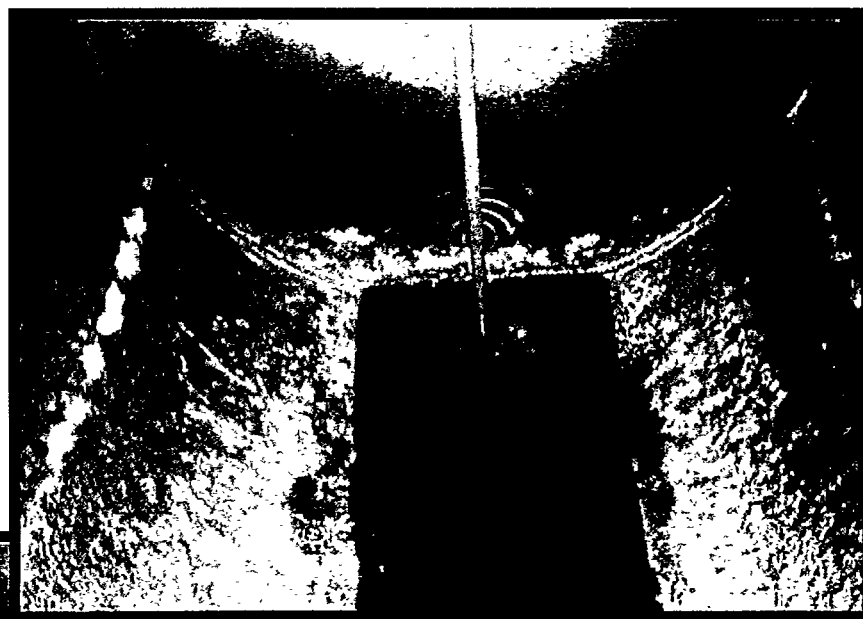
What is a Tank?

Anything That Holds Fuel

Basic Tank Configurations and Sludge Locations
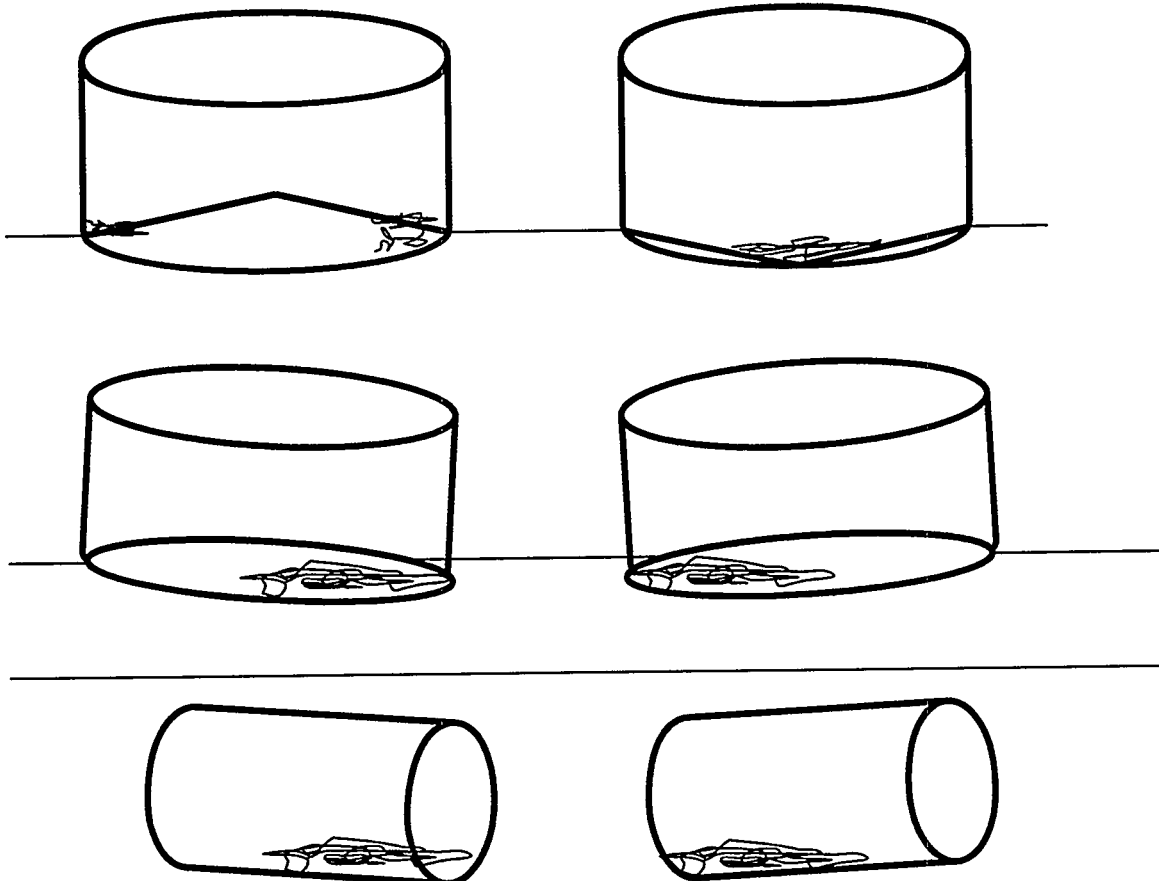
Why Clean A Tank?

Duh!

Tank Cleaning is Not A Cartoon, Tank Cleaning is Solving Problems
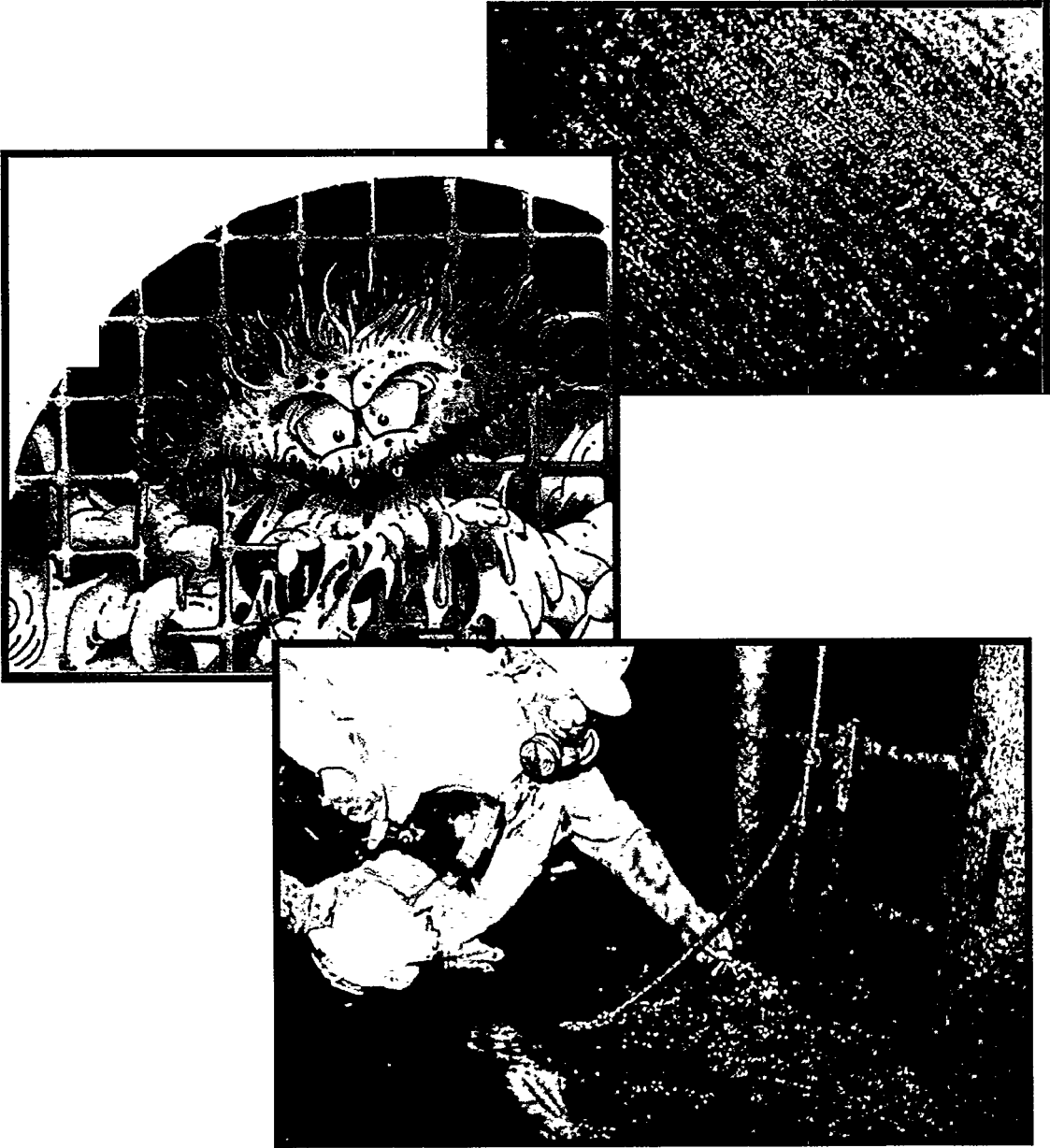
Most Tank Cleaning is

People
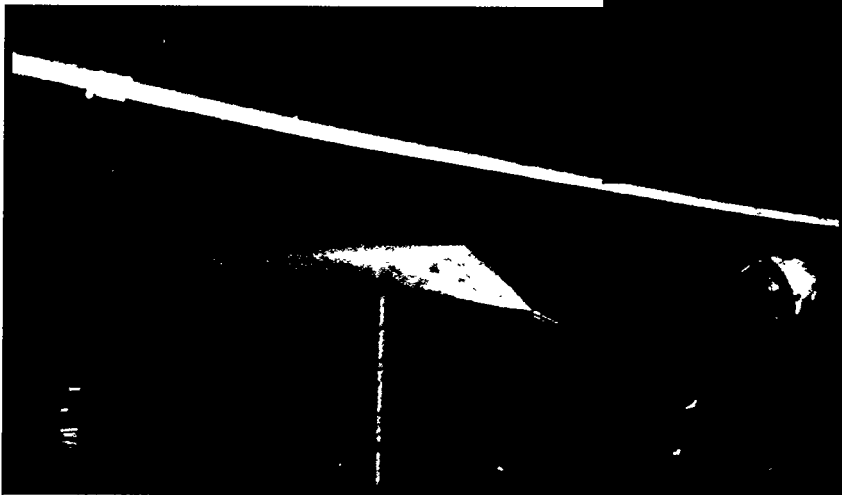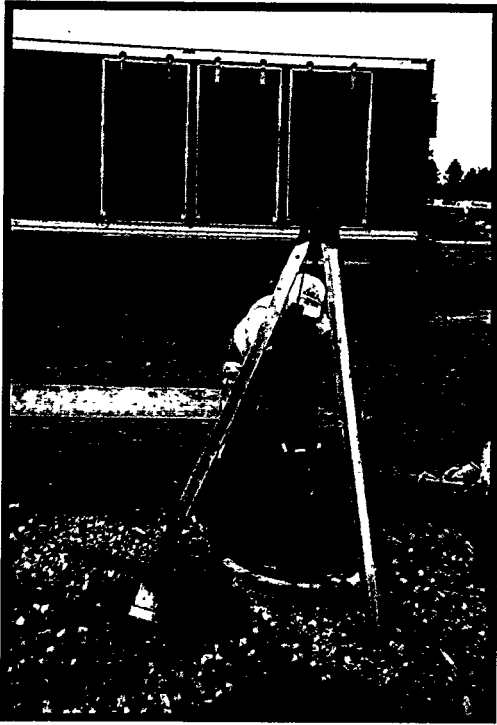
Some Tank Cleaning Requires Extra Planning & Ingenuity
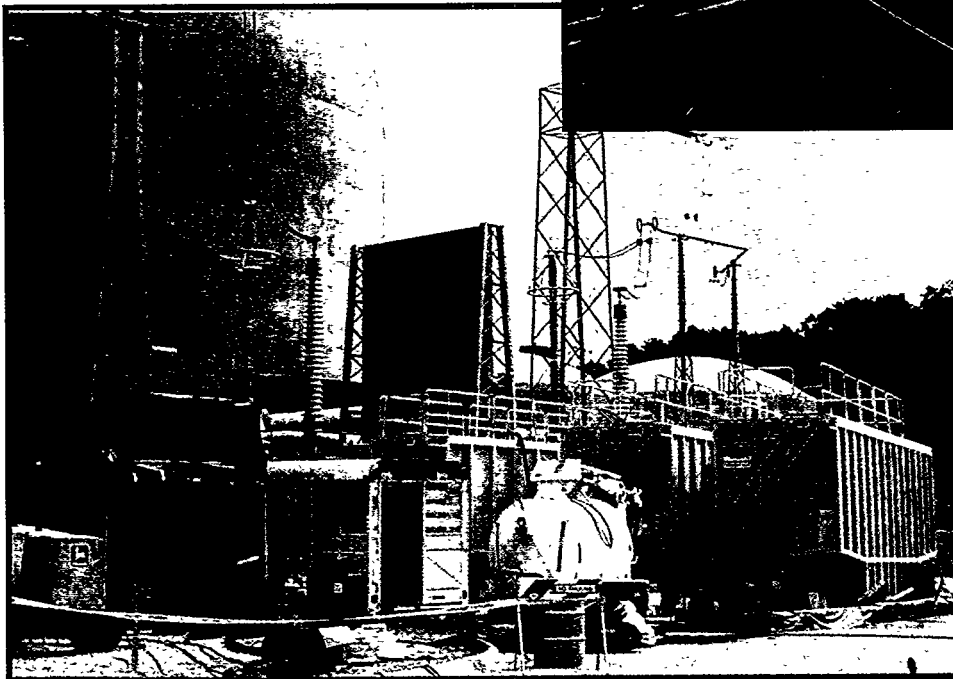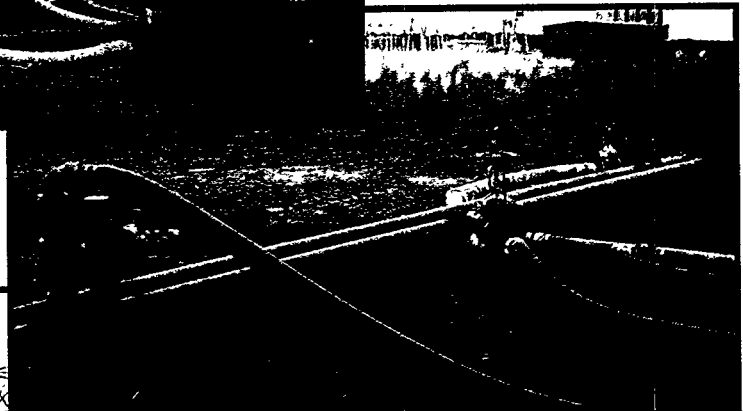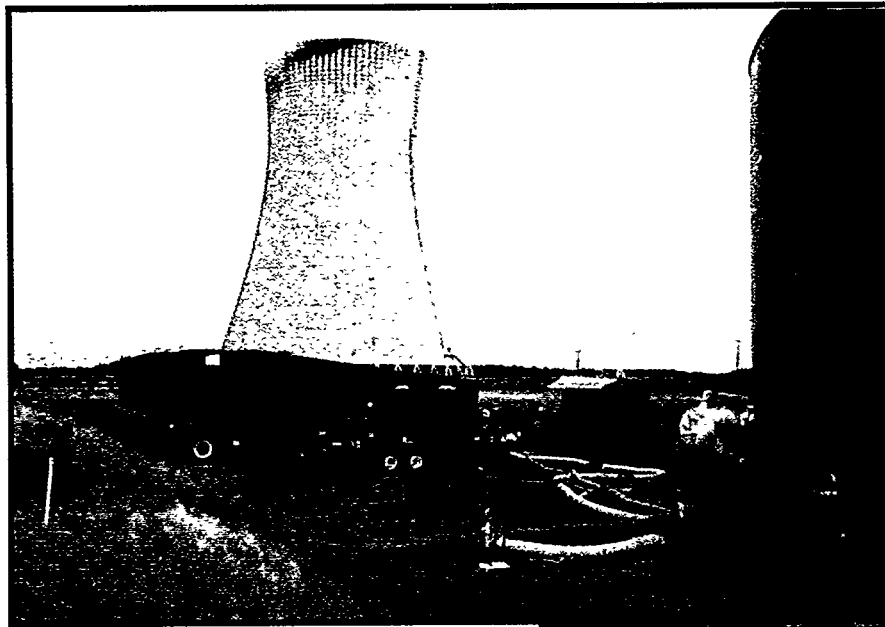
90% of Tank Cleaning is Planning and Preparation
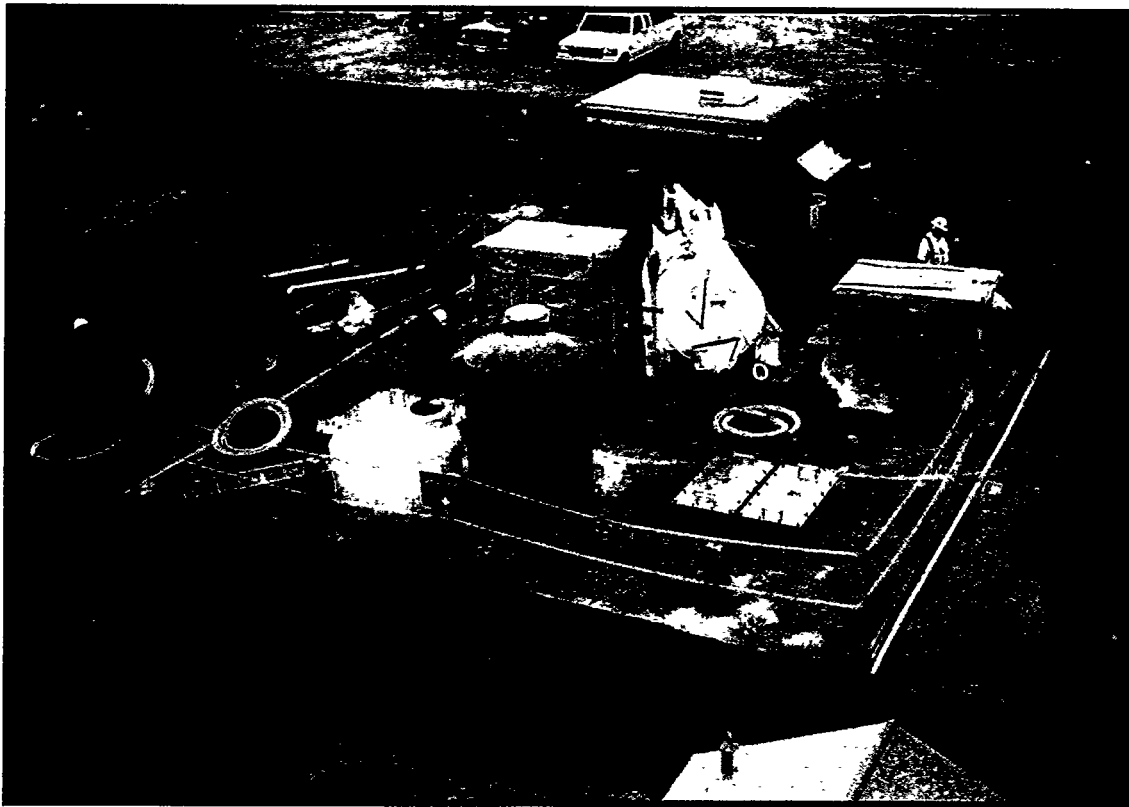
Tank Cleaning Methods

Traditional:

- Squeegee
- Water Washing
- Pressure Washing
- Hydro Blasting

New Technologies:

- CO^2 Blasting (Cryogenic Cleaning)
- Sodium Bicarb Blasting
- Ultra Hydro Blasting
- Robotic Ultra Hydro Blasting

CO^2 Cleaning
(Cryogenic Cleaning)
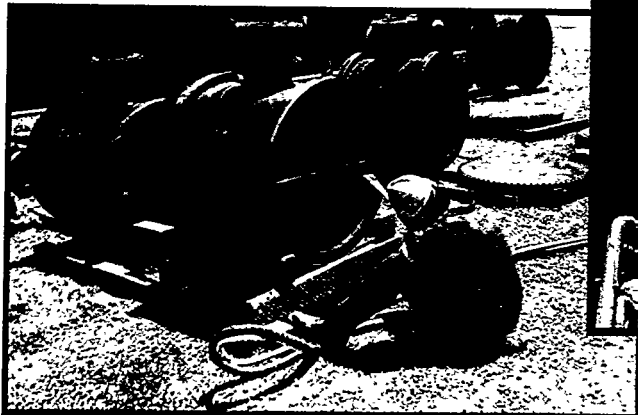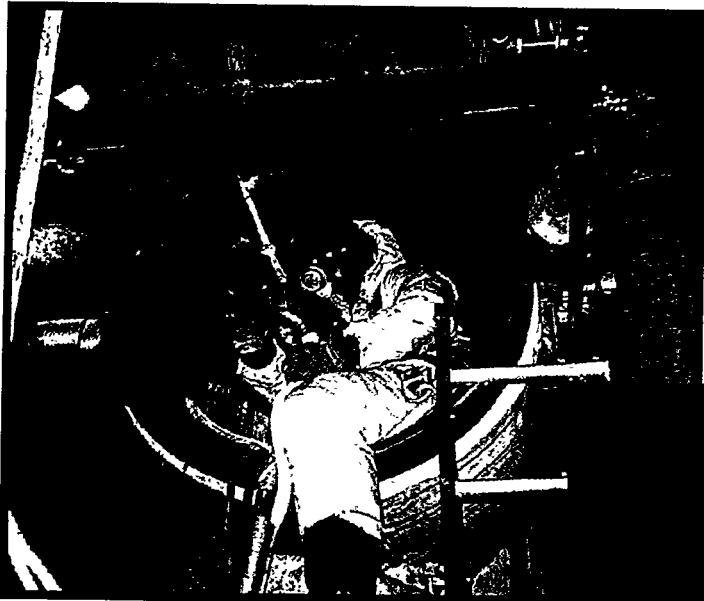
Alternative Cleaning Technology

Sodium Bi-Carb Cleaning
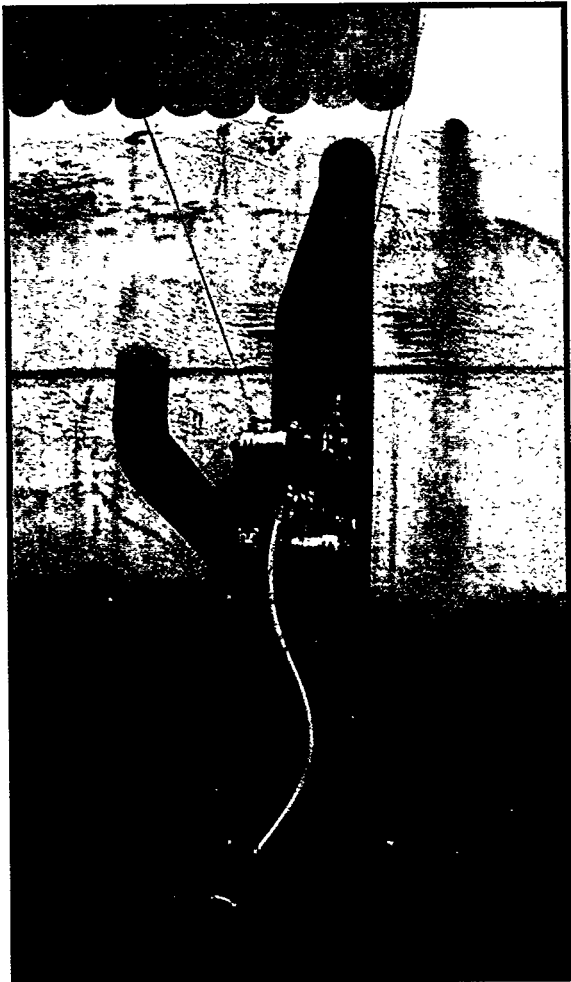
Robotic Ultra- Blast (40,000 psi)

Tank Cleaning Without Personel Entry
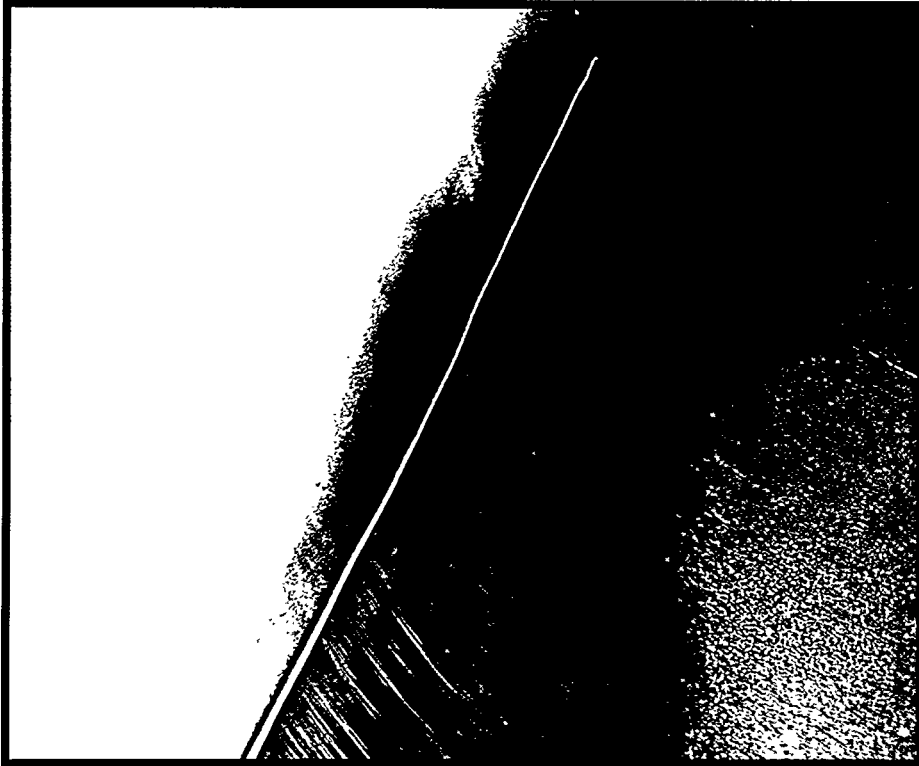
Confined Space Entry?
(Not Without Specialized Equipment and an Egress Plan)
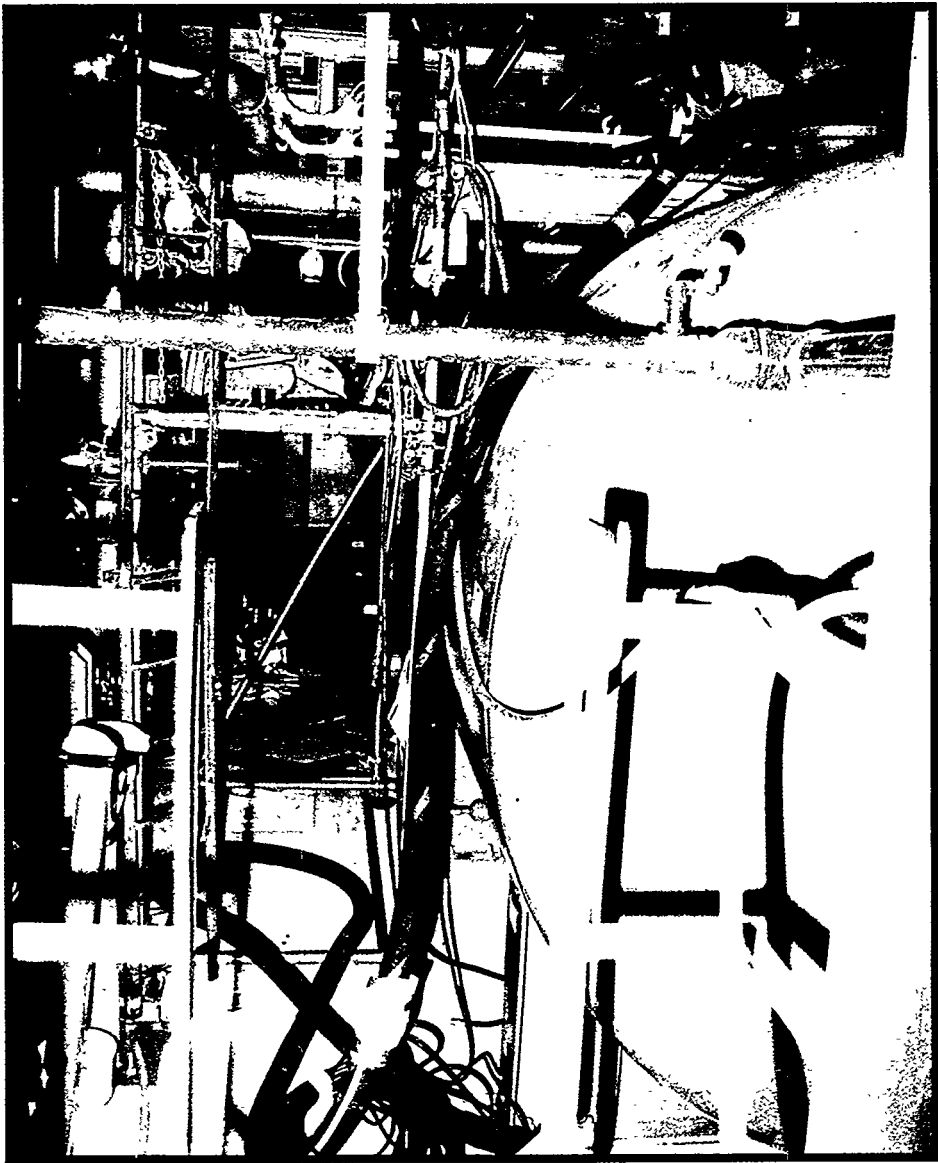
Safety #1 Importance to Confined Space Entry
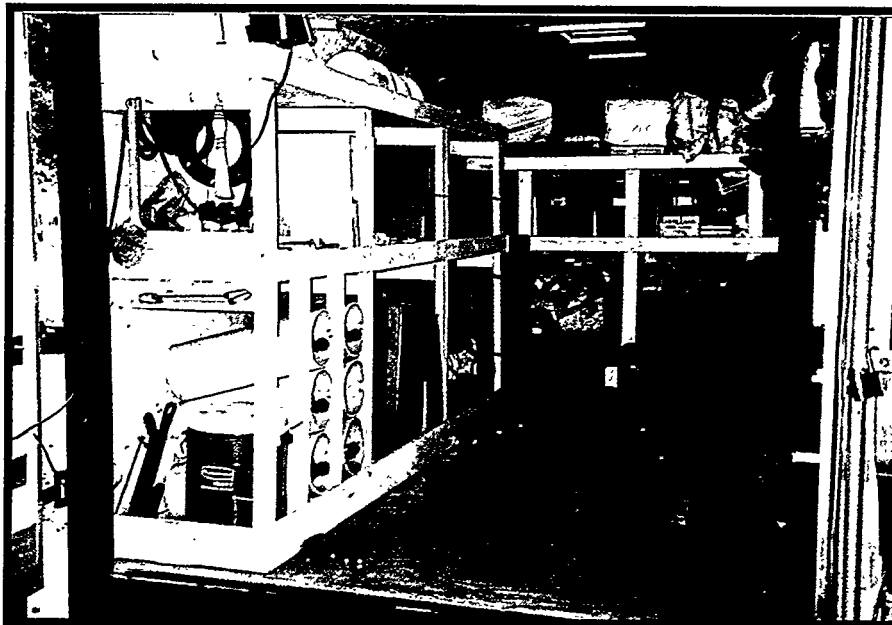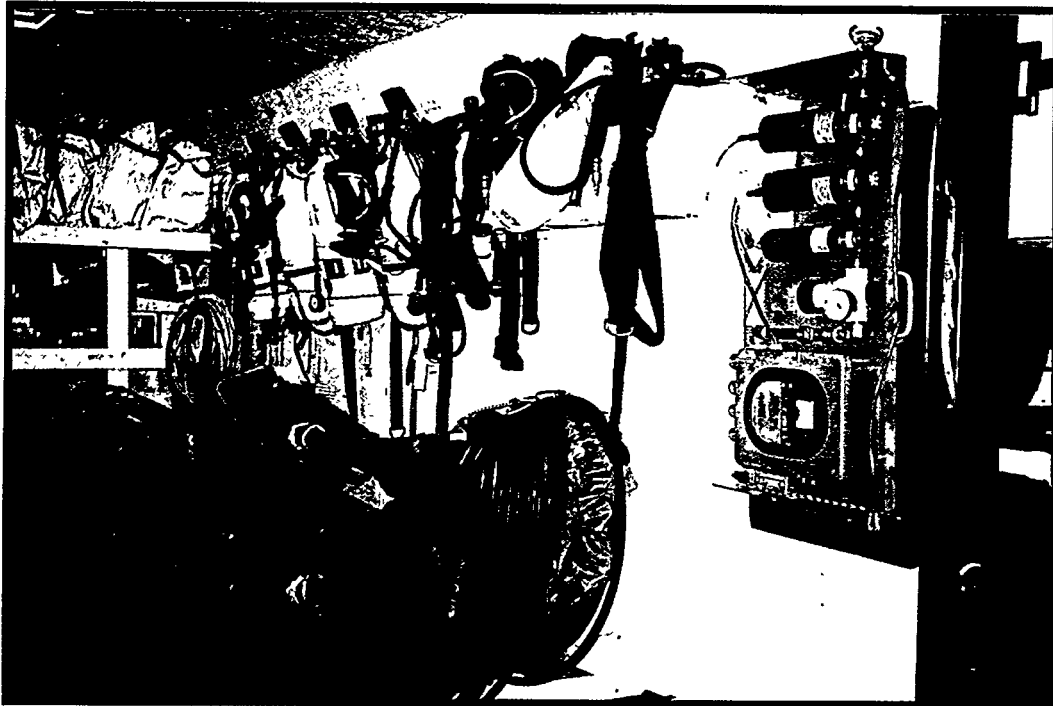
Conclusions:

Housekeeping is easier and cheaper than Tank Cleaning

Preventive Maintenance is Easier than Tank Cleaning

Preventive Maintenance is Easy!

1.De-Watering
2.Periodic Biocide Treatment (3 to 4 times a year)

THE ACID CATALYSED FORMATION OF EXISTENT SOLUBLE GUMS AND PARTICULATE MATTER IN DIESEL FUELS.

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ABSTRACT

In contrast to the many studies on the formation of particulate matter in petroleum fuels, relatively little intention has been paid to the role of soluble gum. This study reports a series of experiments in which the relative amounts of existent gum and particulate matter were determined as a LCGO fuel was aged. These experiments were part of a larger study on the influence of the diesel fuel acid fraction on fuel stability.

As expected, the total insoluble (adherent plus filtered) and soluble gums increase with increasing temperature, time and amount of acid fraction (isolated from LCGO or ADO) added to the fuel. If the neat amount of gum (either total insolubles or solubles) is defined as that due directly to the added acid fraction, it can also be shown that the weight of neat soluble gum formed also increases with time, temperature and amount of acid dopant use as a spike. Whereas the total insoluble gums also behave in the same manner when the LCGO acid fraction is used as dopant, the addition of ADO acid fraction tend to decrease the amount of neat insolubles formed with ageing time. These findings cast doubt on the frequently made assumption that soluble gum is only a more soluble, lower molecular weight version of the more prevalent insoluble matter and is formed as part of the process leading to the formation of insoluble matter.

INTRODUCTION

Development of soluble and/or insoluble gum may be troublesome in engine performance[1]. The soluble gum actually does not cause any particular difficulties in systems in which the fuel is used, but very high values may lead to screen or filter clogging. Commonly, the soluble gum content can be used as a measure of the existent state of the fuel and it may also provide an indicator to the future behaviour of the fuel in storage[2].

The study of the fuel sediment formation initiated by oxygen containing species is the main focus of this work. This work concentrates on the role of the acidic species. The diesel fuel sediment/gum was created artificially under laboratory conditions by doping diesel fuel with acid fraction isolated from a range of fuels by ion chromatography. Light cycle gas oil (LCGO) and automotive diesel oil (ADO), which are classified as unstable and moderately stable fuels respectively, were chosen as the source of the acid fractions and LCGO was used as the raw diesel fuel for doping.

EXPERIMENTAL

Sample preparation

Diesel fuel samples used in this study were obtained from a refinery in Sydney, Australia. Automotive diesel oil (ADO) was a blended product, but with no additive added. Light cycle gasoil (LCGO) was off-cut cracker from the fluid catalytic cracking unit (FCCU). Light waxy gasoil (LWGO) was a diesel oil component from the high vacuum distillation unit (HVU).

All fuel samples were pre-filtered through Activon PTFE filter membranes (0.45 μ

porosity). Fuel samples were stored in a freezer unit at -18 °C before further treatment or investigation. In addition, all fuel samples were stored in clean new borosilicate bottles[3] with screw lids and teflon liners.

Isolation of acids from fuel samples

The separation method was adapted from the method described by Green et al.[4] using Biorad AG MP-1 anion resin, 200-400 mesh (37-75 μm) particle size. The amount of acid fraction was determined using a gas chromatography technique, where the quantity of the solvents was measured using toluene as an internal standard. The acid fraction content was calculated as a percentage (w/w %) of the initial oil. This technique was chosen to avoid the losses of volatile component of the acid fraction.

Ageing method

Amounts of 100, 150, 200 and 250 mg of dopant, if required, was added into 25 mL of fuel and dispersed thoroughly. The procedure used to study the ageing of fuels was adapted from those developed by Jones et al.[5], Bahn et al.[6] and Adiwar[7]. Ageing was carried out by placing the exact volume of the pre-filtered fuel in a clean borosilicate bottle; either 25 mL of sample in a 100 mL bottle or 100 mL of sample in a 250 mL bottle. The fuel sample and upper space in the bottle was saturated with oxygen by bubbling the oxygen gas into the oil for about 15 minutes at a rate of 60 mL per minute. The bottles were then sealed using a teflon liner in the screw cap of the bottle and each bottle was covered with aluminium foil to exclude light. The bottles were let stand for 24 hours at room temperature[8] and after that were stored in an oven at a predetermined temperature (65, 80 and 99 °C) for a fixed period of time (4, 7 or 14 days).

Determination of insoluble particulates and adherence

The method used was adapted from ASTM D 2274-88[9] and the work of Bahn *et al.*[8]. The insoluble particulates of the aged fuels were isolated by filtering the aged fuels gravimetrically through a 25 mm diameter 0.45 μ (pre-weighed) nylon filter by suction. After the filtered fuel sample was removed from the suction flask, the aged fuel sample bottle was washed with 3 x 15 mL portions of *iso*-octane. The total product on the nylon filter was then washed slowly with 5 mL *iso*-octane, removed and placed in a small closed petri dish and dried in a vacuum oven at 40 °C for 2 hours. It was then placed in a desiccator for 1 hour and weighed.

The adherence left on the bottle wall was dissolved in 3 x 5 mL portions of 1:1:1 toluene-acetone-methanol (TAM) and transferred quantitatively into a pre-weighed, clean 20 mL scintillation glass vial wrapped with aluminium foil. The TAM solvent was evaporated at 40 °C under a gentle flow of nitrogen and the bottle weighed after being dried in a vacuum oven at 40 °C for 2 hours. Before weighing, the bottle was left in a desiccator for 1 hour. The values for the insoluble particulates, adherence and total insoluble gums (sum of insoluble particulates and adherence) were recorded as mg/100 mL (either for a 25 mL sample or a 100 mL sample).

Determination of existent soluble gum

The method used was adapted from ASTM D 381-86[10] and from the work of Beranek *et al.*[11]. Filtered fuel (50 mL) was put into a pre-weighed clean 100 mL glass beaker. The beaker was placed into the heating bath of the existent soluble gum apparatus, which had been preheated to 240 °C. A flow of nitrogen, pre-heated to 240 °C, was blown onto the top of the fuel through a round nozzle at a rate of 30 L per minute. The evaporation was

carried out for a further seven minutes after the time when there was no more smoke observed coming out from the oil sample. The glass beaker was then cooled in a desiccator for about 3 hours and then weighed accurately. The value of the soluble gum was reported as mg/100 mL .

RESULTS AND DISCUSSION

Analysis of the acid concentrates

Low voltage high resolution mass spectrometric (LVHRMS) analysis

The mass spectrometric measurement of the LCGO and ADO acid fractions were made by Drs. Richard Sprecher and Garry Veloski of the Pittsburgh Energy Technology Center, US Department of Energy on a Kratos MS50 spectrometer. Table 1 lists a summary of percentages of compound types in the $C_nH_{2n-z}S$ formula class for LCGO and ADO acid fractions based on LVHRMS ion intensity.

The elemental analysis results

The elemental analysis results of the acid concentrates are shown in Table 2. The average molecular composition or empirical formula of these acid concentrates, normalised to one oxygen atom using normal combustion data, are $C_{13.0}H_{13.5}N_{0.3}S_{0.03}O$ and $C_{12.7}H_{14.1}N_{0.2}S_{0.02}O$ for LCGO and ADO acid concentrates respectively.

Sediment formation

Insoluble gums

The amounts of total insoluble gums formed in doped LCGO, when stored under accelerated storage conditions, are shown in Figures 1 and 2. In these studies, 25 mL

samples of LCGO was doped with 100, 150, 200 and 250 mg of LCGO or ADO acid concentrate and stored at 65, 80 and 99 °C for 4, 7 and 14 days. As is usual practice, the total insoluble gums include both the adherent and filtered gums, and the results are reported as per 100 mL. It can be seen that the levels of total insoluble gum increase with increasing amounts of acid concentrate added into the LCGO. Both figures show that the higher the temperature and the longer the time of storage, the higher the amount of total insoluble gum produced.

The weights of neat total insoluble gums formed when doped LCGO stored under these accelerated storage conditions are shown in Figure 3. The neat value is determined by subtraction of the weight of total insoluble gum formed in the control sample from that formed in the doped LCGO. The control is undoped LCGO to which no acid concentrates have been added. The control is also aged together with the doped LCGO. Simply, it means that the neat value is the increased amount of the insoluble gum produced by the addition of the acid fraction.

The neat total insoluble gum data in Figures 4 and 5 show that an increase in the amount of LCGO acid fraction added increases the weight of total insoluble produced, as does increasing both or either the ageing duration time and the ageing temperature. Although the increments are small, it can be seen clearly that the longer the ageing duration and the higher the ageing temperature, the greater is the weigh of insoluble gum produced as a direct result of the added acid fraction.

The data for the formation of neat total insoluble gum in LCGO doped with ADO acid fraction are plotted in Figure 6. In contrast with that found for the addition of the LCGO acid fraction spike, the amount of neat insolubles formed mostly tends to decrease with increasing ageing times and temperatures. It can be seen clearly from Figures 7 and 8 that the longer the ageing duration time and the higher the ageing temperature, the lower will be the amount of neat insoluble formation. This decrease is especially marked in studies at the higher temperatures. Under the experimental conditions used, it can be concluded that, particularly at higher temperatures, the neat insoluble gum formed in LCGO doped with ADO acid fraction initially re-dissolves with the increasing time of

ageing. Furthermore, the data show that the addition of LCGO acid fraction into LCGO generates more insoluble gum than does the addition of ADO acid fraction into LCGO.

Soluble gums

The amounts of soluble gums formed in doped LCGO, when stored under accelerated storage conditions, are illustrated in Figures 9 and 10. Soluble gum is a residue left when the fuel is heated at 240 °C under a flow of nitrogen gas. Soluble gum formation increases with increasing amounts of acid concentrate added into the LCGO, as occurs with insoluble gum formation. Both figures show that the higher the temperature and the longer the time of storage, the higher is the amount of soluble gum produced.

The increment of neat soluble gums is parallel to that of the neat total insoluble gums formed in LCGO spiked with LCGO acid fraction. Both tend to increase with increasing ageing times and ageing temperatures. But, as noted, the increment of neat soluble gums contradicts the increment of neat total insoluble gums formed in LCGO doped with ADO acid fraction. The amount of neat soluble gum formed tends to increase, while the amount of the neat insoluble gum formed mostly tends to decrease with increasing ageing time and temperature. Furthermore, the data illustrated in Figures 9 and 10 show that with increasing temperature and time of ageing, the addition of the LCGO acid fraction into LCGO tends to generate less soluble gum than does the addition of ADO acid fraction into LCGO. At an ageing temperature of 65 °C, the formation of soluble gums by the addition of LCGO acid fraction is slightly higher than for the addition of ADO acid fraction into LCGO. At 80 and 90 °C however, the formation of soluble gum by the addition of LCGO acid fraction is lower than that caused by the addition of ADO acid fraction under the same conditions. This contrasts with the data found for the formation of total insoluble gums when LCGO spiked with acid fractions and aged at those temperatures and times. The addition of LCGO acid fraction into LCGO always produces higher total insoluble gums than does the addition of ADO acid fraction. These observations may support the proposition that the insoluble gum formed in LCGO doped with ADO acid fraction re-dissolves to form soluble gum.

A rationale or chemical mechanism to explain the ADO acid fraction induced dissolution of the particulate matter has yet to be developed. It has been reported[12,13] that the type of sulfur compound, rather than the total sulphur concentration, is the key to fuel instability. When added into a fuel, Morris and Mushrush found[14] thiols accelerate the rate of oxygen reaction without a commensurate increase in peroxidation. In JFTOT (jet fuel thermal oxidation test) studies conducted in dodecane, thiophenol was found to inhibit autoxidation by acting as a radical trap and breaking the autoxidation chain very early in the process[15].

These studies[14] showed that the oxidative addition of thiols to olefins occurred when thiophenol and indene was added into a model fuel and stressed in two model systems at temperatures in the 100-120 °C range and in the JFTOT apparatus at temperatures up to 320 °C. This means that at high temperatures, in the presence of thiophenol, the availability of peroxides needed for further reaction are limited and the reaction stopped at this stage resulting in the increased amounts of the soluble gum. This phenomenon may possibly explain the soluble and insoluble gum formation in LCGO doped with ADO acid fraction. Thiophenols were found by LVHRMS analysis to be a major component of the CHS compound class of the acid fractions. A careful structural study of the soluble gums and particulate matter based on a selective chemical degradation method developed for fuel sediments is currently being conducted.

CONCLUSIONS

It was found that the total insoluble gum formation was increased by increasing the amount of LCGO and ADO acid concentrates added as dopant into LCGO. The higher the temperature and the longer the time of storage, the greater is the amount of total insoluble gum produced. The yield of neat total insoluble gum is increased with increasing amounts of LCGO acid fraction and with both or either the ageing duration time and the ageing temperature.

In contrast with that found for the addition of the LCGO acid fraction, the amount of the neat insolubles formed by the addition of ADO acid fraction mostly tends to decrease with an increasing of ageing times. This decrease is especially marked at elevated

temperatures. Under the experimental conditions used it can be concluded that, particularly at higher temperatures, the neat insoluble gum formed in LCGO doped with ADO acid fraction initially re-dissolves with the increasing time of ageing. Furthermore, the data show that the addition of LCGO acid fraction into LCGO generates more insoluble gum than does the addition of ADO acid fraction into LCGO.

The soluble gum formations were also increased by increasing the amount of acid concentrates added into the LCGO, as occurs with the insoluble gum formations. The higher the temperature and the longer the time of storage, the higher is the amount of soluble gum produced.

The neat soluble gum data show that an increase in the amount of either acid fraction added increases the weight of soluble gum produced, as does increasing both or either the ageing duration time and the ageing temperature. The longer the ageing duration and the higher the ageing temperature, the greater is the weigh of neat soluble gum produced for both the addition of a LCGO and ADO acid fraction spike.

The increment of neat soluble gum parallels that for the neat total insoluble gums formed in LCGO spiked with LCGO acid fraction. Both tend to increase with increasing ageing times and ageing temperatures. But, as noted, the increment of neat soluble gums is in contrast with that found for LCGO doped with ADO acid fraction. The amount of neat soluble gum formed tends to increase, while the amount of neat insoluble gum formed mostly tends to decrease with increasing ageing times and temperature. These facts support the proposition that the insoluble gum formed in LCGO doped with ADO acid fraction re-dissolves to form soluble gum.

Thiols might well be implicated as they are reported to inhibit peroxide formation and were found in the acid fraction, it is presumed that they can explain the decreasing of the neat soluble gum formed in LCGO doped with ADO acid fraction. A synergistic effect between a compound or compounds present in the ADO acid fraction and another compound, possibly sulfur containing, present either in the gum formed initially or in the fuel may be an explanation for this observation.

Table 1. LVHRMS ion intensity of compounds in $C_nH_{(2n-2)}S$ formula class for LCGO and ADO acid fractions (summary).

Z	Example of compound type	LCGO acid fraction		ADO acid fraction	
		% intensity from		% intensity from	
		Class	Total	Class	Total
2	Dihydrothiophenes	1.24	0.04	-	-
6	Thiophenols	33.09	1.05	38.60	0.36
8	Dihydrobenzenethiophenes	5.09	0.16	0.97	0.01
10	Benzothiophenes	10.36	0.33	8.54	0.08
12	Thionaphthols	10.25	0.33	-	-
14	Phenylthioethers	13.09	0.42	-	-
16	Dibenzothiophenes	25.06	0.80	51.9	0.48
20	Bezo(def)dibenzothiophenes	1.51	0.05	-	-
24	-	0.31	0.01	-	-

Table 2. Elemental analysis of diesel fuels and their acid concentrates by Carlo Erba CHNS apparatus method (% w/w) and LVHRMS method (% ion intensity).

Elements	Carlo Erba CHNS apparatus method				LVHRMS method	
	LCGO		ADO		LCGO acid fraction	ADO acid fraction
	Raw fuel	acid fraction	Raw fuel	acid fraction		
C	84.7	81.80	79.5	82.10	85.66	85.57
H	9.2	7.08	11.3	7.62	7.37	7.91
N	<0.1	2.20	<0.1	1.38	2.23	1.21
S	nd	0.55	nd	0.27	0.67	0.26
O	<6.1[1]	8.37[1]	<9.1[1]	8.63[1]	4.07	5.04
H/C ratio	1.3	1.04	1.71	1.11	1.03	1.11
N/C ratio	<0.001	0.02	<0.001	0.01	0.02	0.01
S/C ratio	-	0.003	-	0.001	0.03	0.001
O/C ratio	0.05	0.08	0.09	0.08	0.04	0.04

Note: 1) By difference.

nd = not detected
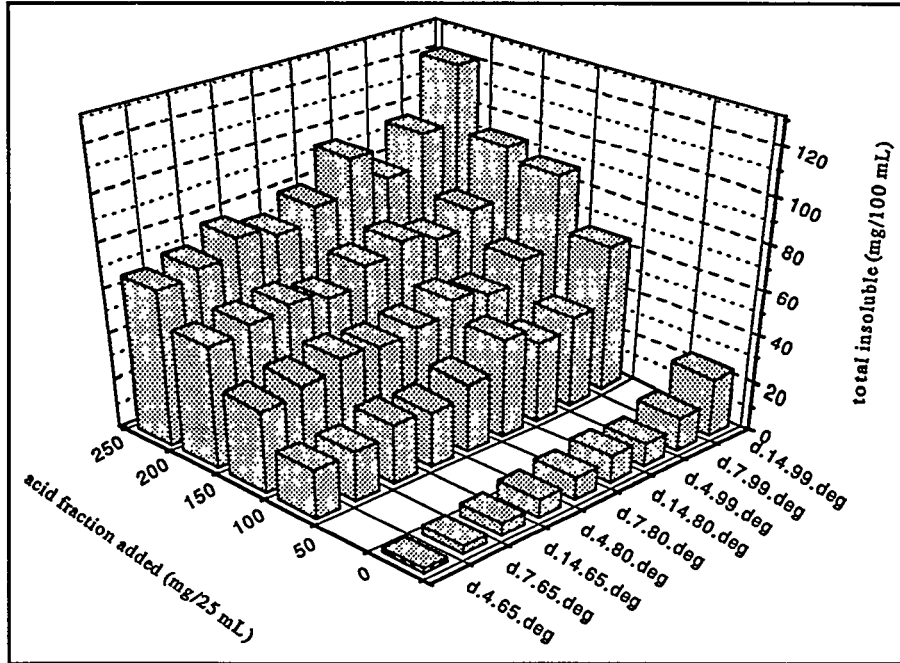
Figure 1   The weight of total insoluble gums formed in LCGO
after ageing at 65, 80 and 99 °C for 4, 7 and 14 days
plotted against the LCGO acid fraction added.
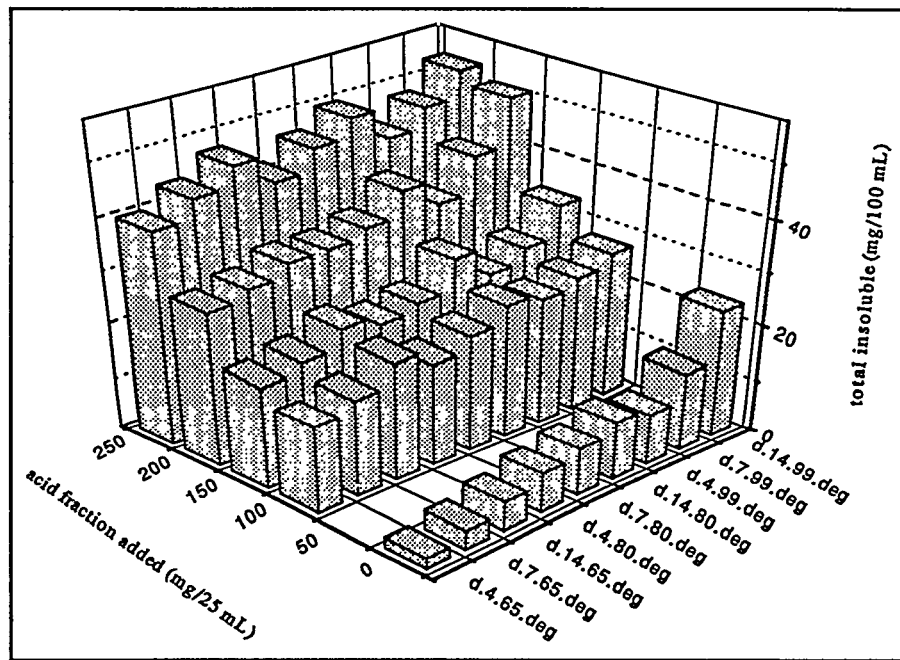
Figure 2   The weight of total insoluble gums formed in LCGO
after ageing at 65, 80, and 99 °C for 4, 7, and 14 days
plotted against the ADO acid fraction added.

Figure 3 The weight of neat total insoluble gums formed in
LCGO after ageing at 65, 80, and 99 °C for 4, 7, and 14
days plotted against the LCGO acid fraction added.

Figure 4   Neat total insoluble gums formed in LCGO doped with 100 (■), 150 (◆), 200 (▲) and 250 (▼) mg of LCGO acid fraction plotted against ageing time at 65, 80 and 90 °C.

Figure 5   Neat total insoluble gums formed in LCGO doped with 100 (■), 150 (◆), 200 (▲) and 250 (▼) mg of LCGO acid fraction plotted against ageing temperature for 4, 7, and 14 days.

Figure 6   The weight of neat total insoluble gums formed in LCGO after ageing at 65, 80, and 99 °C for 4, 7, and 14 days plotted against the ADO acid fraction added.

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Figure 7　Neat total insoluble gums formed in LCGO doped with 100 (■), 150 (♦), 200 (▲) and 250 (▼) mg of ADO acid fraction plotted against ageing time at 65, 80 and 90 °C.

Figure 8   Neat total insoluble gums formed in LCGO doped with
100 (■), 150 (◆), 200 (▲) and 250 (▼) mg of ADO acid
fraction plotted against ageing temperature for 4, 7, and
14 days.

Figure 9 The weight of soluble gums formed in LCGO after ageing at 65, 80 and 99 °C for 4, 7 and 14 days plotted against the LCGO acid fraction added.

Figure 10 The weight of soluble gums formed in LCGO after ageing at 65, 80, and 99 °C for 4, 7, and 14 days plotted against the ADO acid fraction added.
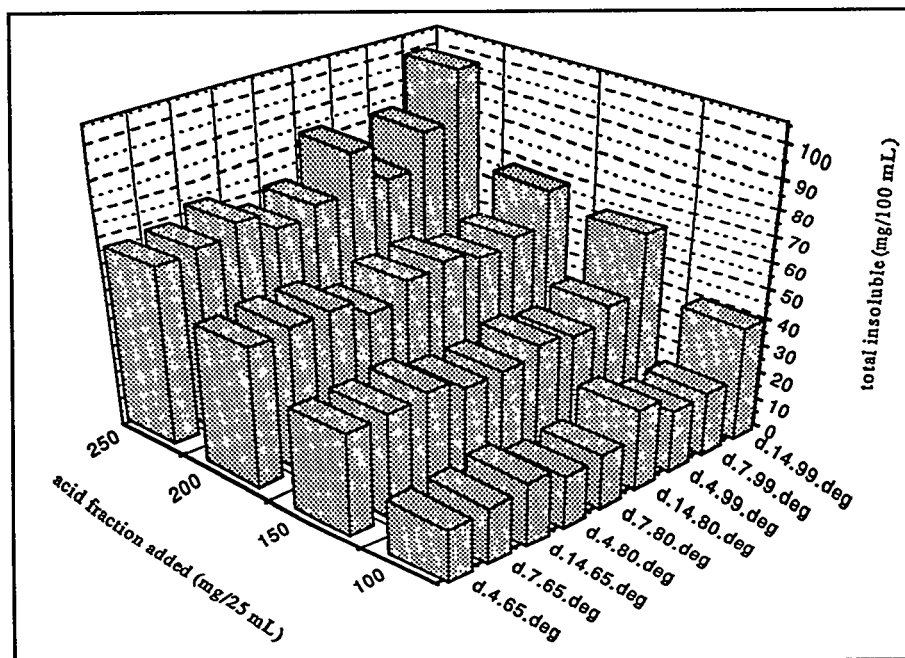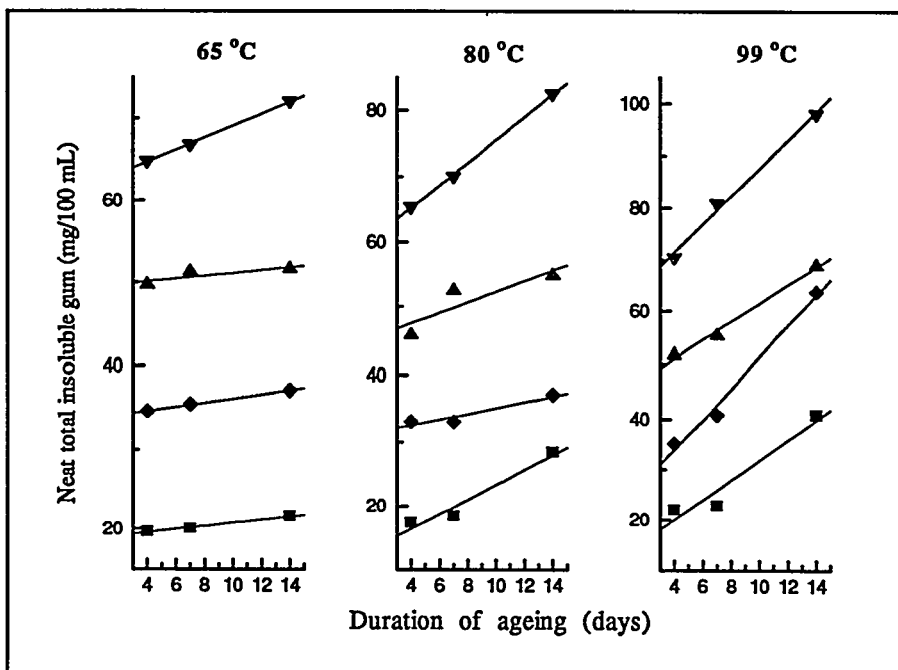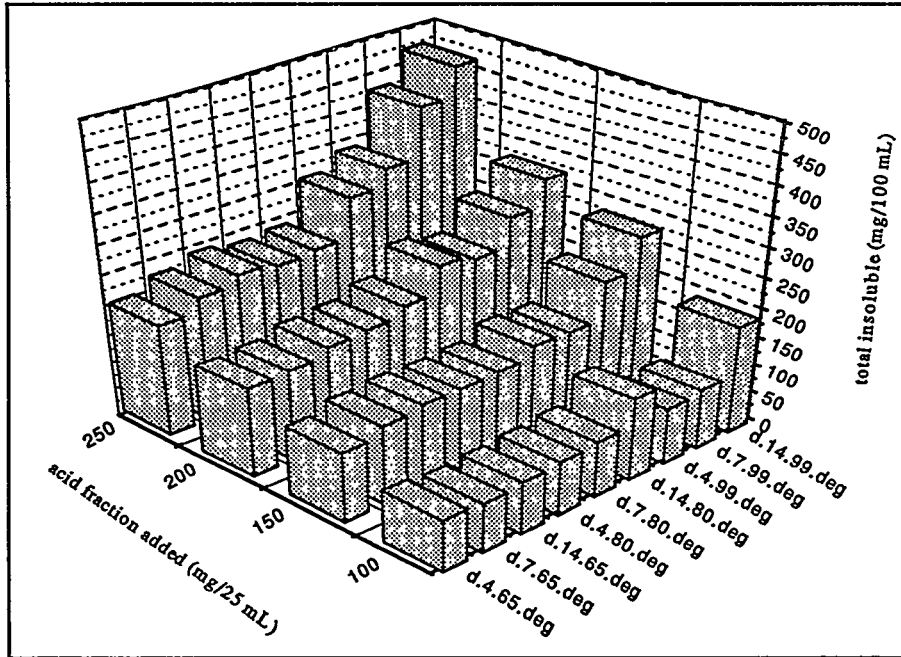
Figure 11 The weight of neat soluble gums formed in LCGO after ageing at 65, 80, and 99 °C for 4, 7, and 14 days plotted against the LCGO acid fraction added.
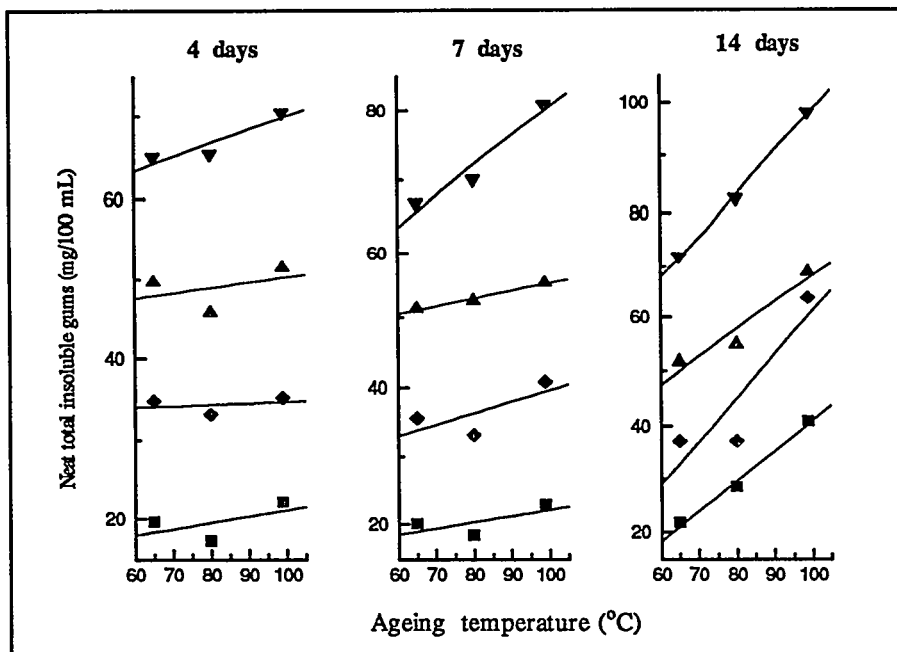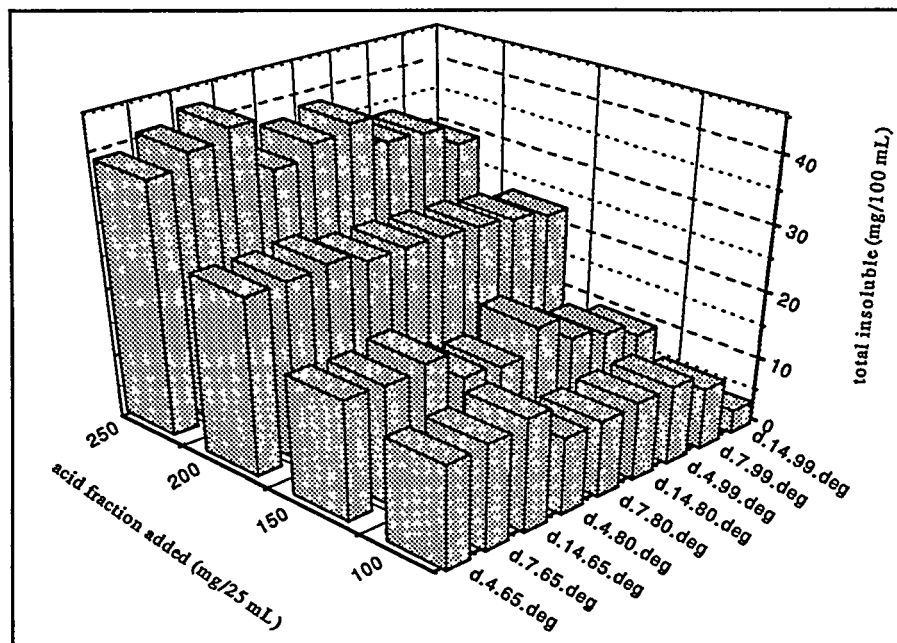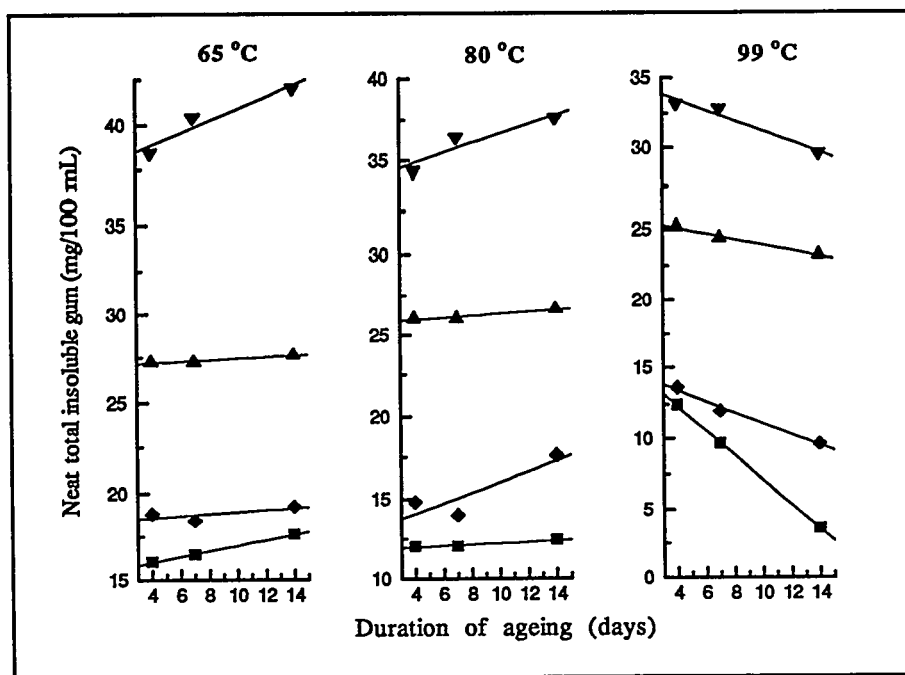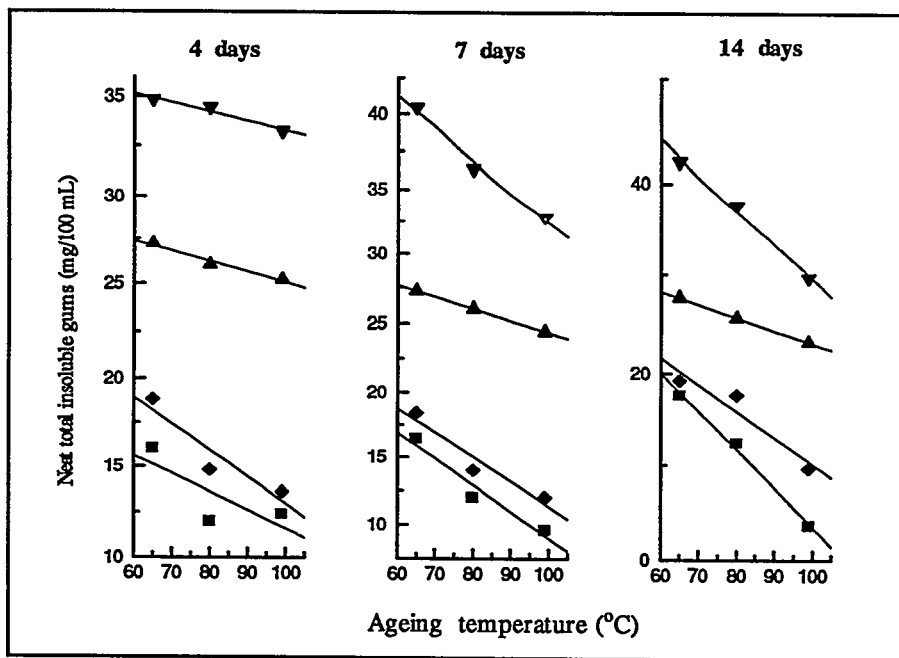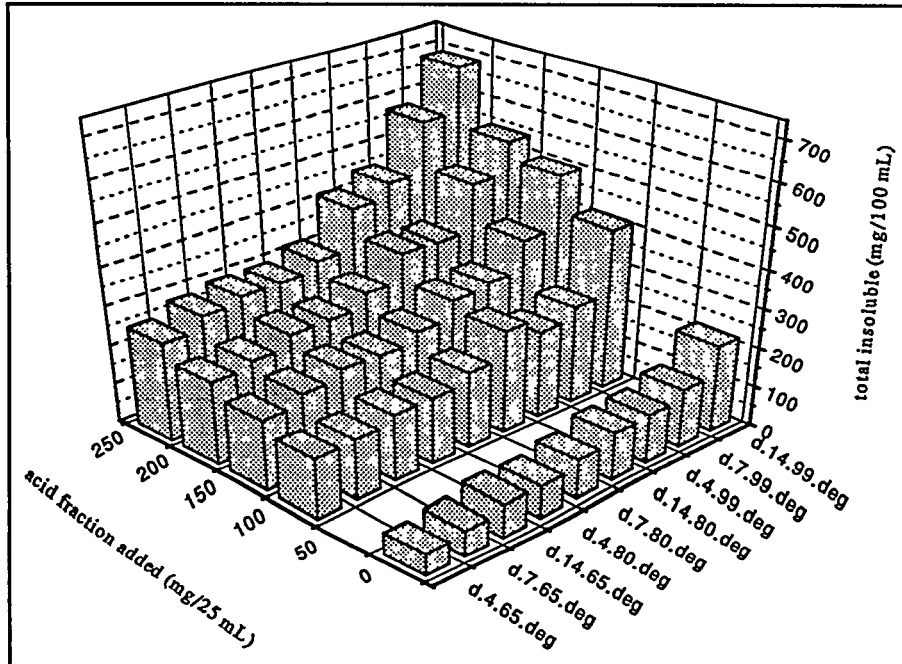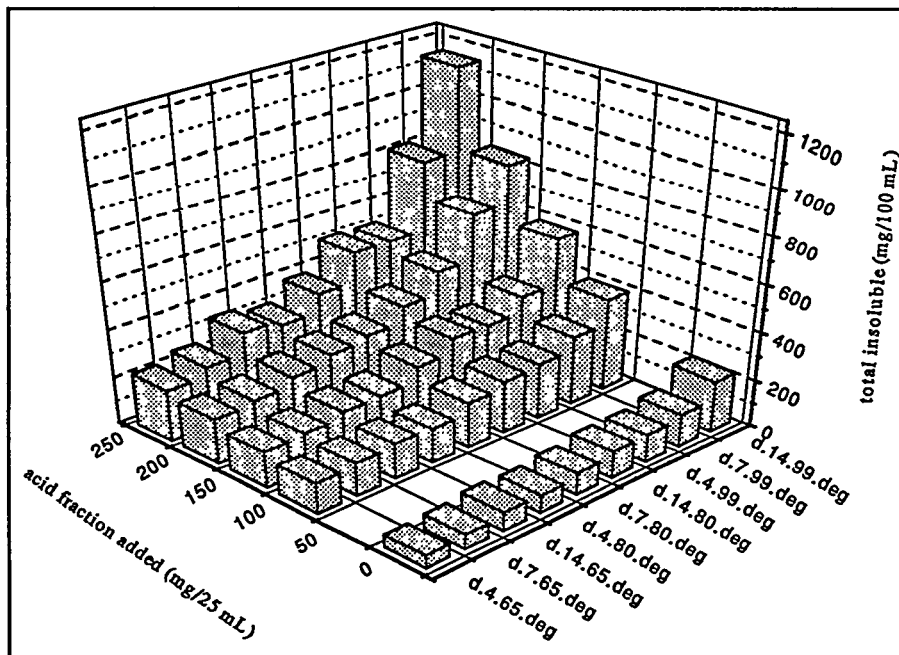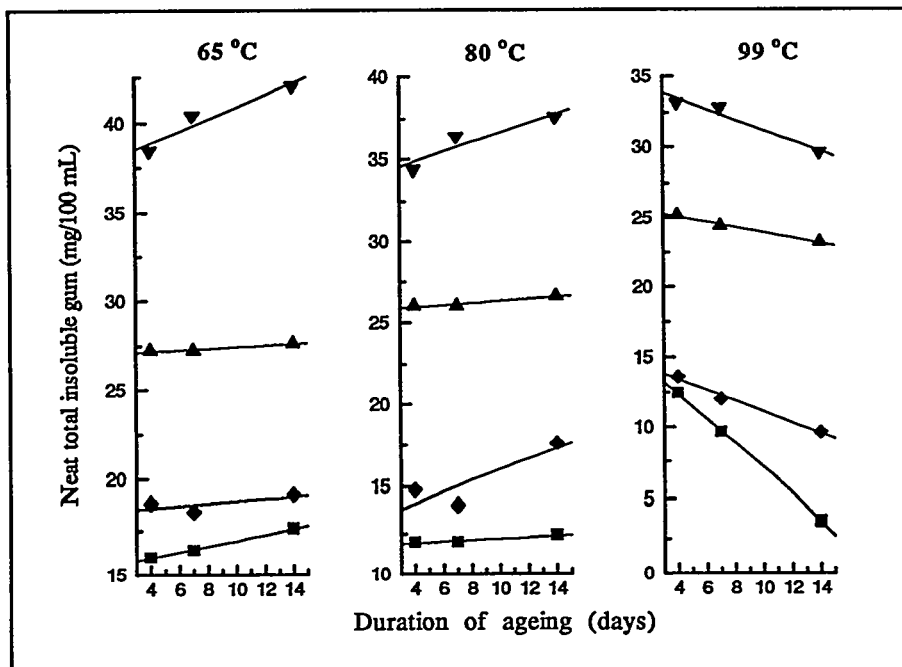
Figure 12   Neat total insoluble gums formed in LCGO doped with
100 (■), 150 (◆), 200 (▲) and 250 (▼) mg of ADO acid
fraction plotted against ageing time at 65, 80 and 90 °C.

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THE RELATIONSHIP BETWEEN CONDUCTIVITY AND LUBRICITY IN "NEW" EUROPEAN ON ROAD DIESEL FUELS

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ABSTRACT

From 1st October 1996 European automotive diesel has been limited to a maximum sulfur content of 0.05% wt. The various processing techniques used to achieve this remove not only sulfur but also nitrogen, oxygen and polyaromatic compounds. It is known that these species provide the fuel with intrinsic natural lubricity, conductivity and protection against peroxide formation. Removal of these compounds from diesel has a well recognised effect on fuel lubricity. It also, however, has an impact on fuel conductivity which may have serious implications when distributing fuel particularly if switchloading with gasoline. The properties of a number of un-additised fuels meeting the current European specification, EN590, were analysed. The relationship between conductivity and lubricity was considered as well as the effects of additives commonly used in retail fuels on these properties. It was shown that fuels with poor lubricity have poor conductivity. The majority of refinery additives have little effect on conductivity, though some do provide lubricity improvement. To ensure that the required levels of lubricity and conductivity are achieved it is necessary to use appropriate additives designed specifically to provide these properties to the fuel. Analysis of forecourt fuels showed that in most cases the requirements of adequate lubricity were addressed but this was not necessarily the case with fuel conductivity.

INTRODUCTION

The introduction of low sulfur diesel fuels (<0.05% wt) has brought new problems for the refiner and petroleum product marketer. The refinery techniques needed to reduce sulfur levels, such as hydrotreating, have a severe effect on other properties of the fuel.

One of the most recognised effects has been the impact on lubricity of removing species that contribute to the natural lubricity of the fuel. This reduction in lubricity can result in catastrophic failure of rotary injection pumps which are lubricated by the fuel. Little attention has been drawn to the other less obvious property changes that have been brought about by hydroprocessing. Certainly the problem of peroxide formation during long term storage has been discussed[1] along with the simple additive solution of adding antioxidant. However, conductivity and the very real problems associated with static discharge have been overlooked by a large number of refiners.

The refiner has had to deal with static discharge problems in jet kerosene for a number of years and in fact the addition of Stadis® 450 is mandated in a number of specifications. Kerosenes needed for the safe operation of jet engines are often hydrotreated to remove impurities. Naturally occurring conductivity improvers would normally dissipate any charges built up in transporting the fuel, negating any risk of static discharge. Their removal by hydrotreatment or clay filtration results in a low rate of dissipation for the static charge generated passing through fitments, tubes and especially filter coalescers. This increases the risk of a spark discharge which could cause fires, or explosions with the potential for loss of life or aircraft.

Ground fuels potentially have the same sort of problem if hydrotreated to remove sulfur. The risk of ignition is normally lower because of the lower flammability of diesel fuels. However, one aspect of their transport, which is not usually seen in jet fuels, where dedicated tankerage is frequently used, is switch loading between fuels of different distillation characteristics.

During the period 1960 to 1981 the API[2] tabulated 121 ignition incidents during tank-loading, 70% of which occurred during switch-loading from gasoline to kerosene (for ground fuel use) or diesel. With switch-loading from gasoline to diesel, a residue of gasoline vapour may be left in the tank. A discharge from electrically charged diesel to the side of the tank may ignite the gasoline vapour, thus starting a fire. Grounding and bonding although essential, are not enough to prevent a fire from starting under these circumstances. The problem is exacerbated by low temperature, since the conductivity of the diesel fuel is further reduced, while the gasoline vapour concentration becomes closer to optimum ignition.

Explosion-like ignitions occurred during filling of road tank trucks on two occasions during one week in April 1997 at Gothenburg, Sweden. The first incident was identified as being due to switchloading of ultra low sulfur diesel with gasoline. In the second incident gasoline had been previously transported in the adjacent compartment. A closed gas return system allowed the transfer of vapours between compartments. The conductivity of the diesel fuels involved had been further reduced by the cold weather experienced during this period. Thorough investigations concluded that static discharge was the likely ignition source.

FUELS USED FOR TESTING

In order to evaluate the relationship between fuel conductivity and lubricity in low sulfur fuels thirty seven fuels were sourced from eight Western European countries. These comprise:

- 16 fuels labelled additised
- 21 fuels labelled un-additised
- 1 prepared fuel blend

All of the fuels were thought to have sulfur levels less than 0.05% and three Scandinavian fuels were expected to have sulfur levels less than 0.005%.

TEST PROCEDURES

Each of the fuels received were tested for sulfur content, lubricity and conductivity. The test methods used were as follows:

Sulfur content

The IP (Institute of Petroleum) 373 "Determination of Sulfur Content - Microcoulometry (Oxidative) Method" test procedure was used.

This test is normally only applicable to sulfur concentrations in the range 1 to 100 mg/kg, unless the fuel sample is diluted or in this case if the linearity of response of the test method and apparatus can be proven. Repeatability is 0.063x where 'x' is the average of the two results being compared, this is only valid for sulfur contents in the range 0 - 110 mg/kg.

Lubricity

The CEC F-06-A-96, "Measurement of Diesel Fuel Lubricity", using the High Frequency Reciprocating Rig (HFRR) test procedure was used.

All wear scars quoted are corrected to give 1.4WS values. Repeatability is calculated using the equation $r = 139 - (0.1648 \times 1.4WS)$.

Conductivity

An Octel in - house test outlined in "Guidelines for Laboratory Evaluation of Stadis® 425 and Stadis® 450", Additive Brief 96-09 was used. This procedure supplements ASTM D2624 "Electrical Conductivity of Aviation and Distillate Fuels", allowing for use of Teflon bottles in place of metal cans. The EMCEE digital model 1152 instrument was used to carry out all analysis.

In the procedure 500 ml of fuel is added to a cleaned Teflon bottle. As Teflon is a perfect insulator, the fuel is grounded using a copper wire. After a suitable relaxation period the fuel is then analysed using the EMCEE digital meter. Repeatability is ± 1 pS/m.

TEST MATRIX

Fuels

All fuels were initially analysed to determine their sulfur content, lubricity and conductivity. Table 1 summarises the results obtained. Fuels 2, 8, 16, 22, 26, 28, 30 and 35 were chosen as base fuels for additisation. Each had generally poor conductivity and lubricity and was available in sufficient volume to enable testing to be carried out.

A large volume of Fuel 31 was available. Its very low wear scar and poor conductivity, however, indicated that it probably contained lubricity improver. The fuel was clay filtered to remove the lubricity improver and other refinery additives to provide a large source of base fuel with the required poor lubricity and conductivity. This clay filtered fuel is reported in Table 1 as Fuel 38.

Additives

The following commonly used refinery additives and possible future blending component were evaluated for their effect on conductivity and lubricity at typical use treat rates:

- 4 cold filter plugging point (CFPP) improvers
- 1 wax anti-settling (WASA) additive
- 5 lubricity improvers
- 1 cetane number improver (CNI)
- 2 dehazer
- 1 corrosion inhibitor
- Rape seed methyl ester (RME)

RME was chosen for inclusion as it is used in France as blending component at levels up to 5% by volume and is believed to have a marked effect on some of the blended fuels properties.

TEST RESULTS AND DISCUSSION

The Canadian diesel fuel specification[3], CAN/CGSB 3-6 M86, mandated a conductivity of 25 pS/m at time and temperature of loading to help minimise the risk of static discharge incidents. The European Committee for Standardisation (CEN) has proposed a wear

scar limit of 460 μm for the European diesel fuel specification, EN 590. This limit is currently under review. These two values are taken as the minimum acceptable performance criteria in all the test work carried out for this paper.

Relationship between conductivity and lubricity

Table 1 shows that of the sixteen fuels received labelled additised, five had conductivities below the Canadian minimum. Of these, two were less than the 3 pS/m level set by Walmsley[4] below which the risk of ignition is at its greatest. Only two of the additised fuels, Fuels 15 and 23, had wear scars greater than 460 μm, and at 474 and 490 μm respectively are within the repeatability of the test when the target value is set at 460 μm.

Table 2 shows that of the 21 un-additised fuels, nine had wear scars less than 460 μm. In eight of these cases the wear scar was less than 400 μm, these are remarkably low. It is obvious that certain of the fuels have been additised with lubricity improver, Fuel 27 a modified Swedish Mk1 with a wear scar of 273 μm certainly contains lubricity improver as do probably Fuels 20 and 21. It is likely also that a number of the fuels with wear scars less than 400 and greater than 300 μm also contain lubricity improver. It is common practice in Europe to add lubricity improvers immediately after fuel blending and it is possible a number of these fuels contain an additive. Figure 1 shows the range of wear scars for the un-additised fuels.

Four un-additised fuels also had high conductivities. Three of these fuels were obtained from Germany and one from the UK. These are the markets in Europe where addition of conductivity improver to ground fuels is most prevalent. Of these, Fuels 13 and 14 also have acceptable wear scars and it is suggested that these fuels are actually additised with lubricity and conductivity improvers. It is possible that Fuels 16 and 34 also contain conductivity improver however as the lubricity of the fuels is poor, the property of the fuel most likely to concern the refiner, it is difficult to make an assumption on whether the fuel contains additive or not. Figure 2 shows the range of conductivities for the un-additised fuels.

Figure 3 illustrates the relationship of sulfur content to lubricity and conductivity. Fuels with sulfur contents less than 350 ppm all have low conductivities. The relationship between sulfur and lubricity is less clear and confusion over whether the fuels contain lubricity improver or not further clouds the issue.

As the refiner is likely to be most concerned with fuel lubricity, if the lubricity of the base fuels received is poor it is likely that they have not been additised with conductivity improver. Figure 4 illustrates the relationship between conductivity and lubricity for fuels with wear scars greater than 460 µm. The results show the majority of the fuels with poor lubricity have conductivities less than ten. Although a number of these fuels do not fall below the 3 pS/m threshold of highest risk, the measurements were taken at summer ambient laboratory temperatures. At colder temperatures it is almost certain that the conductivities of these fuels would drop below the critical 3 pS/m threshold.

Refinery additives

CFPP: All the cold flow additives tested had a small effect on conductivity and at most provided a 4 pS/m increase here. The effect on lubricity was more marked and, in general, a minimum 40 µm decrease in wear scar was achieved. Although this is within the repeatability of the test the trend is consistently down. The most effective of these additives was Additive C which reduced wear scars to an acceptable level in two fuels. The results indicate that these cold flow additives give some lubricity benefit but certainly not to such levels that the use of lubricity improver can be ignored. The results of indicate that response varies from fuel to fuel.

The refiner must consider that any batch to batch variation in fuel may result in a reduced contribution to lubricity improvement from the cold flow additive. This could restrict the refiner's ability to optimise cold flow additive use from blend to blend as is normally practised.

WASA: The one WASA tested gave a performance very similar to that of CFPPs, improving lubricity but not to a sufficient level to remove the need for lubricity improvers. Again there was a very small improvement in conductivity.

Lubricity improver: As would be expected the lubricity improvers provided in most cases more than adequate lubricity at 100 mg/l. In those cases where this did not provide the required performance then the treat rate can be optimised. The additives gave a small but inadequate improvement in conductivity.

RME: RME provided excellent lubricity improving performance at 5%v/v, the maximum allowed in diesel fuels in France. At this treat rate, however, no improvement in conductivity was seen. RME was blended into the fuels at 15% v/v to determine whether higher concentrations would improve the fuels conductivity. The results showed that at least

one fuel attained an adequate level of conductivity, whilst the second showed good improvement. The RME was further tested to see whether adequate conductivity improving performance was retained at temperatures down to -10°C. In both cases adequate conductivity was retained.

CNI: When test accuracy is taken into account, CNI at 0.03% wt had no effect on conductivity.

Dehazer: Dehazer A provided excellent conductivity improving performance at the treat rate of 50 mg/l, providing more than adequate performance at ambient in both fuels. Dehazer B, however, gave negligible improvement in conductivity.

In addition, both dehazers reduced wear scars by a considerable level in Fuel 35 but had little effect in Fuel 8. Lubricity improving performance of these two additives seems to be fuel specific.

Corrosion inhibitor: The corrosion inhibitor used gave little or no improvement in lubricity and conductivity at 10 mg/l. It is well known that corrosion inhibitors can be used as lubricity improvers at higher treat levels, born out by the excellent lubricity results at 100 mg/l. There was, however, no corresponding increase in conductivity.

CONCLUSIONS

- Many of the fuels received labelled un-additised contained additive
- For the majority of the true un-additised fuels, poor lubricity fuels will also have poor conductivity. The reverse is not necessarily the case, it is not determined which of the "good" lubricity un-additised fuels have actually been additised with lubricity improver or possibly even cold flow which has a positive effect on lubricity. Further work needs to be carried out on fuels that are proved to be un-additised
- Majority of Refinery additives have little or no effect on conductivity
- At least one dehazer behaves as a conductivity improver at use treat rates
- A number of additives improve lubricity, however, their effect is inconsistent and fuel dependent. These include cold flow improvers and dehazers. Corrosion inhibitors at their normal treat rates have little or no effect on improving lubricity in the HFRR test.

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Table 1: Source and properties of fuels

Sample	Source	Sulfur content, mg/kg	Lubricity, microns	Conductivity, pS/m
Fuel 1 (additised)	Belgium	387	295	41
Fuel 2 (additised)	Belgium	335	348	4
Fuel 3 (additised)	Belgium	359	403	63
Fuel 4 (additised)	Belgium	322	354	145
Fuel 5 (additised)	Belgium	324	389	93
Fuel 6 (additised)	Belgium	360	432	43
Fuel 7 (additised)	Belgium	334	366	13
Fuel 8 (un-additised)	Finland	31	599	4
Fuel 9 (additised)	France	279	327	1024
Fuel 10 (un-additised)	France	283	399	13
Fuel 11 (additised)	France	382	342	110
Fuel 12 (un-additised)	France	340	390	2
Fuel 13 (un-additised)	Germany	369	460	230
Fuel 14 (un-additised)	Germany	391	348	79
Fuel 15 (additised)	Germany	376	474	8
Fuel 16 (un-additised)	Germany	396	621	46
Fuel 17 (additised)	Germany	369	305	164
Fuel 18 (additised)	Germany	314	302	171
Fuel 19 (additised)	Germany	231	407	178
Fuel 20 (un-additised)	Greece	359	276	1
Fuel 21 (un-additised)	Greece	417	499	1
Fuel 22 (un-additised)	Italy	327	529	2
Fuel 23 (additised)	Italy	370	490	2
Fuel 24 (additised)	Italy	388	368	3
Fuel 25 (un-additised)	Italy	408	359	3
Fuel 26 (un-additised)	Sweden	<1	693	7
Fuel 27 (un-additised)	Sweden	11	273	4
Fuel 28 (additised)	UK	457	313	52
Fuel 29 (un-additised)	UK	212	559	10
Fuel 30 (un-additised)	UK	227	509	9
Fuel 31 (un-additised)	UK	254	280	5
Fuel 32 (un-additised)	UK	390	498	6
Fuel 33 (un-additised)	UK	397	473	5
Fuel 34(un-additised)	UK	421	537	62
Fuel 35 (un-additised)	UK	405	505	0
Fuel 36 (un-additised)	UK	326	364	11
Fuel 37 (un-additised)	UK	237	404	6
Fuel 38 (un-additised)	UK	250	638	0

Table 2: Un-additised by lubricity

Sample	Source	Sulfur content, mg/kg	Lubricity, microns	Conductivity, pS/m
Fuel 26 (un-additised)	Sweden	<1	693	7
Fuel 16 (un-additised)	Germany	396	621	46
Fuel 8 (un-additised)	Finland	31	599	4
Fuel 29 (un-additised)	UK	212	559	10
Fuel 34(un-additised)	UK	421	537	62
Fuel 22 (un-additised)	Italy	327	529	2
Fuel 30 (un-additised)	UK	227	509	9
Fuel 35 (un-additised)	UK	405	505	0
Fuel 21 (un-additised)	Greece	417	499	1
Fuel 32 (un-additised)	UK	390	498	6
Fuel 33 (un-additised)	UK	397	473	5
Fuel 13 (un-additised)	Germany	369	460	230
Fuel 37 (un-additised)	UK	237	404	6
Fuel 10 (un-additised)	France	283	399	13
Fuel 12 (un-additised)	France	340	390	2
Fuel 36 (un-additised)	UK	326	364	11
Fuel 25 (un-additised)	Italy	408	359	3
Fuel 14 (un-additised)	Germany	391	348	79
Fuel 31 (un-additised)	UK	254	280	5
Fuel 20 (un-additised)	Greece	359	276	1
Fuel 27 (un-additised)	Sweden	11	273	4

Table 3: Cold flow improvers and WASAs

Sample	Source	Additive, @ 100 mg/l	Lubricity, microns		Conductivity, pS/m	
			without additive	with additive	without additive	with additive
Fuel 8	Finland	Cold Flow A	599	536	4	4
Fuel 30	UK	Cold Flow A	509	491	9	13
Fuel 38	UK	Cold Flow A	638	544	0	6
Fuel 8	Finland	Cold Flow B	599	544	4	4
Fuel 30	UK	Cold Flow B	509	510	9	13
Fuel 38	UK	Cold Flow B	638	521	0	2
Fuel 8	Finland	Cold Flow C	599	426	4	4
Fuel 30	UK	Cold Flow C	509	430	9	13
Fuel 38	UK	Cold Flow C	638	541	0	3
Fuel 8	Finland	Cold Flow D	599	529	4	3
Fuel 30	UK	Cold Flow D	509	480	9	13
Fuel 38	UK	Cold Flow D	638	523	0	8
Fuel 8	Finland	WASA A	599	560	4	8
Fuel 30	UK	WASA A	509	480	9	12
Fuel 38	UK	WASA A	638	486	0	6

Table 4: Rape Seed Methyl Ester (RME)

Sample	Source	% RME	Lubricity, microns		Conductivity, pS/m	
			without RME	with RME	without RME	with RME
Fuel 8	Finland	5	599	267	8	7
Fuel 16	Germany	5	621	303	31	46
Fuel 26	Sweden	5	693	297	2	7
Fuel 35	UK	5	505	302	2	0
Fuel 8	Finland	15	599	193	4	59
Fuel 38	UK	15	638	305	0	23

Table 5: Conductivity of fuels containing 15% RME at low temperatures

Sample	Source	Temperature, °C	Conductivity	
			without additive	with additive
Fuel 38	UK	Ambient	2	78
Fuel 38	UK	-6	0	71
Fuel 38	UK	-7	0	64
Fuel 38	UK	-8	0	56
Fuel 38	UK	-10	0	48

Table 6: Cetane number improver

Sample	Source	% CNI	Lubricity, microns		Conductivity, pS/m	
			without CNI	with CNI	without CNI	with CNI
Fuel 8	Finland	0.03	599	648	4	2
Fuel 26	Sweden	0.03	693	711	5	4
Fuel 28	UK	0.03	313	274	57	58

Table 7: Lubricity improver

Sample	Source	Additive, @ 100 mg/l	Lubricity, microns		Conductivity, pS/m	
			without additive	with additive	without additive	with additive
Fuel 8	Finland	Lubricity Improver A	599	263	4	2
Fuel 8	Finland	Lubricity Improver B	599	429	4	5
Fuel 8	Finland	Lubricity Improver C	599	352	4	2
Fuel 8	Finland	Lubricity Improver D	599	446	4	2
Fuel 8	Finland	Lubricity Improver E	599	482	4	2
Fuel 30	UK	Lubricity Improver A	509	372	9	2
Fuel 30	UK	Lubricity Improver B	509	456	9	4
Fuel 30	UK	Lubricity Improver C	509	*	9	*
Fuel 30	UK	Lubricity Improver D	509	*	9	*
Fuel 30	UK	Lubricity Improver E	509	364	9	3
Fuel 38	UK	Lubricity Improver A	638	287	0	0
Fuel 38	UK	Lubricity Improver B	638	531	0	2
Fuel 38	UK	Lubricity Improver C	638	353	0	3
Fuel 38	UK	Lubricity Improver D	638	452	0	4
Fuel 38	UK	Lubricity Improver E	638	348	0	12

* No Low Sulfur Diesel 30 for further analysis

Table 8: Dehazer

Sample	Source	Additive, @ 50 mg/l	Lubricity, microns		Conductivity, pS/m	
			without additive	with additive	without additive	with additive
Fuel 8	Finland	Dehazer A	599	520	4	213
Fuel 35	UK	Dehazer A	505	282	4	85
Fuel 8	Finland	Dehazer B	599	571	4	20
Fuel 35	UK	Dehazer B	505	252	4	2

Table 9: Corrosion inhibitors

Sample	Source	Additive, @ 10 mg/l	Lubricity, microns		Conductivity, pS/m	
			without additive	with additive	without additive	with additive
Fuel 8	Finland	Inhibitor A	599	558	3	4
Fuel 35	UK	Inhibitor A	505	515	0	1

Table 10: Corrosion inhibitors

Sample	Source	Additive, @ 100 mg/l	Lubricity, microns		Conductivity, pS/m	
			without additive	with additive	without additive	with additive
Fuel 8	Finland	Inhibitor A	599	376	3	8
Fuel 35	UK	Inhibitor A	505	288	0	3

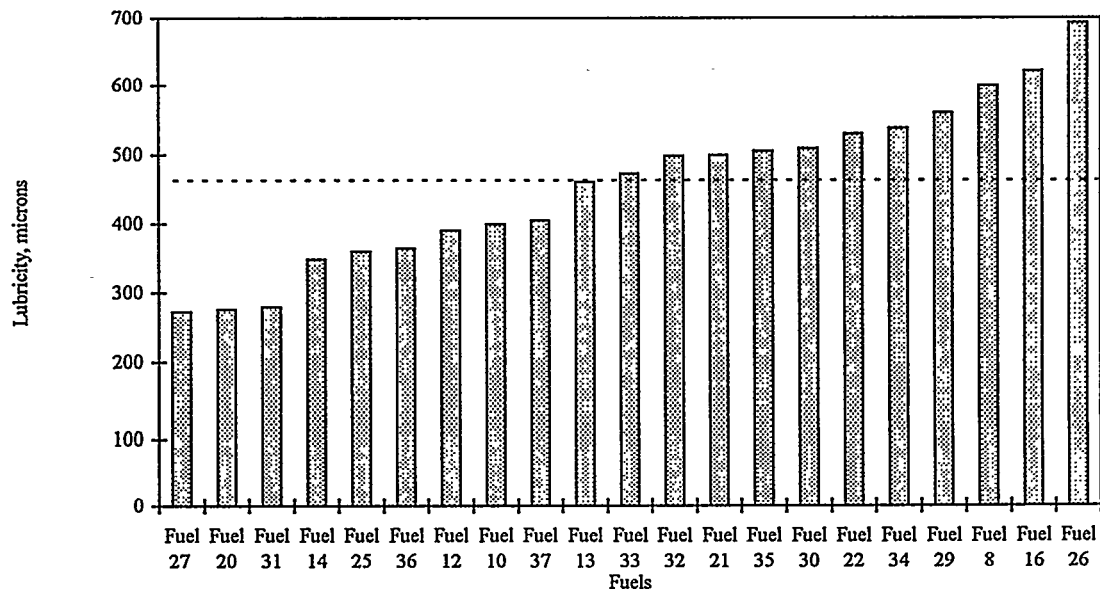Figure 1: Lubricity wear scars for the un-additised fuels

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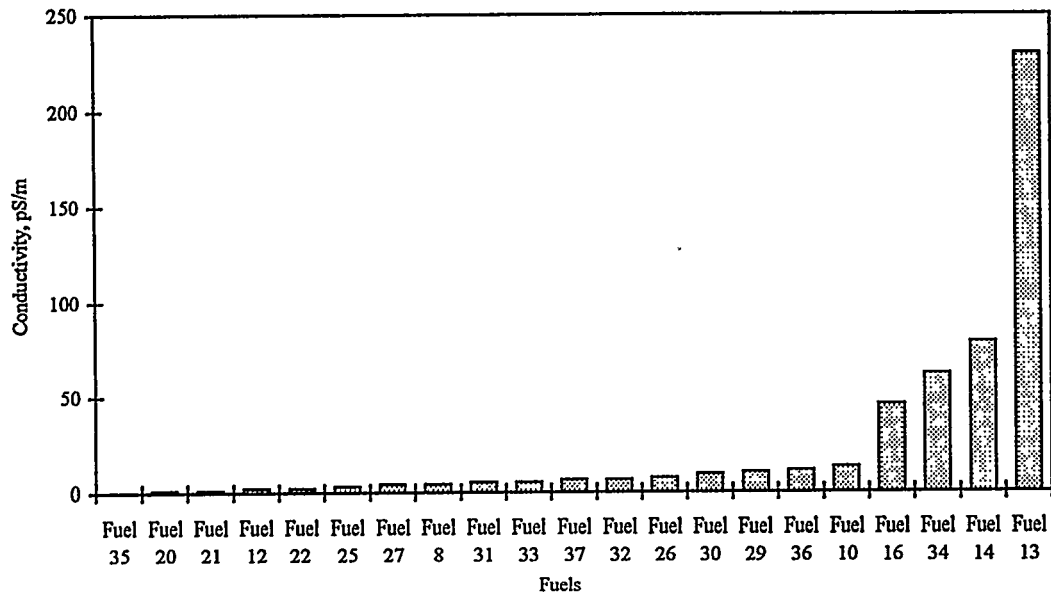Figure 2: Distribution of conductivity for the various un-additised fuels

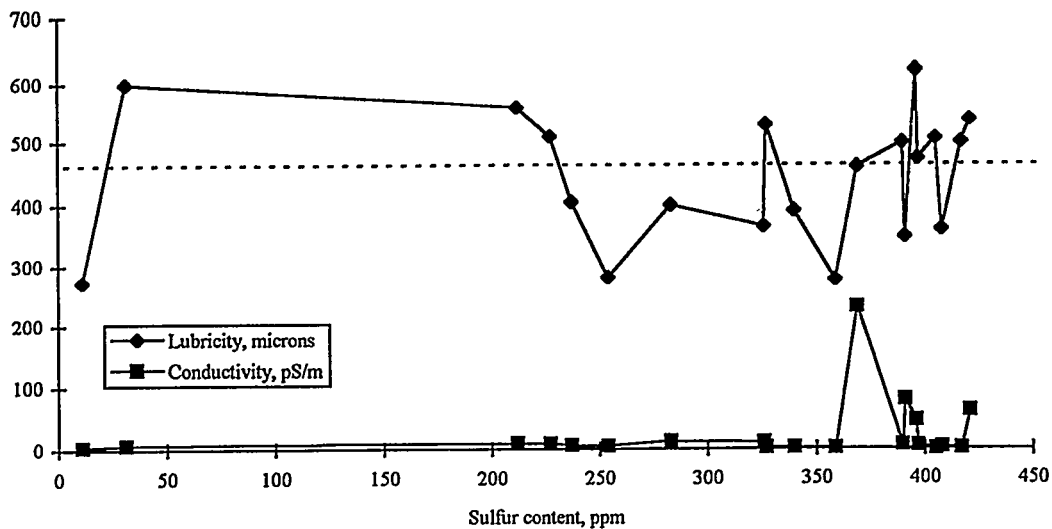Figure 3: Lubricity and conductivity versus sulfur content for the un-additised fuels

Figure 4: Lubricity versus Conductivity for un-additised fuels with lubricity greater than 460 microns
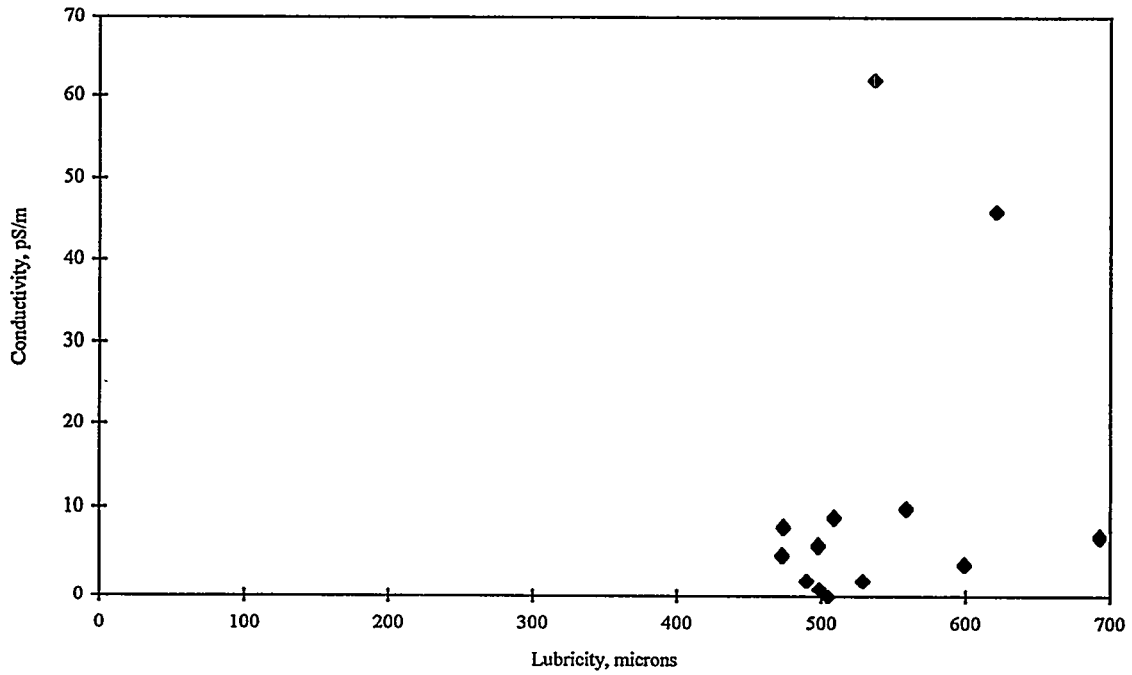

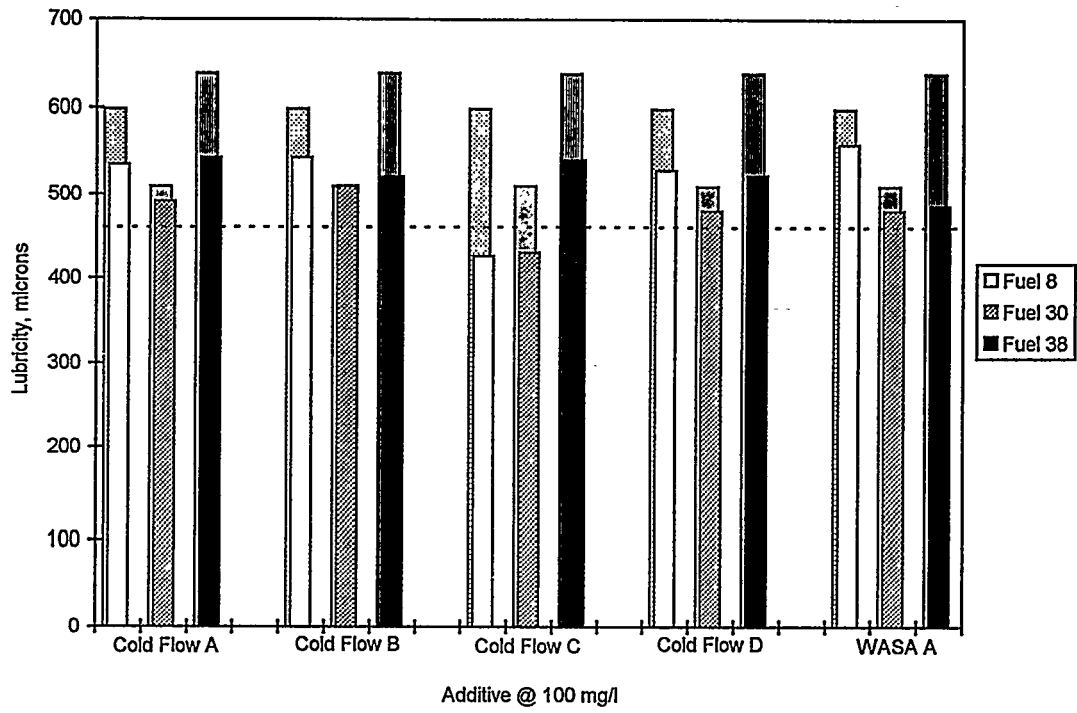Figure 5: Effect of cold flow and WASAs on lubricity of base fuels

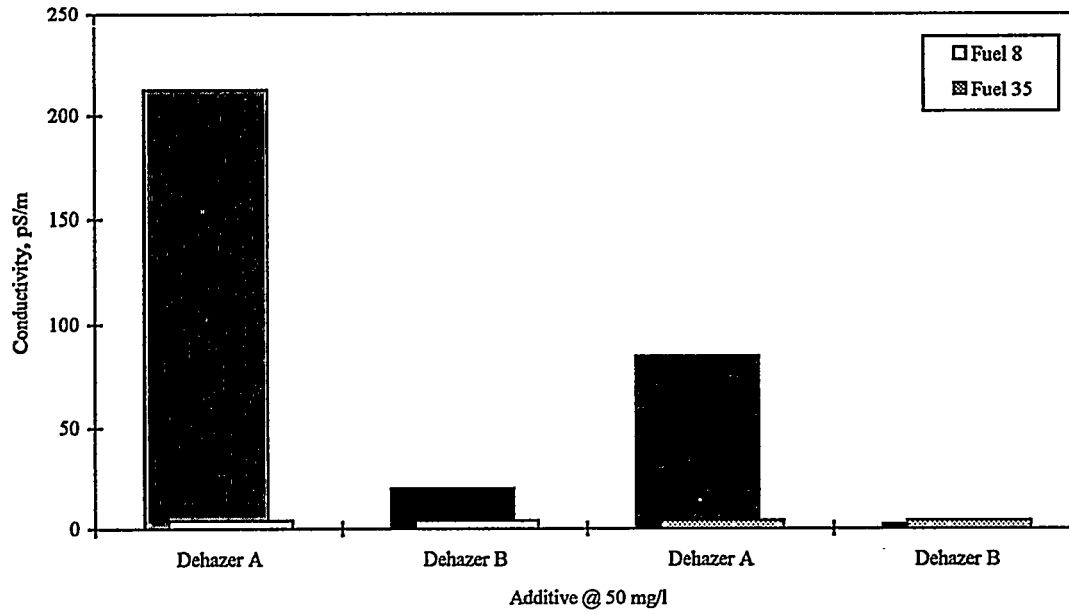Figure 6: Effect of Dehazers A and B on fuel conductivity

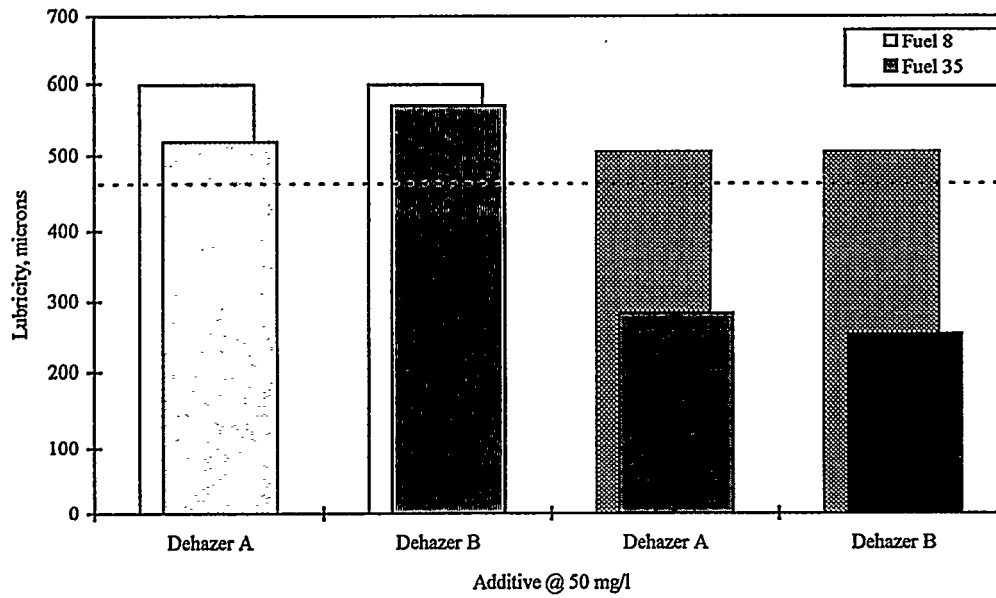Figure 7: Effect of Dehazers A and B on lubricity

THE EFFECTS OF MODERATE TO SEVERE HYDROTREATING ON DIESEL FUEL PROPERTIES AND PERFORMANCE

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Hydrotreating is currently the most viable refining process for lowering sulfur and aromatic contents of diesel streams to conform with environmental regulations. Although the individual aromatic ring saturation and desulfurization reactions occurring during hydrotreating are relatively straightforward, some of the overall changes in stream composition and properties are not. A major objective of this work was to correlate properties and composition as a function of stream origin and hydrotreating severity. The initial sample pool included seven straight run distillates (SR), eight light cycle oils (LCO), one coker distillate, and three finished diesel fuels. Individual streams or blends of two or three streams were hydrotreated to various levels of total aromatics— nominally 10, 20, and 30 percent. Compositions of feeds and products were determined by high resolution mass spectrometry (HRMS) and other methods. Properties investigated included storage stability, lubricity, cetane number, cetane index, viscosity, boiling point distribution, flash point, and specific gravity. In general, hydrotreating improved storage stability and cetane number/index, but lowered lubricity, viscosity, boiling point, and flash point. However, in some cases, notably SR and severely hydrotreated LCO, storage stability and peroxide formation were significantly worse after hydrotreating. Negative effects of hydrotreating on storage stability and lubricity were largely attributed to removal of minor polar constituents which act as antioxidants and coatings on metal surfaces. Removal of beneficial constituents appeared to be less if raw SR/LCO/coker streams were blended and then hydrotreated, rather than hydrotreated separately and then blended.

Introduction

Hydrotreating is the main refining process used to lower sulfur and aromatic contents of diesel fuels and diesel blending components below limits set by environmental regulations. Known or anticipated effects of hydrotreating on fuel properties include: improvement in storage stability, lower boiling range (especially IBP), lower flash point, lower conductivity, improvement in cetane number/index, poorer lubricity, lower viscosity, greater tendency toward peroxide formation, and of course, lower heteroatom (N, O, S) and higher hydrogen contents. Many of these effects were reported at the *5th International Conference on Stability and Handling of Liquid Fuels.*[1-4]

Hydrotreating is a mature process; many proven process designs, catalysts, etc., are available for a wide variety of applications and product specifications.[5] However, in the case of middle distillate hydrotreating, various options exist for hydrotreating individual diesel blending streams or combinations of streams depending on individual refinery configurations. One objective of this

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work was to examine the relative merits of hydrotreating individual streams versus blended streams at various levels of severity. Another was to determine interrelationships between fuel properties and composition as a function of hydrotreating severity.

Experimental

Hydrotreating. The initial sample pool included seven straight run distillates (SR), eight light cycle oils (LCO), one coker distillate, and three finished diesel fuels obtained from several refineries. Preliminary inspection properties, lubricity, and storage stability data were obtained on each stream, largely using ASTM methods. Based on those results, representative SR, LCO, and coker distillates were selected as feedstocks for subsequent hydrotreating and testing.

Hydrotreating was carried out on a small scale flow-through pilot unit containing a nominal 1/2 (i. d.) x 96 inch (1.27 x 244 cm) reactor. The reactor was loaded with equal volumes of Crosfield (Chicago, IL, USA) 599 catalyst and Crosfield 465 catalyst. The catalysts were presulfided using carbon disulfide under 450 psi (3.2 MPa) H_2 pressure using a temperature program from 25 to 343°C. All subsequent hydrotreating was performed at 343°C (650°F).

Hydrotreating conditions (pressure, space velocity) were varied to obtain, as a minimum, a sulfur content below 0.05 wt% and a targeted aromatics content ranging from 1–35 wt%. The majority of runs targeted aromatic contents ranging from 10–30 wt%. For highly aromatic streams such as LCO, H_2 pressures up to 3,000 psi (20.8 MPa) and space velocities as low as 0.25 LHSV were required to reduce aromatic contents to 10 wt% or below.

Feed and Product Testing. High resolution mass spectrometry (HRMS) was used to determine hydrocarbon types in hydrotreater feeds and products. Details of the methodology are described elsewhere.[6] Storage stability was evaluated using a combination of procedures, including oxygen overpressure (ASTM D 5304), storage at 43°C for 13 or 18 weeks (ASTM D 4625), storage at 80°C for two weeks,[7] and ambient storage for periods of up to four years. Relative lubricity was assessed using the BOCLE procedure (ASTM D 5001). Distillation curves, elemental composition, specific gravity, cloud point, pour point, flash point, viscosity, acid number, peroxide content, cetane number and cetane index were measured using standard methods.

A few feeds/products were subjected to liquid chromatographic separation into acidic, basic, and neutral types using nonaqueous ion exchange liquid chromatography.[8] The acid fractions were trifluoroacetylated and analyzed by GC/MS.[9,10] In some cases, total phenols were also estimated on whole feeds/products using infrared spectroscopy in conjunction with trifluoroacetylation.[11]

Results

Tables 1–4 list hydrotreating conditions and feed/product properties for an SR, LCO, 75/25% SR/LCO blend, and 75/17/8% SR/LCO/coker blend, respectively. In general, each series of data follows the expected trends with increasing hydrotreating severity. The following parameters increase with severity: hydrogen content, BOCLE wear scar, and cetane number/index. Conversely, heteroatom (N, O, S) content, aromatic content, boiling point, specific gravity, flash point, and viscosity decrease with increasing severity. No significant trends were evident for the following parameters: cloud point, pour point, and acid number. All products were reduced in sulfur content to well below the maximum acceptable limit of 0.05 wt% (500 ppm) for U. S. on-road diesel fuels. The catalysts employed typically reduced nitrogen content to below 1 ppm for streams hydrotreated to aromatic contents ≤ 20 wt%. Sulfur content for 10–25 wt% aromatic products typically ranged near 50 ppm.

Interpretation of storage stability data for feeds and products was complicated by the fact that results from the various accelerated and long-term stability tests did not always agree. For example, Figure 1 compares data for several untreated SR and LCO obtained by various methods. For SR, the oxygen overpressure test (90°C, 16 hr, 100 psig O_2) tended to yield higher sediment values than all other methods. However, this was not the case for LCO. For LCO, no consistent biases in results as a function of methodology were evident.

Figure 2 compares storage stability under extreme conditions (90°C, 96 hr, 100 psig O_2) for feeds and products listed in Tables 1–4 as well as for blends of hydrotreated SR products with selected hydrotreated LCO products. That is, in one case the raw SR and LCO were blended and subsequently hydrotreated (Table 3, data in middle of Figure 2); in the other, the two streams were hydrotreated independently (Tables 1 and 2, data at far right of Figure 2) and then reblended. The latter case is referred to as "reblended" in Figure 2 as well as in subsequent figures.

Taking into account the severe aging conditions and inherent uncertainty of accelerated stability tests, several conclusions are nonetheless evident from Figure 2. First, even mild hydrotreating markedly improves stability of either the 75/25% SR/LCO or 75/17/8% SR/LCO/coker blends. In fact, the stability of either blend is better than that of the hydrotreated SR alone. Secondly, severe hydrotreating of the LCO reduced its storage stability compared to mild hydrotreating. Finally, the reblended hydrotreated SR/LCO samples were significantly less stable than those from stocks which were preblended and then hydrotreated together.

Figure 3 compares storage stability at 16, 40, and 96 hours under conditions of the oxygen overpressure test (90°C, 100 psig O_2) for hydrotreated 75/25% SR/LCO blends versus reblended 75/25% hydrotreated SR/LCO streams. As seen in the figure, stability for both sample sets is acceptable up to 40 hrs after which the reblended samples alone form appreciable quantities of

sediment. Based on these test data, storage for very long periods (> 2 years) under ambient conditions would probably be necessary before any difference in storage characteristics of hydrotreated blends versus reblends would be noticeable.

Figure 4 compares peroxide formation at 96 hours under oxygen overpressure conditions. The much higher degree of peroxide formation achieved during aging of the hydrotreated SR and severely hydrotreated LCO samples compared to either the 75/25% SR/LCO or 75/17/8% SR/LCO/coker blends is quite evident and correlates nicely with the pattern of sediment formation shown earlier in Figure 2. Peroxide data were not obtained on aged reblended SR/LCO samples; in all probability their peroxide levels would have been near those observed for the aged hydrotreated SR samples.

Enhanced peroxide formation for moderate to severely hydrotreated diesel fuels has been noted previously.[1,2] Waynick and Taskila attributed this trend to increased proportions of secondary and benzylic carbons formed in the process of ring saturation.[1] Figures 5 and 6 summarize results from HRMS analysis of SR and SR/LCO/coker feeds and products, respectively. Results for other sample types were comparable. The figures clearly indicate that the main structural effect of hydrotreating was simple saturation of aromatic rings. Side reactions such as ring opening or cracking were minimal. Based on HRMS data for hydrocarbon types alone, there is no apparent reason for the improved storage stability or resistance to peroxide formation for hydrotreated SR/LCO or SR/LCO/coker blends versus reblended streams.

Figure 7 shows distributions of phenolic homologs ranging from phenol itself to alkylphenols containing up to 4 carbons in alkyl substituents in the untreated 3222 SR/3215 LCO 75/25% blend, a hydrotreated product from the blend (1,060 psig H_2, 1.25 LHSV) and a hydrotreated 3222 SR product (1,000 psig H_2, 1.0 LHSV). The distributions are based on computer reconstructed selected ion chromatograms from GC/MS analysis of trifluoroacetylated acid concentrates isolated from each sample. The peaks shown in the figure correspond to molecular ions of each homolog, which are resolved during GC elution owing to differences in boiling points attributable to both isomeric form and carbon number. The total acid yield (wt%) from liquid chromatographic separation of each sample was: 1.12 (untreated SR/LCO), 0.12 (hydrotreated SR/LCO), and 0.09 (hydrotreated SR).

The hydrotreated SR/LCO contains a much stronger distribution of alkylphenols than the hydrotreated SR. In fact, only three phenol isomers were detectable in the hydrotreated SR; furthermore, they are present at levels only slightly above that of instrumental noise. The greater phenol concentration in the hydrotreated blend may in turn be attributed to the higher phenol levels in the raw 3222 SR/3215 LCO feed, compared to the neat 3222 SR feed, because of the appreciable phenol content of LCO.[12] Thus, the improved storage stability and resistance to peroxide formation for hydrotreated products derived from feeds containing LCO and coker

streams may arise from the antioxidant properties of low levels of phenolic compounds which survive hydrotreating.[12]   Since the neat 3215 LCO was hydrotreated at very high severity conditions (Table 2) to obtain targeted aromatic concentrations, the reblended SR/LCO samples were likely deficient in phenols relative to products obtained from preblended feeds. For example, infrared analysis indicated that the phenolic oxygen content of the hydrotreated LCO containing 25 wt% aromatics (Table 2) was only 56 ppm O, whereas the product from the 75/25% 3222 SR/3515 LCO blend containing 17.9 wt% aromatics (Table 3) contained 73 ppm O. Considering that the hydrotreated LCO was in turn diluted 3:1 during reblending with hydrotreated SR, it is likely that the reblended SR/LCO samples had an appreciably lower phenol content than the corresponding hydrotreated blends.

Figure 8 relates the decrease in apparent lubricity, as measured by wear scar diameter in the standard BOCLE test (D 5001) with decreasing viscosity resulting from hydrotreating. Available data for all feeds and products in Tables 1–4 are plotted in the figure. Although viscosity is used in the figure, many other parameters which correlate with hydrotreating severity give rise to similar plots. The most important feature of Figure 8 is the fairly rapid decrease in lubricity with mild to moderate hydrotreating severity, followed by more or less constant lubricity at high severity. It is likely that this region of sharply declining lubricity primarily reflects removal of minor polar constituents, which adhere to and thus protect metal surfaces, as well as a secondary contribution from viscosity lowering. Low lubricity for hydrotreated diesel fuel has been noted previously.[3,4]

The improvement in cetane index or cetane number observed with hydrotreating (Tables 1–4) directly reflects conversion from aromatic to saturated hydrocarbon types as illustrated in Figures 5 and 6. Satisfactory correlations were developed for both parameters, where N_1-A_2 were calculated from HRMS data.

$$\text{Cetane Number} = 140.093 - 1.152\,N_1 - 1.113\,N_2 - 1.310\,A_1 - 1.299\,A_2 \qquad (1$$

$$\text{Cetane Index} = 83.354 - 0.176\,N_1 - 0.525\,N_2 - 0.580\,A_1 - 0.696\,A_2 \qquad (2$$

N_1 = 1-ring naphthenes
N_2 = $\geq$ 2-ring naphthenes
A_1 = compounds with 1-aromatic ring
A_2 = compounds with $\geq$ 2-aromatic rings + all sulfur compounds

Figure 9 illustrates the correlation for cetane index obtained using Equation 2 applied to streams in Tables 1–4 as well as for other fuels included in the overall research program. Other researchers have developed similar correlations for cetane index and related fuel properties.[12–16]

Discussion

Although hydrotreating generally improves diesel fuel properties and overall quality, negative effects can also arise, particularly with severe hydrotreating or with processing straight run distillates. For example, mild hydrotreating improves storage stability of LCO largely through removal of heteroatomic species such as alkylindoles and phenalenones which are believed to cause sediment formation in raw LCO.[17,18] However, in the case of moderate to severe hydrotreating required to meet environmental regulations, particularly limits on aromatic content, diesel storage stability can actually worsen through concurrent production of hydrocarbon types prone to peroxide formation as well as removal of beneficial polar compounds such as alkylphenols which can act as antioxidants. In this work, even mild hydrotreating of neat SR was detrimental to storage stability (Figure 2), whereas it significantly improved stability of blends containing LCO. Generally, in the case of neat SR or other streams with inherently good storage stability, the negative effects of antioxidant removal usually outweighed any potential benefits of hydrotreating. This same generalization holds for lubricity, where removal of minor polar constituents as well as lowering viscosity through ring saturation significantly lowered the fuels' lubricating ability.

Loss of potentially beneficial polar compounds appears to be less in the case of hydrotreating blends rather than when individual refining streams are treated separately. Further investigation and exploitation of this point may become more critical if environmental restrictions on diesel become more stringent. On the other hand, bulk properties such as cetane number or cetane index, which depend solely on hydrocarbon composition, should be relatively insensitive to minor changes in process methodology.

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Table 1. Properties of Feed and Hydrotreated SR3222

	Feed	Product Stream				
Hydrotreating conditions						
H$_2$ pressure, psi		750	750	1000	1500	1750
H$_2$ pressure, MPa		5.3	5.3	7.0	10.4	12.2
LHSV		1.5	1.5	1.0	1.1	1.0
Total aromatics by HRMS, wt%	32.1	26.6	25.8	19.1	13.1	8.8
Simulated distillation, °F (D 2887)						
10% off	447	431	434	418	418	409
50% off	581	573	574	566	566	561
90% off	688	677	677	674	674	673
Elemental composition,						
C, wt%	86.6	87.0	87.1	86.5	86.5	86.0
H, wt%	13.3	13.5	13.4	13.7	13.8	14.0
N, ppm	177	3.3	8.1	<1	<1	<1
S, ppm	5,800	61	54	40	73	6
Specific gravity @ 60°F (D 4052)	0.8674	0.8547	0.8554	0.8490	0.8470	0.8440
Cloud pt, °F (D 2500)	22	20	20	18	20	16
Pour pt, °F (D 97)	5	15	5	0	0	-5
Flash pt, °C (D 93)	85	67.5	69.5	58.5	66.5	55
Viscosity, cSt @ 100°F	4.500	4.115	4.154	3.877	3.944	3.815
(D 445), cSt @ 210° F	1.510	1.437	1.433	1.404	1.415	1.408
Acid No. mgKOH/g (D 664)	0.03	0.01	<0.01	0.02	0.02	0.02
BOCLE wear scar, mm (D 5001)	0.58	0.74	-[a]	0.84	0.82	0.84
Cetane number (D 613)	49.0	51.1	49.0	51.3	54.4	-

[a] Dash denotes not available.

Table 2. Properties of Feed and Hydrotreated LCO3215

	Feed	Product Stream		
Hydrotreating conditions				
H$_2$ pressure, psi		2000	3000	3000
H$_2$ pressure, MPa		13.9	20.8	20.8
LHSV		1.5	0.5	0.25
Total aromatics by HRMS, wt%	78.7	25.5	12.8	1.2
Simulated distillation, °F (D 2887)				
10% off	485	405	385	381
50% off	596	529	513	506
90% off	757	704	687	680
Elemental composition,				
C, wt%	88.3	87.4	87.0	85.5
H, wt%	10.4	13.1	13.6	14.0
N, ppm	1100	<1	<1	<1
S, ppm	13,000	114	172	3
Specific gravity @ 60°F (D 4052)	0.9488	0.8718	0.8571	0.8482
Cloud pt, °F (D 2500)	-ᵃ	34	38	36
Pour pt, °F (D 97)	-	25	30	30
Flash pt, °C (D 93)	116	50.5	50	49.5
Viscosity, cSt @ 100°F	5.878	3.616	3.170	3.116
(D 445), cSt @ 210° F	4.729	1.323	1.242	1.230
Acid No. mgKOH/g (D 664)	<0.01	0.02	0.02	0.02
BOCLE wear scar, mm (D 5001)	0.55	0.84	0.84	-
Cetane number (D 613)	25.9	44.1	46.3	48.4

ᵃ Dash denotes not available.

Table 3. Properties of Feed and Hydrotreated SR3222/LCO3215 Blend (75/25%)

	Feed	Product Stream			
Hydrotreating conditions					
H$_2$ pressure, psi		750	1060	1875	2250
H$_2$ pressure, MPa		5.3	7.4	13.0	15.6
LHSV		1.5	1.25	0.95	0.8
Total aromatics by HRMS, wt%	43.7	38.8	30.1	17.9	12.2
Simulated distillation, °F (D 2887)					
10% off	456	440	432	420	412
50% off	585	573	567	559	554
90% off	705	692	686	679	681
Elemental composition,					
C, wt%	86.2	86.8	86.5	86.7	86.5
H, wt%	12.5	13.1	13.3	13.9	13.8
N, ppm	514	62	9	<1	<1
S, ppm	7000	104	49	50	52
Specific gravity @ 60°F (D 4052)	0.8878	0.8700	0.8653	0.8570	0.8519
Cloud pt, °F (D 2500)	_a	20	22	30	24
Pour pt, °F (D 97)	15	15	20	25	20
Flash pt, °C (D 93)	91	63	60	56	57.5
Viscosity, cSt @ 100°F	4.729	4.229	4.135	4.016	3.871
(D 445), cSt @ 210° F	1.553	1.443	1.440	1.420	1.398
Acid No. mgKOH/g (D 664)	0.02	0.01	<0.01	0.01	<0.01
BOCLE wear scar, mm (D 5001)	0.59	0.64	0.67	0.84	0.84
Cetane number (D 613)	46.3	46.2	46.4	48.5	51.3

a Dash denotes not available.

Table 4. Properties of Feed and Hydrotreated SR3222/LCO3215/Coker 3237 Blend (75/17/8%)

	Feed	Product Stream			
Hydrotreating conditions					
H_2 pressure, psi		750	1060	1875	2250
H_2 pressure, MPa		5.3	7.4	13.0	15.6
LHSV		1.5	1.25	0.95	0.80
Total aromatics by HRMS, wt%	43.6	31.0	27.7	16.6	10.5
Simulated distillation, °F (D 2887)					
10% off	443	419	418	411	403
50% off	579	565	563	556	550
90% off	694	683	683	678	675
Elemental composition,					
C, wt%	86.6	86.7	87.0	86.6	86.2
H, wt%	12.9	13.4	13.7	14.0	13.9
N, ppm	469	38	7	<1	<1
S, ppm	8900	93	57	29	26
Specific gravity @ 60°F (D 4052)	0.8804	0.8630	0.8599	0.8526	0.8473
Cloud pt, °F (D 2500)	-[a]	24	18	28	28
Pour pt, °F (D 97)	10	20	10	20	20
Flash pt, °C (D 93)	86	60	66	64	59.5
Viscosity, cSt @ 100°F	4.354	3.909	3.886	3.816	3.697
(D 445), cSt @ 210° F	1.470	1.388	1.390	1.386	1.362
Acid No. mgKOH/g (D 664)	0.03	0.01	0.01	<0.01	0.01
BOCLE wear scar, mm (D 5001)	0.57	0.65	-	-	0.85
Cetane number (D 613)	43.0[b]	51.2[b]	50.7[b]	53.2[b]	53.6[b]

[a] Dash denotes not available.

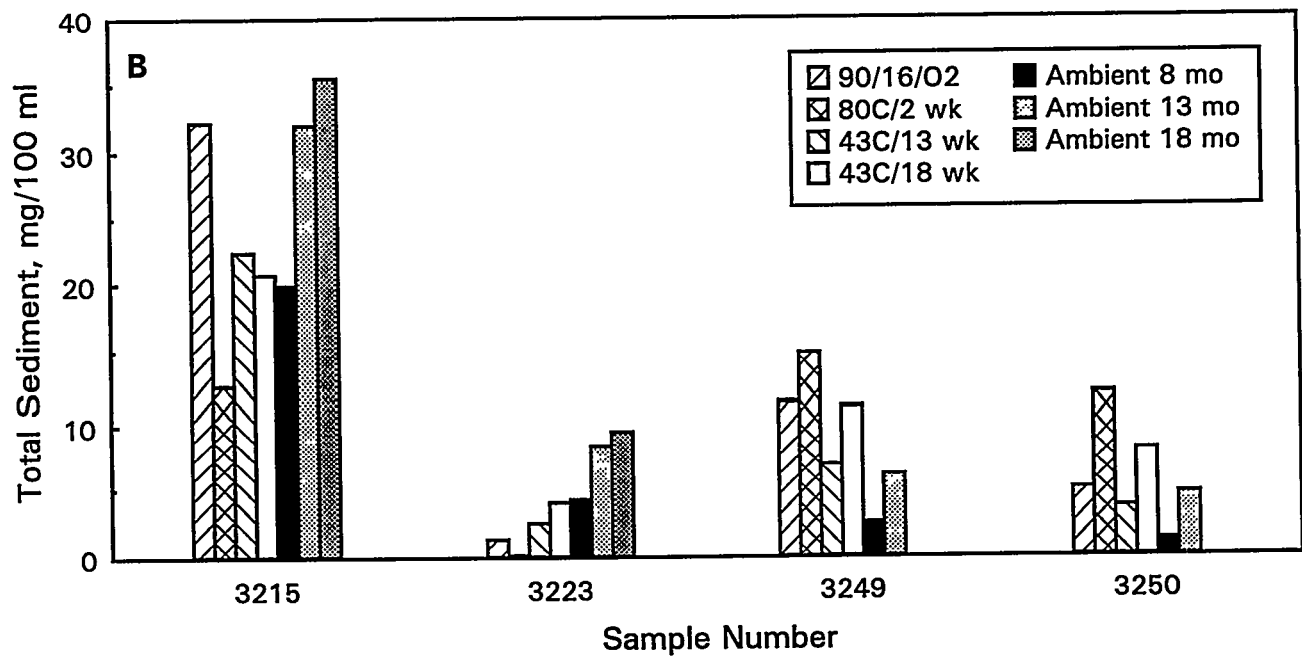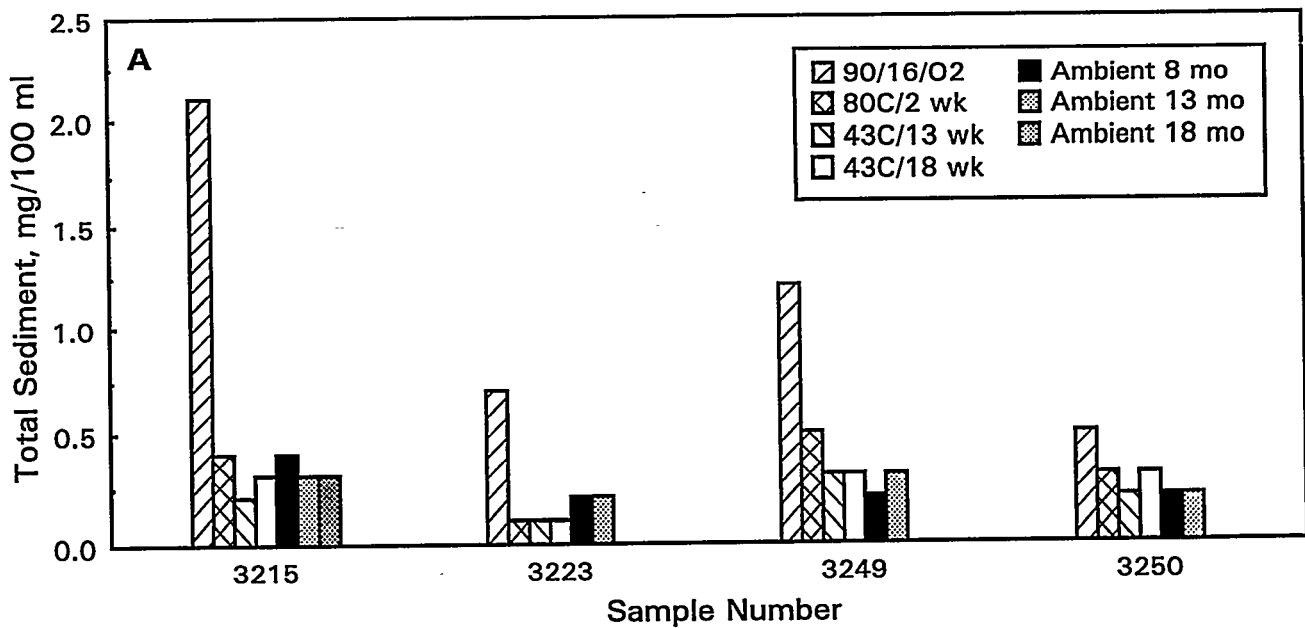[b] Calculated using equation 1.

Figure 1. Comparison of storage stability test methods for
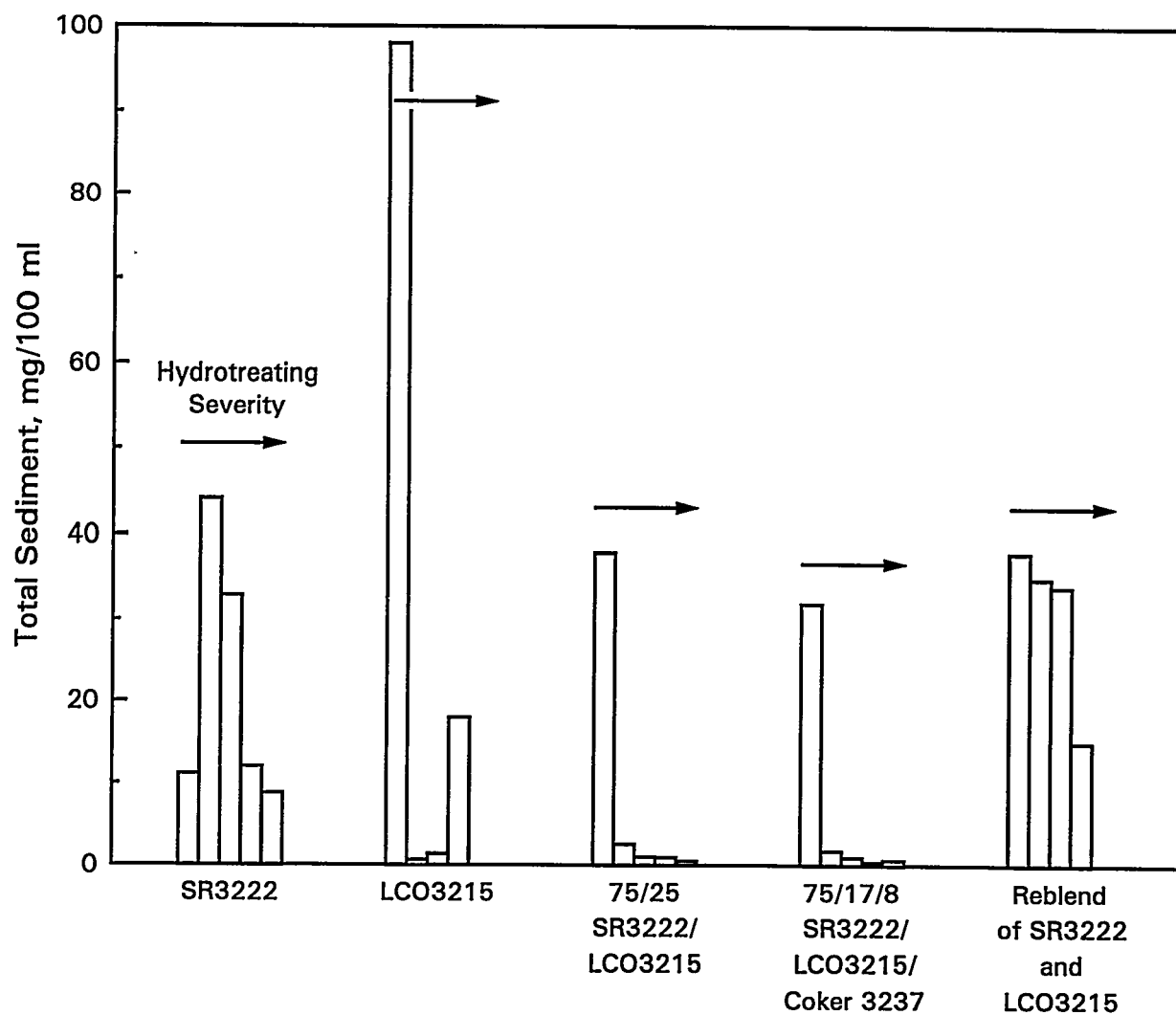(A) Straight Run and (B) LCO Streams

Figure 2. Storage stability as a function of hydrotrating severity. Verticle axis is total sediment after 96 hours at 90° C/ 100 psig Oxygen (ASTM D5304)
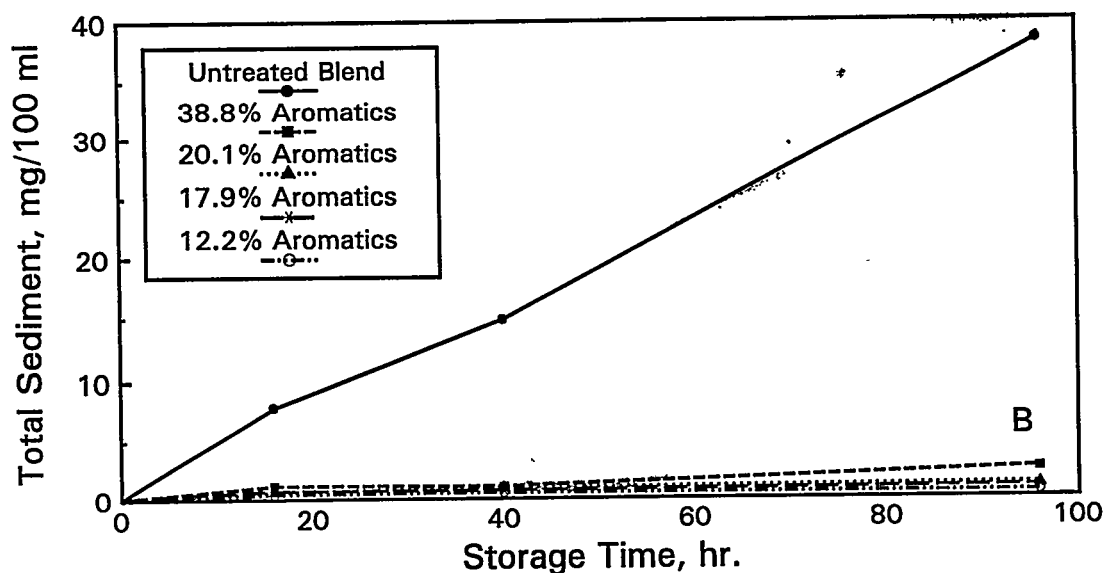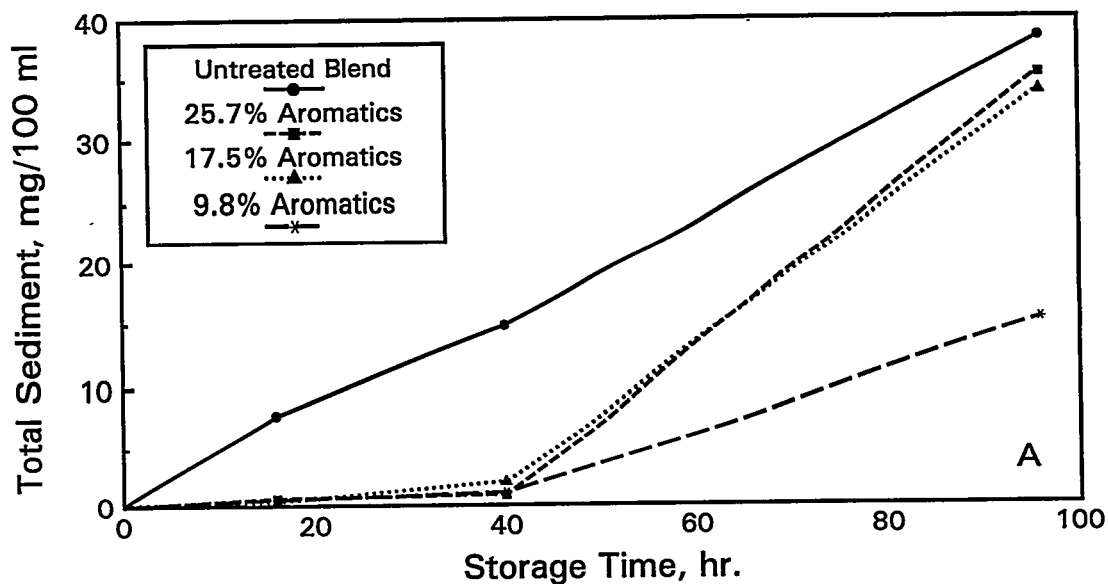
Figure 3. Comparison of storage stability of 75/25 SR3222/ LCO3215 (A) hydrotreated separately, reblended and aged vs. (B) blended, hydrotreated and aged
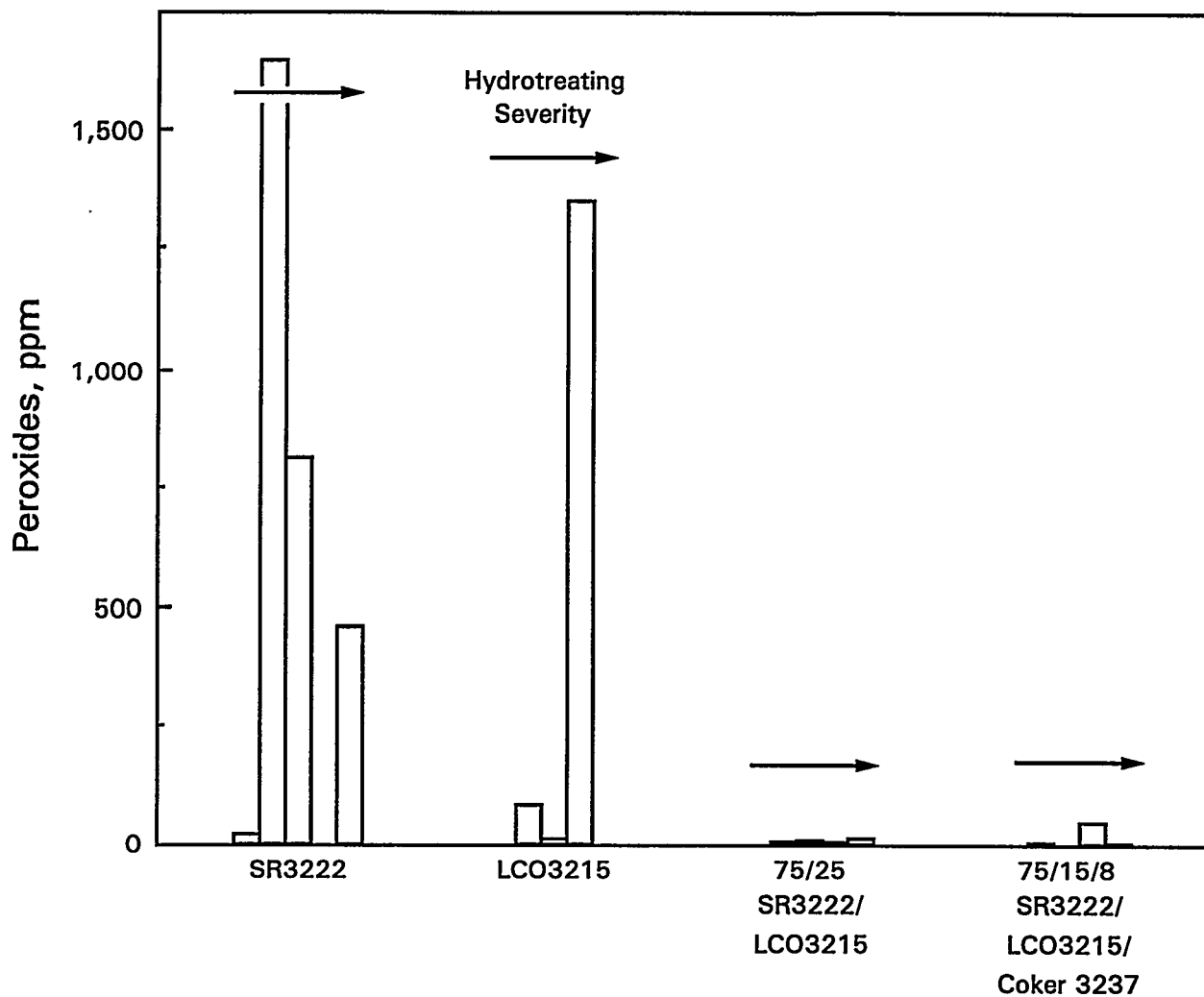
Figure 4. Peroxide formation as a function of hydrotreating
severity. Verticle axis is total peroxides after
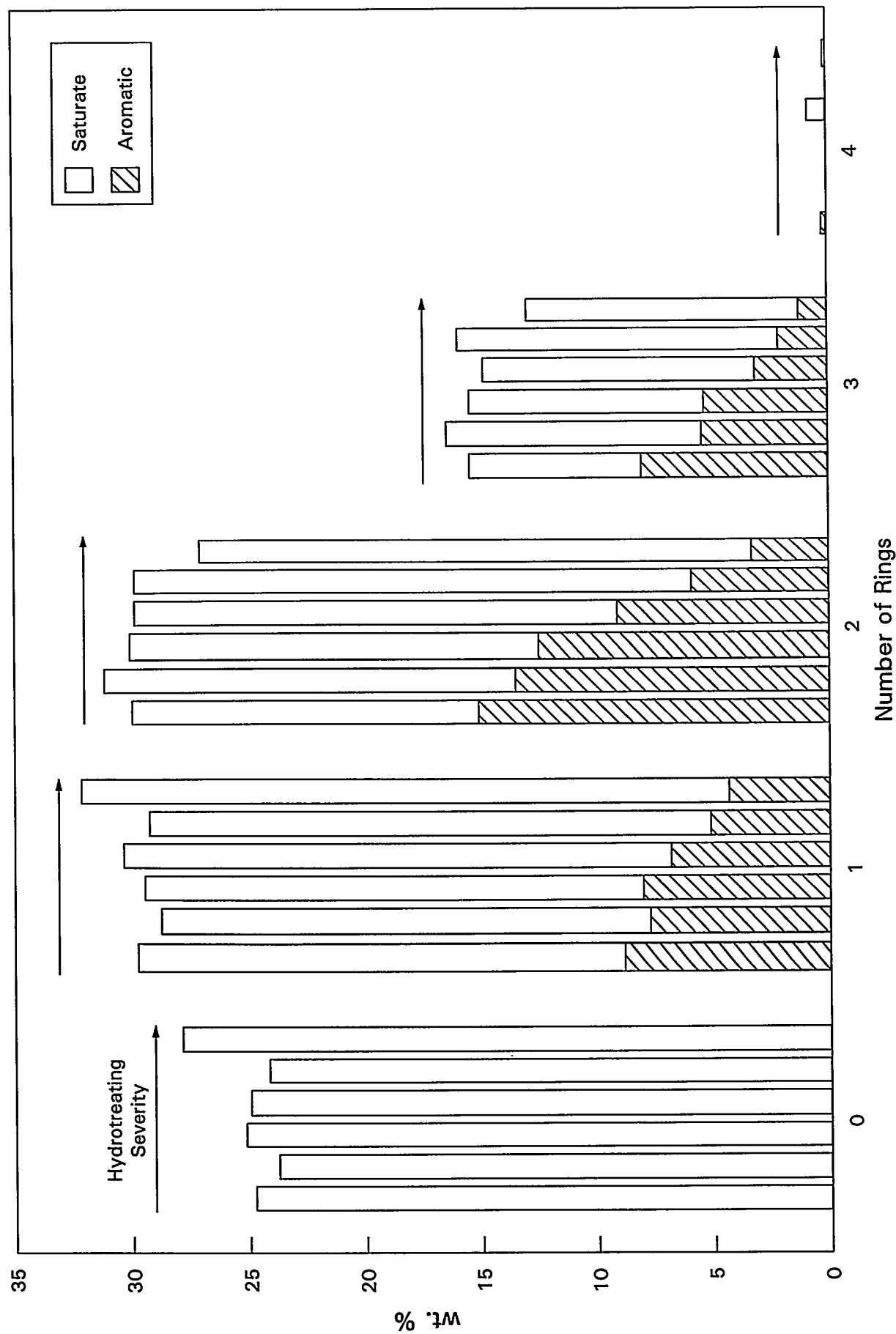96 hours at 90° C/100 psig oxygen (ASTM D5304)

Figure 5. HRMS composition of SR3222 as a function hydrotreating severity (data for feed at far left for each ring number)

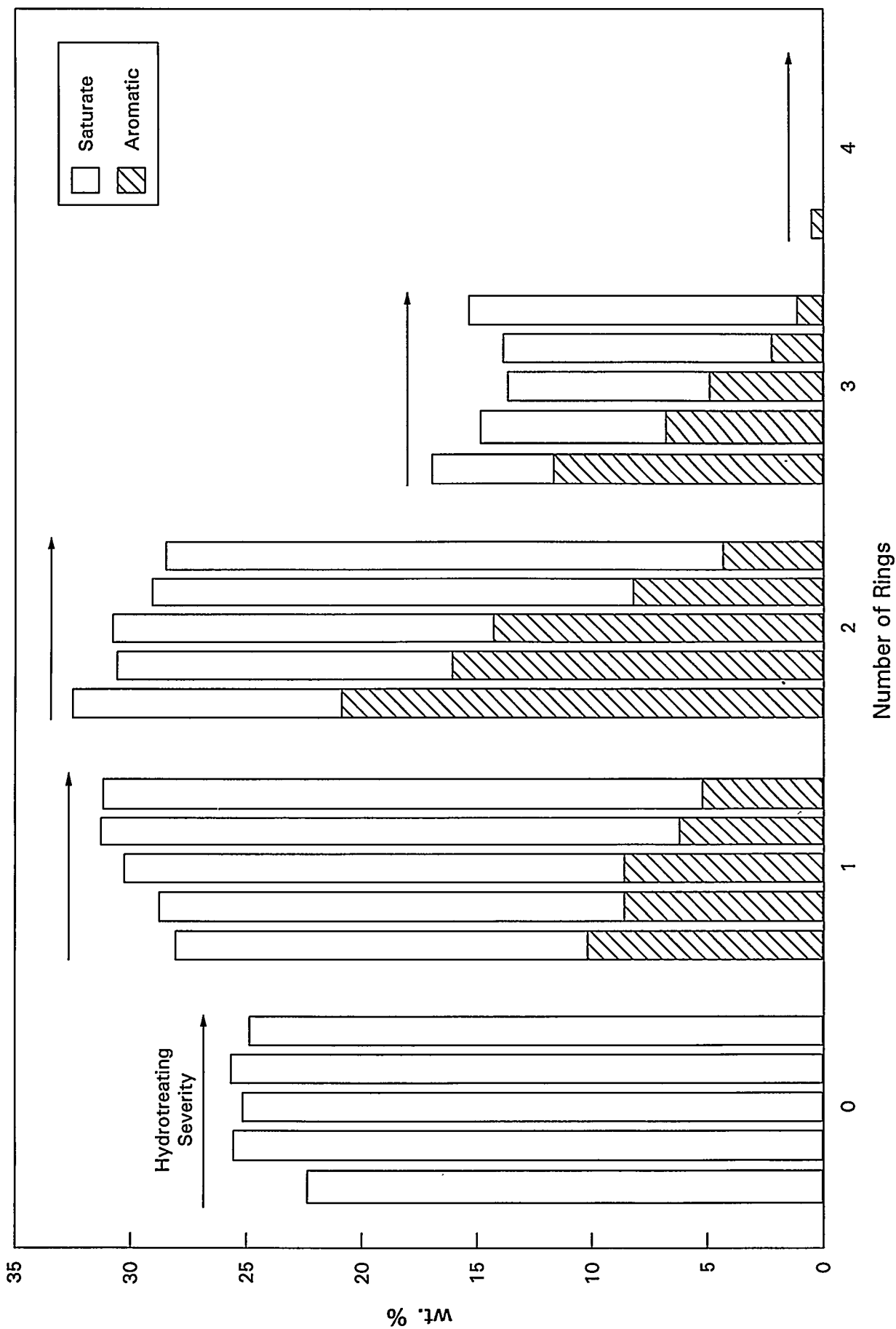Figure 6. HRMS composition of SR3222/LCO3215/Coker3237. (75/17/8%) blend as a function of hydrotreating severity (data for feed at far left for each ring number)

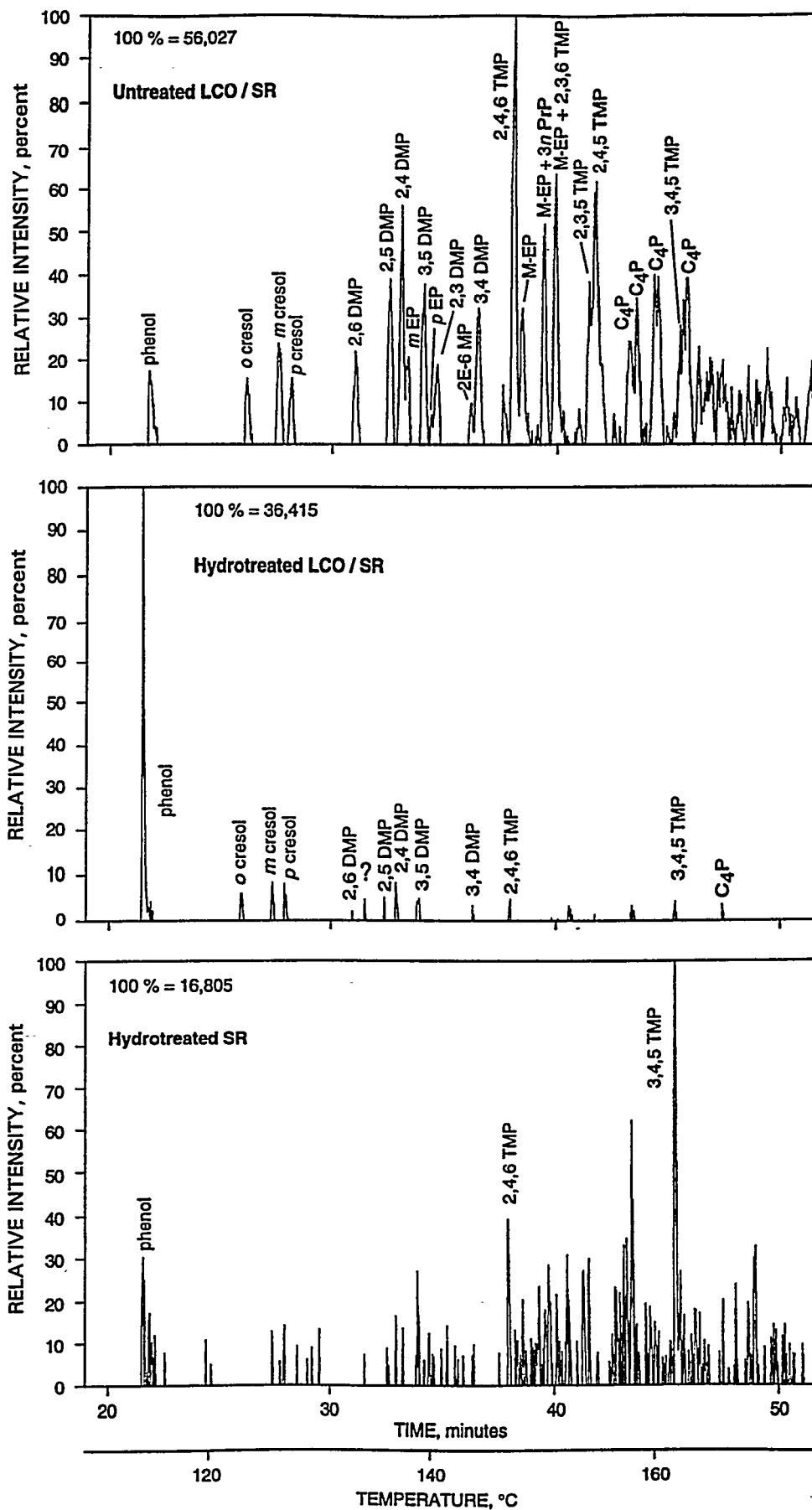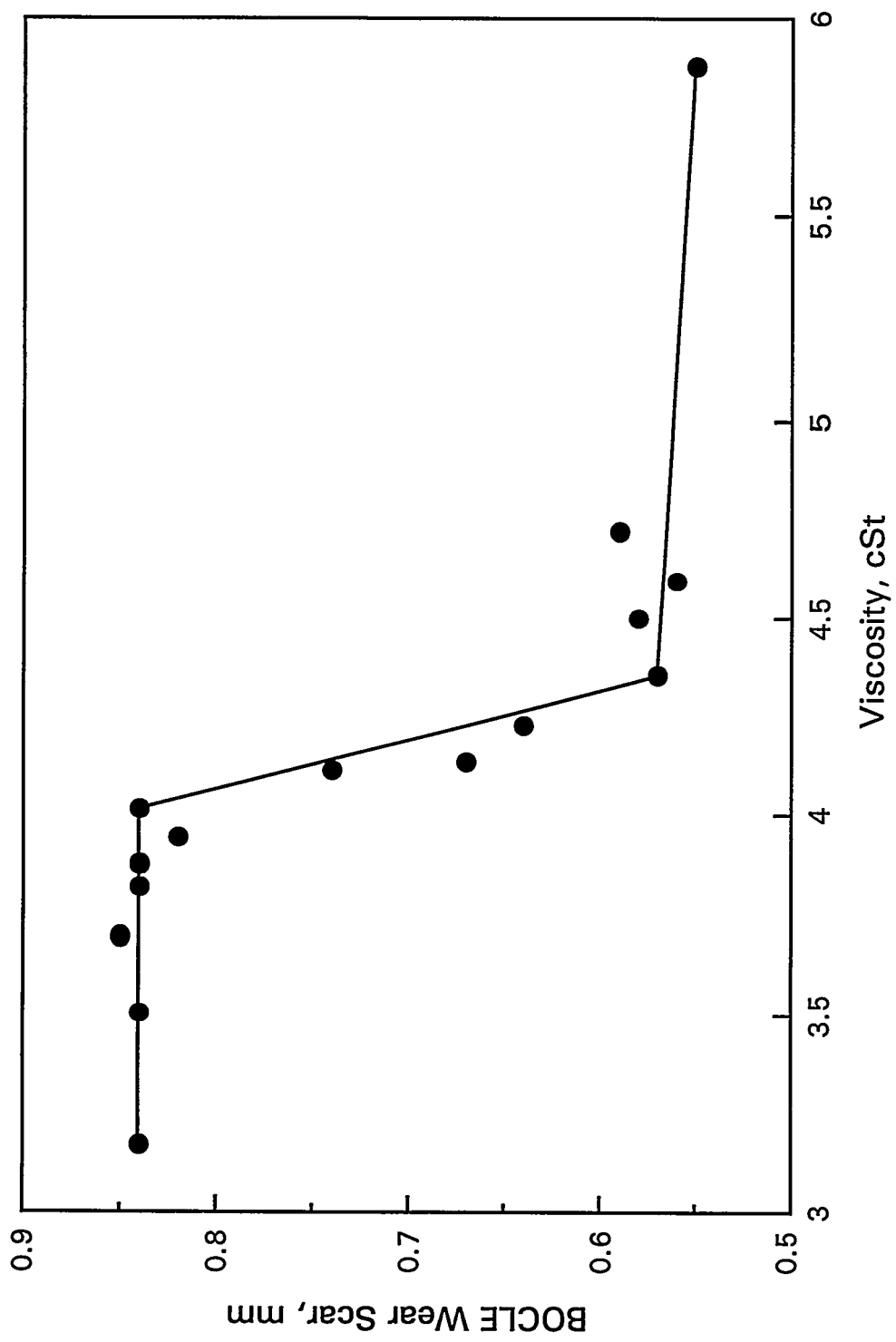Figure 7. GC/MS selected ion chromatograms showing phenol distributions.
DMP = dimethylphenol, TMP = trimethylphenol, C_4P = C_4-alkylphenol

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Figure 8. Correlation of lubricity (BOCLE) versus viscosity at 100 ° F for feed and hydrotreated streams
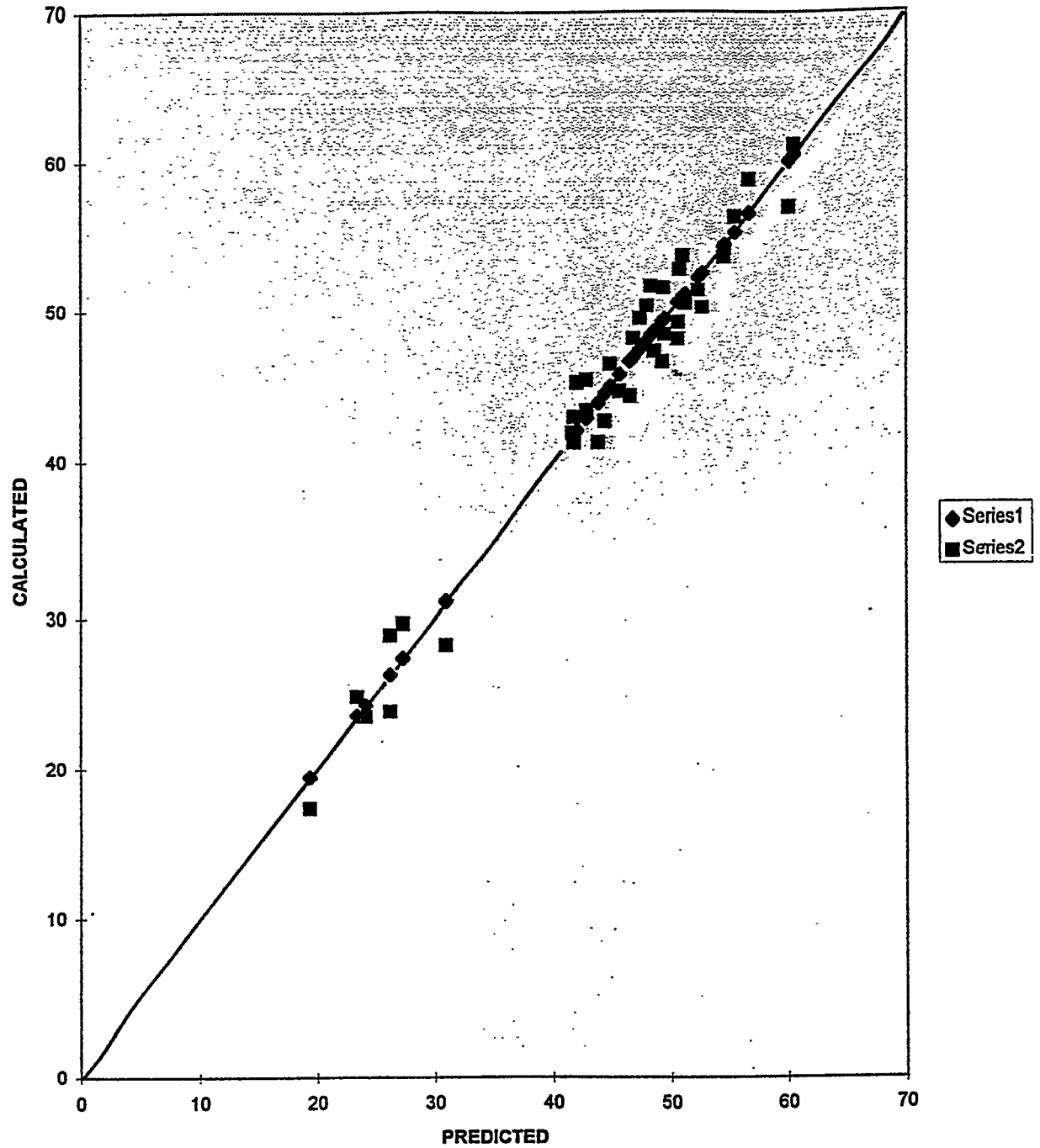
CETANE INDEX CORRELATION

Figure 9. Comparison of cetane index calculated via ASTM D976 versus that predicted from HRMS hydrocarbon type analysis

EFFECT OF INCREASINGLY SEVERE HYDROTREATING

ON STABILITY-RELATED PROPERTIES OF NO. 2 DIESEL FUEL

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ABSTRACT

This paper reports the effect of increasingly severe hydrotreating on the compositional and stability-related properties of four No. 2 diesel fuels ranging in sulfur level from 222 ppm to 11 ppm. The effect of the most commonly used phenylene diamine antioxidant on fuel properties was also determined. Denitrification was essentially complete when the fuel sulfur level had been reduced to 86 ppm. At 222 ppm sulfur (similar to current U.S. low sulfur diesel fuels), fewer multi-ring but similar total aromatics were present compared with the high sulfur feed. With further sulfur removal, total aromatics were reduced as well, due to removal of mono-ring aromatics. Storage stability was excellent for all four fuels. Hydroperoxide susceptibility appeared adequate to excellent under conditions similar to commercial transport and storage. Phenylene diamine (PDA) antioxidant appeared to be directionally detrimental to storage stability for diesel fuels with sulfur levels as low as 86 ppm. However, storage stability was still acceptable, due to the excellent stability of the non-additized diesel fuels. Tests currently used in many refinery, pipeline, and end-user specifications did not detect the adverse effect of PDA antioxidants on storage stability. Additional information concerning diesel fuel instability chemistry was also demonstrated.

INTRODUCTION

Before October 1993, No. 2 distillate fuel sold in the United States contained 0.2-0.4%(wt) sulfur.[1-3] As of October 1993, No. 2 distillate fuel used for on-highway vehicles was required to have a sulfur level no greater than 0.05%(wt), i.e. 500 ppm(wt).[4-5] This sulfur level reduction has been achieved by increasing the severity by which diesel fuel feedstocks are hydrotreated. Several areas of concern have arisen over these increasingly hydrotreated No. 2 distillate fuels:

1. Potential decreased storage stability.

2. Potential increased hydroperoxide susceptibility.

3. Potential decreased cold flow properties.

Limited early data indicated that such low sulfur diesel fuels would have improved storage stability,[6-8] i.e. form less sediment and dark-colored fuel-soluble materials. A more recent study verified this conclusion.[9]

However, there have been concerns that resulting low sulfur diesel fuels may exhibit increased hydroperoxide susceptibility, i.e. from increased levels of hydroperoxides upon storage. This concern stems from problems observed in some hydrotreated jet fuels over the last thirty years.[10-12] Increased hydroperoxide levels found in those fuels were reputed to have degraded elastomers in jet aircraft fuel systems. Those and other similar observations led to a military specification requiring all hydrotreated jet fuels to contain antioxidants,[13-14] and limiting initial peroxide number to less than one milliequivalent active oxygen per kilogram of fuel (meq O/Kg).

A few studies have been published to date concerning the effect of hydrotreating on No. 2 diesel fuel peroxidation tendency.[7-8] One study found that high sulfur diesel fuel samples taken from the field had no measurable hydroperoxides. Researchers concluded that high sulfur diesel fuel was stable with respect to hydroperoxide formation. The study also observed that initial hydroperoxide levels in fresh low and high sulfur diesel fuel were essentially zero. However, low sulfur diesel fuel was much more susceptible to form hydroperoxides under accelerated storage conditions.[8] This increased hydroperoxide susceptibility did not correlate with increased storage instability (sediment formation and color darkening); all low sulfur diesel fuels had excellent storage stability as measured by the reliable ASTM D4625 (13 week, 43 C, 1 atm air) procedure. Another study showed that hydrotreated diesel fuels exhibited increased oxygen uptake, and that this tendency became more pronounced as the severity of hydrotreatment was increased.[7] The most significant and most recent study was reported at the 5th International Conference on Stability and Handling of Liquid Fuels in Rotterdam.[9] This report indicated that commercial U.S. low sulfur diesel fuels did have increased hydroperoxide susceptibility compared with commercial

U.S. high sulfur diesel fuels under sufficiently accelerated conditions. However, no such tendency was observed under ordinary field conditions of fuel transport and storage.

One obvious method to control any perceived increase in hydroperoxide susceptibility would be to use traditional antioxidants. However, use of certain aryl antioxidants (phenylene diamines) in high sulfur diesel fuels has been shown to greatly decrease storage stability by increasing the amount of sediment formed.[15] The effect of those antioxidants in low sulfur diesel fuel has not yet been established in the literature. Nonetheless, at least one major fuel antioxidant supplier has suggested using those antioxidants in low sulfur diesel fuel to address perceived increased hydroperoxide susceptibility.[16]

The concern over reduced cold flow properties stems in part from a reduction in the aromatic profile of the diesel fuel resulting from increased hydrotreating. However, little work has been reported to determine if increased hydrotreating will negatively impact cloud point and pour point.

The primary objective of the work reported in this paper was to evaluate an already available set of four hydrotreated No. 2 diesel fuels made from the same feedstock. Since finished fuel sulfur levels began at 222 ppm and went as low as 11 ppm, trends in fuel properties as a function of hydrotreating severity could be examined. Resulting data could provide useful insight not possible by looking only at commercial U.S. low sulfur (LS) and high sulfur (HS) diesel fuels. Also, the data could provide important information for future U.S. diesel fuel production, which might be required to attain even lower sulfur levels. A secondary objective was to evaluate the effect of the most commonly used aryl amine fuel antioxidant on the stability of LS No. 2 diesel fuel.

EXPERIMENTAL

Fuel Samples

Each of the four No. 2 diesel fuel samples used in this work was obtained by hydrotreating a highly aromatic feedstock having the following gross compositional properties as measured by mass spectrometry:

Aromatics, %(wt)	
Total	46.5
Mono	17.6
Di	23.5
Tri	2.9

The hydrotreating was done in two stages as follows:

Stage	First	Second
Catalyst	Co/Mo	Pt/Pd on Mol. Sieve
Psig H2	500	900
lhsv	2.1	1.0
Temperature, °F	650	500-550
H2 Circulation rate, scf/bbl	1,500	5,000

The samples were about one year old when testing began. During that year, they had been stored in clear, sealed glass bottles at ambient laboratory temperature.

Portions of the four fuel samples were additized with 50 ppm of N,N'-di-sec-butyl-p-phenylene diamine antioxidant. This antioxidant and its concentration were chosen since they were used in the original published work showing an adverse effect on HS diesel fuel storage stability.[15,17]

Tests

The four additive-free fuel samples were tested for chemical composition, physical properties, and stability using the following procedures:

Chemical Composition

Total Sulfur by Dispersive X-Ray Fluorescence (ASTM D4294)

Total Nitrogen (ASTM D4629, modified)

Basic Nitrogen (ASTM D2896)

SMORS

Phenalenones

Aromatics by Mass Spectrometry

Physical Properties

Initial Color (ASTM D1500)

Cloud Point (ASTM D2500)

Pour Point (ASTM D97)

Stability

Oxidative Stability (ASTM D2274)

Nalco Pad Stability

Storage Stability (ASTM D4625)

40-Hour Stability

Initial Peroxide Number (ASTM D3703)

Peroxide Number after ASTM D4625 (ASTM D3703)

Hydroperoxide Potential, CRC Procedure

Hydroperoxide Potential, Oxygen Overpressure (OP) Procedure

The ASTM procedures are well documented and will not be described further here. The Nalco Pad stability procedure measures thermal stability and has been described elsewhere.[18] ASTM D2274 and the Nalco Pad test are known not to correlate with real storage stability. However,

they were included since they continue to be used as specification tests by many diesel fuel marketers and customers. The 40-Hour Stability test is a procedure developed and used by Amoco Oil Company. Over ten years of use and hundreds of No. 2 distillate fuel samples have shown this procedure to correlate well with the reliable ASTM D4625. During this test, a 350 ml sample of distillate fuel is stressed at 80°C for 40 hours in a mineral oil bath while oxygen is bubbled through the sample at a rate of 3 liters/hour. The sample is then removed from the oil bath and allowed to cool for two hours in the dark. After determining the final color, the sample is diluted to 1, 225 ml with N-pentane, mixed thoroughly, and filtered through a tared 0.8 micron filter. After rinsing with N-pentane, the filter is dried and weighed to determine the total insolubles. Initial Peroxide Number should actually be regarded as a Peroxide Potential (susceptibility) test with a one year, ambient temperature storage period. The CRC Hydroperoxide Potential procedure was originally developed for jet fuels[19] and involves heating a 100 ml fuel sample at 65°C and 1 atmosphere air for four weeks. Peroxide number is then determined as an indication of the fuel's hydroperoxide susceptibility. The OP procedure for hydroperoxide potential was adapted from previously documented work involving jet fuels.[20] The procedure involves heating a 50 ml fuel sample at 100°C and 690 kPa (100 psia O2) for 24 hours. The peroxide number is then determined. The modification to the total nitrogen procedure was that the fuel sample was delivered to the combustion tube by a platinum boat rather than by standard syringe injection. SMORS (soluble macromolecular oxidatively reactive species) are believed to be sediment precursors,[21-22] and the procedure for measuring them has been previously documented.[23] Mass spectrometric analysis was based on the Robinson procedure as reported elsewhere.[24-25] Phenalenones are believed to be SMORS and sediment precursors,[26] and the analytical method for measuring them was based on a previously reported procedure.[27]

The additized fuel samples were evaluated with only those test procedures relating to fuel stability.

RESULTS AND DISCUSSION

Chemical Composition

Chemical composition test results are given in Table I. Total and basic nitrogen levels dropped significantly as the fuel was hydrotreated from 222 ppm to 86 ppm sulfur. Further reductions in sulfur did not result in much further decrease in nitrogen levels. No phenalenones were detected in any of the four hydrotreated diesel fuels. Since phenalenones are formed by the facile oxidation of phenalene, this indicates that the hydrotreating process was probably severe enough to reduce all phenalenes that may have been present in the original feed. Only the 222 ppm sulfur fuel had a high level of SMORS. The other three fuels had SMORS that were similar to the mean values of both LS and HS commercial U.S. diesel fuels.[9] This indicates that by hydrotreating the feed to 86 ppm sulfur, SMORS precursors were nearly removed. Since phenalenones are believed to be SMORS precursors, the absence of phenalenones and the high SMORS level in the 222 ppm sulfur fuel is interesting. It implies that either phenalenones initially present in the feed were not removed by hydrotreating and then completely reacted to form SMORS during the one year storage, or else the SMORS formed in the 222 ppm sulfur fuel were formed from precursors other than phenalenones. As will be shown in the subsequent section on stability, the latter explanation is the more likely one.

Gross hydrocarbon analysis indicated that the main change in going from the feed to the 222 ppm sulfur fuel was to reduce polycyclic aromatics to monocyclic aromatics, with no overall reduction in aromatic content. This is consistent with earlier U.S. commercial diesel fuel survey data.[9] However, as hydrotreating became progressively severe, both poly- and mono-cyclic aromatics significantly decreased.

Physical Properties

Physical property test results are given in Table II. Initial color was good for all samples and did not vary much between them. The Saybolt color measurement on two of the fuels had more to do

with color intensity than with the actual tint that is usually measured in the ASTM test. All fuels were light yellow in color.

There were no real trends for cloud point or pour point among the four diesel fuels. Specifically, cloud point and pour point did not seem to increase (become worse) as the fuel was more severely hydrotreated. This should not be too surprising since hydrotreating will not produce the straight-chain wax that contributes to diesel fuel cloud and pour point behavior. Interestingly, the significant fuel solvency change that accompanied going from 53% to 7% aromatics did not change the temperature at which visible wax precipitates (cloud point) or immobilizes the fuel (pour point). However, there is evidence reported elsewhere that suggests that such changes in aromatic content could reduce the effectiveness of cold flow improver additives in the resulting diesel fuels.[9]

Stability

Stability test results are given in Table III. Trends in hydroperoxide potential tests are displayed in Figures 1 and 2. All four samples showed excellent thermal and storage stability. As sulfur level decreased, overall results remained constant.

SMORS measured on the filtered samples after D4625 storage showed a decreasing trend with decreasing sulfur level. Only the 222 ppm sulfur and 86 ppm sulfur fuels developed significant additional SMORS relative to the amounts initially present. The 222 ppm sulfur fuel developed a quite high level of SMORS. Since all four fuels prior to D4625 testing contained no measurable phenalenones, the SMORS developed during D4625 testing must have been formed from other precursors. Also, since ASTM color did not darken much during D4625 testing, the SMORS formed must not have been very dark. This is in contrast to HS diesel fuel, where previous work indicates that SMORS contribute to aged color formation[9,28] and can correlate to aged sediment formation.[29-31] The major implication of this result is that SMORS formed in LS diesel fuel are different from SMORS formed in HS diesel fuel. In fact, the SMORS formed in HS diesel fuel may include a wide range of compounds beyond the indolyl phenalenes and indolyl phenalenones

typically suggested in the literature.[32] This wide range of compounds may include some of the SMORS formed in LS diesel fuels. Although not published, some of these conclusions concerning the diversity of SMORS in diesel fuel have been suggested by one of the researchers who first discovered SMORS.[33]

Hydroperoxide susceptibility of the four progressively hydrotreated fuels was profiled by measuring the peroxide number developed after four increasingly severe storage conditions. Based on the one year ambient data, it appears that "real world" hydroperoxide susceptibility of U.S. LS diesel fuel will improve as sulfur levels are further reduced beyond the current typical levels. Although the 7 meq O/Kg value for the 222 ppm sulfur fuel is within the "problem" range cited in prior jet fuel literature, it is unlikely that much on-highway diesel fuel will be stored for one year. Previous data indicated that commercial U.S. LS fuel (with similar sulfur levels) gave negligible levels of hydroperoxides.[9] Those fuels represented what the end user would likely receive. Whatever level of hydroperoxide stability exists in today's LS diesel fuel, further reductions in required sulfur levels should improve that stability.

Looking at the entire peroxide number data, an interesting trend can be seen, as depicted in Figures 1 and 2. As test storage conditions increased in severity, the maximum peroxide number observed among the four fuels shifted towards lower sulfur diesel fuel. For instance, the initial peroxide number (after one year storage in the laboratory) showed the highest level in the 222 ppm sulfur fuel. A similar pattern was observed for peroxides measured after D4625 storage (43°C, 13 weeks, 1 atm. air), although overall values after D4625 were higher than the initial values. However, after the even more severe CRC conditions (65°C, 4 weeks, 1 atm air), the maximum peroxide level shifted towards the 86 ppm sulfur fuel. After the most severe OP storage condition (100°C, 24 hours, 690 kPa O2), the maximum peroxide number was observed in the 39 ppm sulfur fuel, with much lower values for the other three fuels. These test results can be best understood by remembering that a fuel's peroxide number reflects the difference between the rates of two processes: hydroperoxide formation and hydroperoxide decomposition. Factors promoting hydroperoxide formation are apparently more important under the less severe test storage conditions. One such factor is the concentration of compounds most prone to

hydroperoxide formation. As indicated in several previous reports,[8,9] compounds containing benzylic carbon are among the most prone to hydroperoxide formation. As poly-cyclic aromatics are reduced to mono-cyclic aromatics with total aromatic content remaining constant, benzylic carbon content increases. This fact has been proposed as a primary reason why hydroperoxide susceptibility under accelerated conditions is greater in commercial LS diesel fuels compared with HS diesel fuels.[9] However, when hydrotreating is severe enough to reduce all aromatic species, benzylic carbon content will decrease, replaced by carbons less susceptible to hydroperoxide formation. This would explain why peroxide number decreased under lower test severity as the fuel was more severely hydrotreated.

However, as test storage conditions become more severe, factors promoting hydroperoxide decomposition apparently become more important for the less hydrotreated diesel fuels. One factor that may contribute to this effect is the concentration of naturally occurring hydroperoxide decomposers in the fuels. These compounds are removed as the fuel is progressively hydrotreated. So, at higher test severity, hydroperoxide decomposition by naturally occurring hydroperoxide decomposers will be greater in the less hydrotreated diesel fuels. Also, there is some evidence that benzylic hydroperoxides are somewhat less kinetically stable compared with non-aromatic hydroperoxides.[34-38] If so, this would also tend to increase the rate of hydroperoxide decomposition in the less hydrotreated diesel fuels.

More data will be required to fully explain how these and other factors contribute to the peroxide number trends evident in Figures 1 and 2.

It is interesting to note that the most severely hydrotreated diesel fuel (11 ppm sulfur) gave only about 0.5 meq O/Kg for all test storage conditions. Without further analysis for final oxidation products, it can only be concluded that for that fuel the rates of hydroperoxide formation and decomposition were nearly equal under all test storage conditions.

Effect of Phenylene Diamine Antioxidant

Test results on the four diesel fuels containing 50 ppm N,N'-di-sec-butyl-p-phenylene diamine are given in Table IV. Graphical displays of this data with comparative test results of the non-additized fuels (from Table III) are given in Figures 3-8. The phenylene diamine (PDA) antioxidant decreased D4625 stability for the 222 ppm and 86 ppm sulfur fuels, but had no effect on the two lowest sulfur fuels (Figure 3). However, the increased D4625 total insolubles levels for the 222 ppm and 86 ppm sulfur fuels were still within commonly recommended limits of not more than 2.0 mg/100 ml. It is unclear whether this deleterious effect of PDA antioxidant was of the same magnitude as was observed in the high sulfur diesel fuels of the previously reported study.[15] In that study, the non-additized fuels were far more unstable than the non-additized fuels evaluated here. However, the two- to sixfold increase in D4625 total insolubles observed in those high sulfur diesel fuels was within the same range as the two- to fourfold increase observed in the 222 ppm and 86 ppm sulfur diesel fuels. The role of test reproducibility in this comparison cannot be precisely determined.

The PDA antioxidant also decreased stability in the 40-Hour Stability test, but only for the 86 ppm sulfur fuel (Figure 4). However, the increase in total insolubles for that fuel was much greater for the 40-Hour Stability test than for the D4625 test. Oxidative stability as measured by D2274 and thermal stability as measured by the Nalco Pad test were not affected by addition of PDA antioxidant to the four low sulfur diesel fuels. This observation further demonstrates the unreliable nature of these two tests in predicting real world storage stability. Since these tests are the specification tests most commonly used by refineries, pipelines, and end-users to check diesel fuel stability, any decrease in stability caused by future use of PDA additives in low sulfur diesel fuels may not be detected.

SMORS could be determined for only the 222 ppm sulfur diesel fuel with PDA antioxidant. Emulsion problems prevented determinations for the other three additized fuels. The SMORS after D4625 storage for the additized 222 ppm sulfur fuel (0.5 mg/100 ml) was much less than the same non-additized fuel (11.0 mg/100 ml). The SMORS after D4625 storage for the additized

222 ppm sulfur fuel was also much less than the initial SMORS level for the same non-additized fuel (2.5 mg/100 ml). Also, the concentration of PDA in the fuel (50 ppm, or about 5 mg/100 ml) was in excess of initial or potential SMORS. This indicates that the PDA additive was more likely reacting with SMORS or SMORS precursors to form other species not measured in the SMORS procedure. Some of those new species may have been responsible for the increased D4625 total insolubles that were observed in the additized fuel.

The PDA antioxidant generally decreased final hydroperoxide levels compared with non-additized diesel fuels when stored under D4625 and CRC conditions (Figures 6 and 7). However, the additive generally increased hydroperoxide levels in the most severe OP storage conditions (Figure 8). Looking at just the additized fuels, the trends in hydroperoxide potential data parallel those observed in the non-additized fuels. As test storage severity increased, maximum peroxide number shifted towards lower sulfur diesel fuel. Under the most severe OP storage conditions, the very large peak in final peroxide number for the 86 ppm additized fuel coincides with the peak in 40-Hour total insolubles observed in the same fuel. It is interesting to note that the storage conditions in the 40-Hour Stability test and the OP Hydroperoxde Potential test are similar. It has already been observed that hydroperoxide potential and storage stability do not correlate in commercial LS diesel fuel.[9] Therefore, the apparent correlation between those two test procedures in the additized 86 ppm sulfur diesel fuel strongly suggests that PDA antioxidants are introducing new mechanisms for hydroperoxide and insolubles formation in low sulfur diesel fuel. This idea is also suggested in the SMORS data that were previously discussed. The new hydroperoxide and insolubles formation mechanisms may also be linked, although further work will be required to establish that.

CONCLUSIONS

The work reported in this paper supports the following conclusions:

1. Current U.S. commercial LS diesel fuel has less multi-ring aromatics than HS diesel fuel, but similar total aromatic levels. With further hydrotreating, total aromatics are reduced as well, due to removal of mono-ring aromatics.

2. Hydrotreating of diesel fuel to low aromatic levels does not significantly change cloud and pour points. However, fuel response to cold flow additives may be adversely affected.

3. As diesel fuels are hydrotreated to and beyond current U.S. commercial LS diesel fuel sulfur levels, storage stability remains excellent.

4. As diesel fuels are hydrotreated to current U.S. commercial LS diesel fuel sulfur levels, hydroperoxide susceptibility remains acceptable under normal conditions of commercial transport and storage. As diesel fuels are further hydrotreated, hydroperoxide susceptibility under those same conditions should improve.

5. Addition of PDA antioxidants such as N,N'-di-sec-butyl-p-phenylene diamine may reduce the storage stability of commercial LS diesel fuel, although the resulting stability may still be acceptable if the non-additized diesel fuel stability was excellent. Currently used refinery stability tests will probably not detect any decrease in diesel fuel storage stability caused by PDA antioxidants.

6. PDA antioxidants such as N,N'-di-sec-butyl-p-phenylene diamine will reduce hydroperoxide susceptibility of LS diesel fuels under conditions of commercial fuel transport and storage. However, hydroperoxide susceptibility may increase under sufficiently severe test conditions.

7. SMORS in non-additized LS diesel fuel do not significantly contribute to color darkening. Neither are they sediment precursors. LS diesel fuel SMORS are either chemically distinct from HS diesel fuel SMORS, or they are an innocuous subset of HS diesel fuel SMORS. A reaction of LS diesel fuel SMORS with PDA antioxidant may be one pathway by which PDA antioxidants cause increased sediment formation.

ACKNOWLEDGMENTS

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TABLE I

CHEMICAL COMPOSITION

Sulfur, ppm (wt)	222	86	39	11
Total Nitrogen, ppm (wt)	75	8	4	<1
Basic Nitrogen, ppm (wt)	12	<5	<5	<5
SMORS, mg/100 ml	2.5	0.4	0.4	0.2
Phenalenones, ppm (wt)	ND[1]	ND[1]	ND[1]	ND[1]
Aromatics by Mass Spec., % (wt)				
Total	53	28	13	7.2
Mono-cyclic	43	24	11	5.3
Di-cyclic	9.7	3.3	1.1	0.8
Tri-cyclic	0.6	0.7	0.9	1.0

[1] Not detected

TABLE II

PHYSICAL PROPERTIES

Sulfur, ppm (wt)	222	86	39	11
Initial Color, ASTM[1]	<1.5	-6[2]	-16[2]	<1.0
Cloud Point, °F	11	8	10	8
Pour Point, °F	5	5	0	5

[1] ASTM D1500 except where noted

[2] Saybolt color

TABLE III

STABILITY

Sulfur, ppm (wt)	222	86	39	11
Initial Color, ASTM[1]	<1.5	-6[2]	-16[2]	<1.0
Stability, D2274				
Total Insolubles, mg/100 ml	0.2	0.1	0.0	0.0
Final Color, ASTM	<2.0	<0.5	<0.5	<1.0
Nalco Pad Rating	1	1	1	1
40-Hour Stability				
Total Insolubles, mg/100 ml	0.4	0.1	0.0	0.0
Final Color, ASTM	<1.5	-6[2]	-16[2]	<1.0
Stability, D4625				
Total Insolubles, mg/100 ml	0.3	0.2	0.2	0.2
Final Color, ASTM	<2.0	<0.5	0.5	<1.0
SMORS, mg/100 ml				
Initial[3]	2.5	0.4	0.2	0.2
After D4625	11.0	1.0	0.4	0.3
Hydroperoxide Potential, meq O/Kg				
Initial[3]	7.6	1.7	0.43	0.50
After D4625	193	24	1.4	0.55
CRC[4]	26	28	2.0	0.43
OP[5]	1.3	21	199	0.68

[1] ASTM D1500 except where noted

[2] Saybolt color

[3] Measured on fuels after 1 year ambient laboratory temperature storage

[4] CRC Hydroperoxide Potential Method as described in EXPERIMENTAL section

[5] Oxygen Overpressure Method as described in EXPERIMENTAL section

TABLE IV

EFFECT OF PHENYLENE DIAMINE ANTIOXIDANT ON FUEL STABILITY[1]

| Sulfur, ppm (wt)	222	86	39	11
Initial Color	<0.5	<1.5	<1.0	<0.5
Stability, D2274				
Total Insolubles, mg/100 ml	0.1	0.2	0.0	0.1
Final Color, ASTM	<0.5	<2.0	<1.0	0.5
Nalco Pad Rating	1	1	1	1
40-Hour Stability				
Total Insolubles, mg/100 ml	0.1	2.5	0.0	0.1
Final Color, ASTM	<0.5	<1.5	<1.0	<0.5
Stability, D4625				
Total Insolubles, mg/100 ml	0.8	0.9	0.2	0.1
Final Color, ASTM	<0.5	<2.0	<1.0	<0.5
SMORS, mg/100 ml				
After D4625	0.5	ND/E[2]	ND/E[2]	ND/E[2]
Hydroperoxide Potential, meq O/Kg				
After D4625	4.2	0.45	0.42	0.49
CRC[3]	5.9	36	0.46	0.61
OP[4]	13	220	41	4.8

[1] All four fuels were additized with 50 ppm (wt) of N,N'-di-sec-butyl-p-phenylene diamine, as described in EXPERIMENTAL section

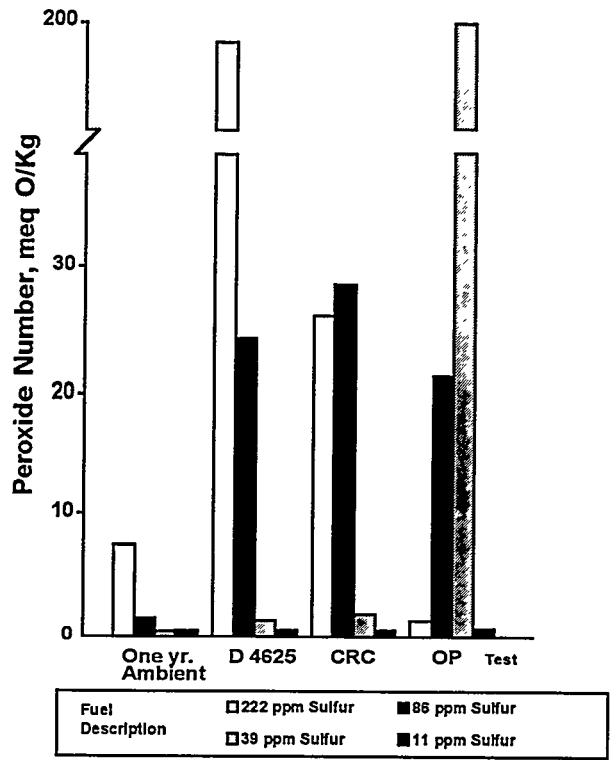[2] Not detectable due to formation of an emulsion during the test procedure

[3] CRC Hydroperoxide Potential Method as described in EXPERIMENTAL section

[4] Oxygen Overpressure Method as described in EXPERIMENTAL section

Figure 1
Effect of Hydrotreating Severity
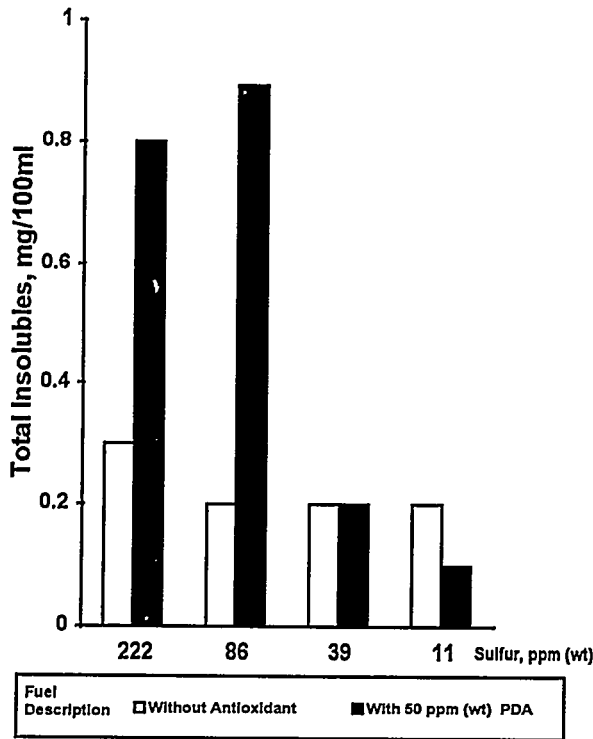### on Hydroperoxide Potential

Test Description	☐One Year, Ambient Temp	■43 Deg. C, 13 Weeks
	☐CRC	■OP
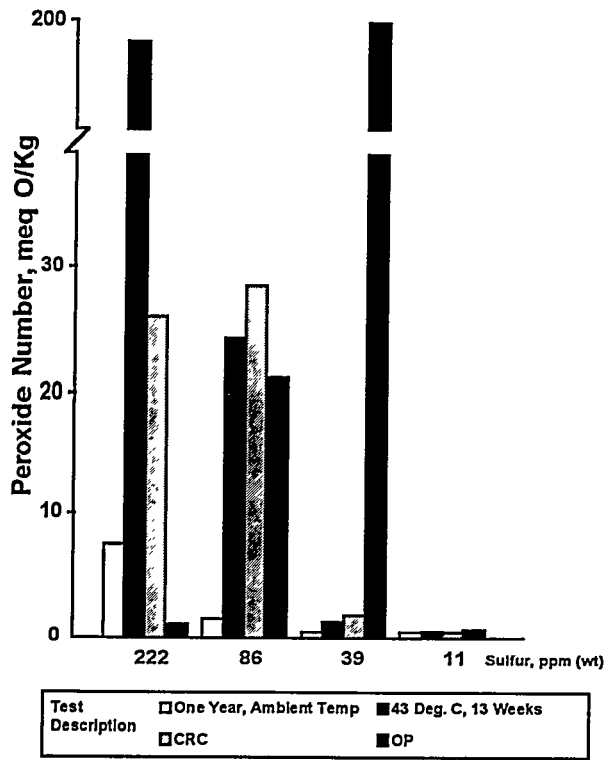
Figure 2
Effect of Test Severity
on Hydroperoxide Potential

Fuel Description	☐222 ppm Sulfur	■86 ppm Sulfur
	☐39 ppm Sulfur	■11 ppm Sulfur

Figure 3
Effect of Phenalene Diamine Antioxidant
on D4625 Total Insolubles

Fuel Description	☐Without Antioxidant	■With 50 ppm (wt) PDA

Figure 4
Effect of Phenalene Diamine Antioxidant
on 40-Hour Stability Total Insolubles

Fuel Description	☐Without Antioxidant	■With 50 ppm (wt) PDA
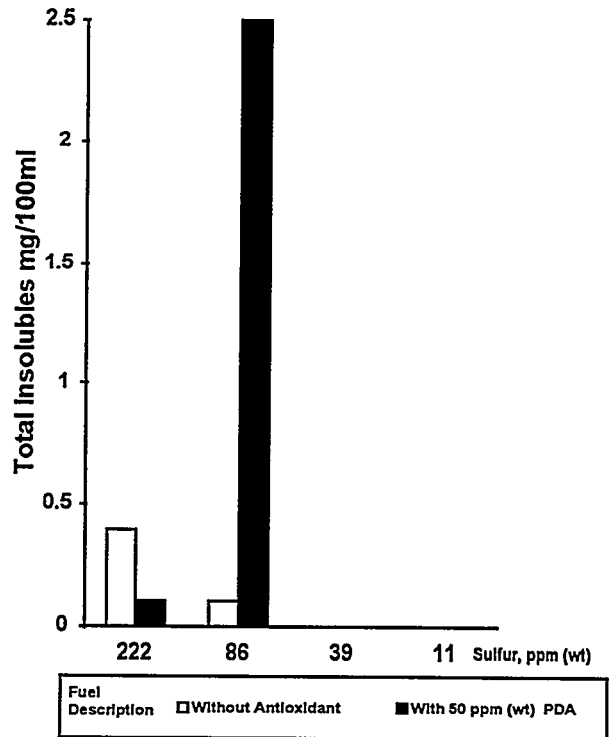
Figure 5
Effect of Phenalene Diamine Antioxidant on SMORS

Fuel Description: □ Initial without antioxidant ■ After D4625, Without Antioxidant □ After D4625, With 50 ppm(wt) PDA
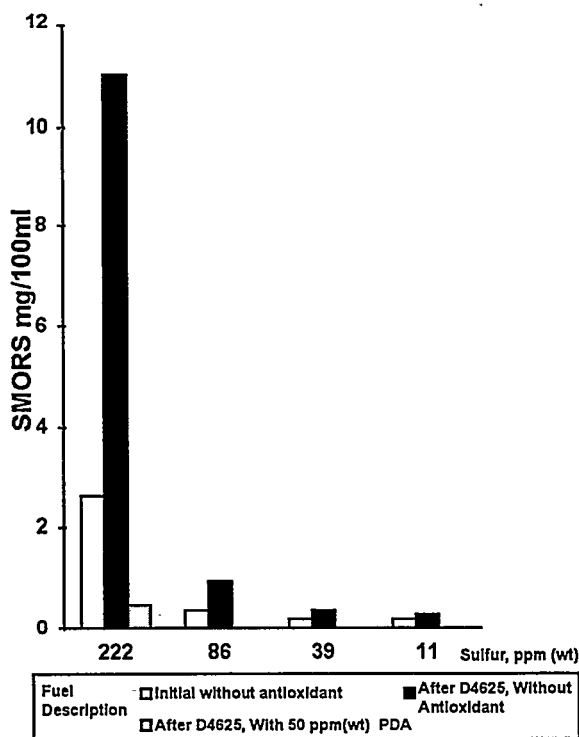
Figure 6
Effect of Phenalene Diamine Antioxidant on Hydroperoxide Potential After D4625

Fuel Description: □ Without Antioxidant ■ With 50 ppm(wt) PDA
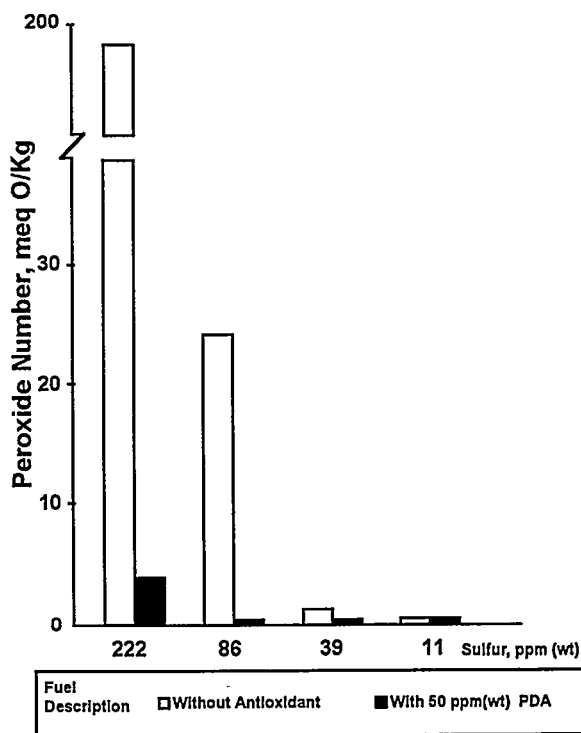
Figure 7
Effect of Phenalene Diamine Antioxidant on CRC Hydroperoxide Potential

Fuel Description: □ Without Antioxidant ■ With 50 ppm (wt) PDA
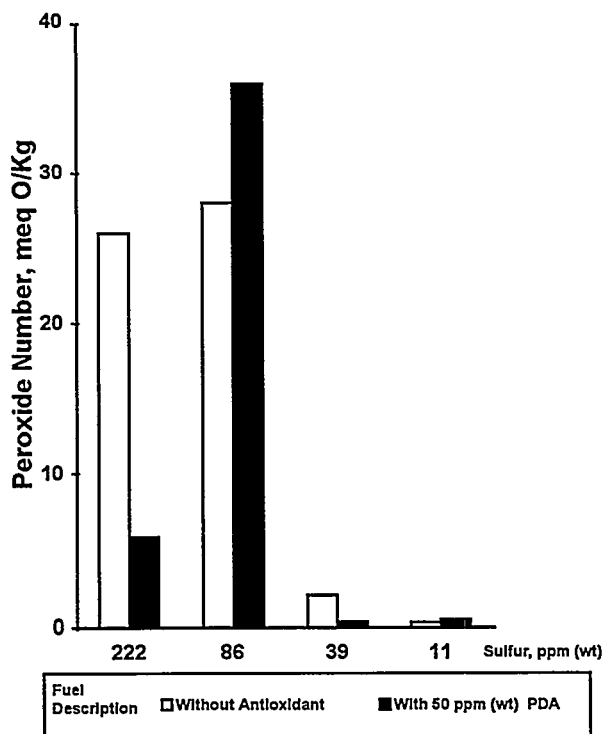
Figure 8
Effect of Phenalene Diamine Antioxidant on Hydroperoxide Potential After OP

Fuel Description: □ Without Antioxidant ■ With 50 ppm (wt) PDA