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Potential for Peroxide and Gum Formation in Ultra-Low-Sulfur Diesel Fuels

HEATHER D. WILLAUER

DENNIS R. HARDY

ROBERT E. MORRIS

FREDERICK W. WILLIAMS

*Navy Technology Center for Safety and Survivability
Chemistry Division*

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14. ABSTRACT This report summarizes an open literature survey that was conducted to determine the level of risk associated with using Ultra Low Sulfur Diesel (ULSD) Fuels in Naval operations. The findings show the level of risk for hydroperoxide and soluble gum formation in these fuels is not well understood. Thus, specific test methods have been identified for determining if these fuels will meet the Navy's long-term storage requirements. In addition, approved antioxidants formulations for jet fuel (MIL-DTL-5624R) have been recommended as a potential solution to mitigating peroxide and gum formation in ULSD.					
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POTENTIAL FOR PEROXIDE AND GUM FORMATION IN ULTRA-LOW SULFUR DIESEL FUELS

1.0 STATEMENT OF THE PROBLEM

In order to guarantee ample fuel reserves necessary for combat operations, the U.S. Navy maintains facilities for storage of mobility fuels for extended periods of time (1-3 years), in regions that differ vastly in climate and storage conditions. The storage stability specification for ship propulsion fuel (MIL-PRF-16884L) is used to ensure suitability for use. In order to meet the requirements for Ultra-Low Sulfur Diesel (ULSD) fuels with 15 ppm S or less, the sulfur is removed by hydrotreating and other processes. Since some naturally occurring sulfur compounds will decompose hydroperoxides, there are concerns that as ULSD is introduced into the fleet, that these fuels may undergo greater rates of peroxide and/or soluble gum formation during long-term storage, similar to the process that occurs in aviation fuels [1-8]. In addition, hydrotreatment can also remove other naturally occurring fuel constituents that can also function as antioxidants. Historically, it is generally accepted that when hydroperoxide concentrations exceed the specification level of 8 ppm, fuel system elastomeric materials such as o-rings and seals are attacked. Hydroperoxides have also been shown to initiate fuel autoxidation under long-term ambient temperature storage conditions (storage instability) and short-term high-temperature stress (thermal oxidative stability). These hydroperoxides greatly accelerate, as well as, lower the temperature at which gums and sediments can form. With the increased production of ULSD, the Navy may receive more ULS F-76 which will carry the same possible risk of peroxide and soluble gum formation. Due to the Navy's long-term storage stability requirements, it is necessary to determine the level of risk and ways to mitigate risk due to peroxide and soluble gum formation.

The Naval Research Laboratory was tasked by the Naval Fuels and Lubricants Integrated Product Team (IPT) in January of 2007 to conduct a survey of the open literature to determine if there is an increased level of risk associated with using ULSD fuels in shipboard propulsion systems. This report summarizes and evaluates the literature findings as a first step towards confirming the potential for peroxide and soluble gum formations in ULS fuels. This report also identifies any additional information that is required in order to develop strategies to mitigate any risks that are found to be associated from the use of ULSD in Navy ship propulsion systems.

2.0 BACKGROUND

The Environmental Protection Agency (EPA) has established a comprehensive program to lower the combustion emissions from diesel engines [9,10]. As a part of this federally mandated program, vehicles for highway use were required to use ULSD by June of 2006. ULSD is defined by the EPA as diesel fuel having a sulfur content that is equal to or less than 15 parts per million (ppm). The American Society of Testing and Materials (ASTM) designates diesel fuel that meets 15 ppm, 500 ppm, and 5,000 ppm maximum sulfur content as S15, S500, and S5000. Table 1 summarizes the manufacturing compliance schedule mandated by EPA for reducing the sulfur concentration of diesel fuels used for specific applications [9].

Similarly the European Union has mandated a 50 ppm sulfur limit that took effect in 2003. Part of this proposal called for a zero-sulfur fuel to be implemented over a period of six years [8].

Table 1. EPA ULSD Compliance Schedule.

Fuel Type	Sulfur Content (ppm)	Compliance Date
Highway (diesel trucks, cars)	≤ 15	June 2006
Non-road, Locomotive, Marine	≤ 500	June 2007
Non-road engine use (farm, construction and industrial applications (generators, forklifts,))	≤ 15	June 2010
Marine and Locomotive engine use	≤ 15	June 2012

As ULSD enters the U.S. commercial market, the diesel fuel community and engine manufacturers have expressed concern over the changes in diesel fuel properties that have resulted from the severe hydroprocessing used to reduce sulfur concentrations to 15 ppm or less. These affected fuel properties include lubricity, energy content, and cetane number [9-11].

The process of hydrotreating involves the interaction of heated liquid fuel with hydrogen in the presence of a catalyst. Mild processes produce fuel with lower sulfur and nitrogen content and little or no olefinic unsaturation. Severe hydroprocessing uses a different class of catalysts and uses higher temperatures and hydrogen partial pressures. This process removes olefins, heteroatomic and metal species, and reduces the overall aromatic content of the fuel [12,13]. This significant removal of aromatic content and oxygen-containing compounds from the fuel causes the fuel to lose many of the natural lubricity agents [14].

Fuel stability issues also arise with severity of the hydrotreating process. In this context, fuel stability refers to the resistance of a fuel to undergo deleterious chemical changes during storage or use. These chemical changes can have an impact on both the physical and chemical properties of the fuel. These chemical processes can lead to changes in color; the development of insoluble reaction products, including soluble and adherent gums, sediments, and other thermal deposits; , changes in combustion, and changes in compatibility with other fuels [12]. This can lead to engine system fouling, clogged filters, fuel lines, and an overall loss in engine performance [12,15].

Naval distillate fuel (F-76) is procured in accordance with MIL-PRF-16884L, which differs from the ASTM D975-06 specification for diesel fuel oils as shown in Table 2 [16,17], in addition to key property requirements that are specific to the Navy [16].

One such property unique to the Navy is storage stability. The Navy maintains a large strategic petroleum reserve to guarantee fuel for its combat operations. This fuel is stored for extended periods of time (1-3 years) in areas that differ vastly in climate and storage conditions. The

storage stability specification is just one measure to ensure the combat readiness of the fuel [1,18]. With the anticipation of ULSD entering the fuel supply, concerns have been raised about

Table 2. General Properties Required by Specifications for Commercial and Military Diesel.

Property	Military MIL-PRF-16884K	ASTM (D975) Grade Low Sulfur no. 1-D	ASTM (D975) Grade Low Sulfur no. 2-D
Viscosity at 40 °C, mm ² /s	1.7 - 4.3	1.3 - 2.4	1.9 - 4.1
Sulfur content, wt. % (max)	0.5	0.05	0.05
Flash point, °C (min)	60	38	52
Cloud point, °C (max)	-1		
Pour point, °C (max)	-6		
Hydrogen content, wt. % (min)	12.5		
Cetane number, (min)	42	40	40
Carbon residue, 10% bottoms, wt. % (max)	0.20	0.15	0.35
Storage Stability, total insolubles, mg/100mL (max), ASTM D5304	3.0		
Trace Metals, ppm (max) Calcium, Lead, Sodium + Potassium, Vanadium	1.0, 0.5, 1.0, 0.5		

the relative stability of these diesel fuels with respect to increased peroxide and soluble gum formation [6-11]. Severe hydroprocessing of fuels is employed to reduce aromatic content in order to reduce emissions and catalytic cracking is used to maximize fuel yield. These processing procedures increase the concentrations of more highly branched hydrocarbons and unsaturated compounds, which are susceptible to autoxidation, leading to the formation of hydroperoxides [1]. Historically hydroperoxides in fuel will chemically attack and degrade fuel system elastomeric materials such as o-rings and seals [1,9]. Hydroperoxides have also been shown to initiate fuel autoxidation during long-term ambient storage (storage instability), as well as short-term high-temperature stress in engine systems (thermal oxidative stability). Hydroperoxides act to greatly accelerate the rate of fuel autoxidation as well as lower the initiation temperature at which fuel degradation occurs to form soluble gums and sediments [2,4,5].

The first reported problems associated with hydroperoxides in fuels occurred in the early 1960's [1,8]. Hydrotreated jet fuels having hydroperoxide concentrations that exceeded 16 ppm caused failure of fuel system elastomers in Rolls Royce dart engines [1,8]. The U.S. Navy experienced similar problems with the failure of a neoprene fuel pump diaphragm that caused an A-7E aircraft engine to stall [1]. To minimize these and other hydroperoxide-related problems, the Navy amended the jet fuel specification (MIL-T-5624K) in November 1976 to require the addition of an approved antioxidant to all JP5 and JP4 containing hydrotreated components. Similar hindered phenol antioxidants to those currently approved for JP5 are also approved for use in commercial jet fuels per ASTM D1655 [19]. The specification was also modified to include a maximum peroxide number of 8 ppm [1]. In addition, the Navy's use limit was specified as 16 ppm in the predecessor to the MIL-STD-3004, MIL-HDBK-210. As of March

1995, the Navy removed the peroxide number requirement from the MIL-DTL-5624R specification [20] along with the use limit.

Since the early 1960's a significant amount of research effort has gone into developing test methods for predicting and measuring hydroperoxide concentrations and their effects on jet fuel stability [1-5]. The Navy designed a Low Pressure Reactor (LPR) test method to evaluate storage characteristics of jet fuels. The LPR test uses elevated temperatures (100 °C) and air overpressures (50 psi) to increase the rate of oxidation reactions in the fuel. The test method effectively predicts long-term storage stability of jet fuels (24 hours predicts about 9 months of ambient) without altering the actual oxidation reaction mechanisms [1]. This and other test methods allowed researchers to study hydroperoxide formation and remediation in jet fuel [1-5]. These studies have led to a series of approved antioxidant formulations designed to control hydroperoxide formation in jet fuels [20]. To date, few extensive hydroperoxide studies have been performed on ULSD fuels [7]. Thus, from a Navy perspective, their rate and potential for formation along with the degree of problems they could cause in ULSD fuel is not yet known with any certainty.

3.0 ULSD STABILITY STUDIES

3.1 Ethyl Petroleum Additives Inc.

Ethyl Petroleum Additives Inc. published a study of hydroperoxide formation in ULSD fuels in 2003 [8]. One objective of that study was to determine the conditions under which high concentrations of hydroperoxides would be formed in USLD. Another objective was to evaluate the ability of current ASTM stability test methods to predict damaging hydroperoxide concentrations during storage and use. Table 3 lists the physical and chemical properties of the two different ULSD fuels used in those studies.

Table 3. Physical and Chemical Properties of ULSD Fuels.

Property	ASTM Method	Fuel A	Fuel B
Cetane number	D 613	42	59
Aromatics, vol %	D 1319	25	22
Saturates, vol%	D 1319	74	76
Olefins, vol%	D 1319	2.0	2.0
Sulfur, ppm (wt.)	D 5453	1	17
Specific Gravity	D 4052	0.8	0.8
Kinematic visc., 40°C, cSt	D 445	2.5	4.0

Fuel A was obtained from a U.S. refinery and all tests were performed one month after it had been manufactured. Fuel B came from an Asian refinery and had been stored at 10 °C for a year prior to testing. A common additive, 2-ethylhexyl nitrate (2-EHN) that is used to increase the cetane number of diesel fuels, is thermally unstable and was examined to determine if it had any

effect on the formation of hydroperoxides. The hydroperoxide concentrations were measured by ASTM D3703, and are summarized below in Table 4.

Table 4. Hydroperoxide Concentrations (in ppm) Measured in ULSD Samples after Various Conditions of Stress.

Test Condition	Fuel A	Fuel B	Fuel A + 2500 ppm EHN	Fuel B + 2500 ppm EHN
None (unheated sample)	2.5	0	2.5	0
D2274 Oxidative Stability (16 hrs, 95°C)	11	0.5	43	0.8
D4625 Storage Stability (13 weeks, 43°C)	2.2	0.1	3.0	0.5
D5304 Storage Stability (16 hrs, 90°C)	17	2.4	14	7.0
D6468 Thermal Stability (90 min, 150°C)	348	395	385	323
D6468 Thermal Stability (180 min, 150°C)	940	800	600	280

Table 4 shows that the levels of hydroperoxide concentrations reached in these tests depended heavily on the conditions of stress and stability test method used for each fuel. Fuel A, which contained the lowest sulfur concentration, also generated the largest concentration of hydroperoxides. The peroxide concentrations reached in Fuel A exceed the Navy's use limit of 16 ppm for each test method with the exception of D2274 and D4625. Fuel B, which had 17 ppm sulfur, generated significantly lower levels of hydroperoxides. The addition of the cetane improver proved to have little impact on peroxidation in each fuel. The large hydroperoxide concentrations generated for both fuels under test conditions used for ASTM D6468 suggested there would be a problem of peroxide formation during engine use. To test this prediction, Fuel A was run in three different diesel engines. No significant formation of hydroperoxides was measured in Fuel A indicating that the fuel system did not heat the fuel to temperatures and residence times used in D6468. Measuring the thermal stability of the fuel is important because the fuel in diesel vehicles is exposed to high temperatures (130 °C) and pressures (1500 bar) in the fuel injection system [21]. This causes the fuel temperature in the fuel tank to gradually increase as the fuel is re-circulated in the fuel system. The temperatures in the fuel tank increase as a function of engine operation time and fuel volume in the tank [8].

Kinetic experiments were carried out by Ethyl Petroleum Additives Inc. under ambient conditions at atmospheric air pressure to establish Arrhenius parameters for both fuels with and without the cetane improver additive. These results are shown in Table 5.

The kinetic studies indicated that the activation energies (E_a) of hydroperoxide formation for the two fuels were higher (130 and 117 kJ/mol) than those reported in the literature for jet fuels (79 kJ/mol – 92 kJ/mol), and that the hydroperoxide formation rates for a given temperature were slower [7]. It was also concluded from the kinetic studies that the cetane improver acted to

promote autoxidation at high temperatures (65-150 °C) and as an oxidation inhibitor at lower temperatures (65 °C).

Table 5. Arrhenius Parameters for Fuels A and B.

Fuel	Additive	E _a (kJ/mol)
A	None	130
B	None	117
A	2500 ppm EHN	170
B	2500 ppm EHN	154

3.2 Amoco Petroleum Products

Amoco Petroleum Products published a study in 1997 on the effects of increasing the severity of hydrotreatment on the storage stability of No. 2 diesel fuel [7], in a series of accelerated stability tests. In their study, a highly aromatic fuel feedstock was hydrotreated to achieve four No. 2 diesel fuels ranging in sulfur content from 222 ppm to 11 ppm. A separate sample of each of the four fuels was taken and 50 ppm of the antioxidant phenylene diamine (PDA) (N,N'-di-sec-butyl-p-phenylene diamine) was added to determine the effect of this additive on storage stability. The fuels had been stored for a year in clear sealed glass bottles under ambient conditions prior to testing.

The measured physical and chemical properties of the fuels are shown in Table 6. These data show that as the severity of hydrotreatment was increased, the sulfur content dropped from 222 ppm to 86 ppm and the aromatic content, total and basic nitrogen levels also decreased significantly. The data in Table 6 also indicate a considerable reduction in SMORS (soluble macromolecular oxidatively reactive species) precursors [22] measured as the fuel was hydrotreated to reach a sulfur content of 86 ppm.

A series of ASTM and industrially developed stability tests were performed on the hydrotreated diesel fuels that did not contain the antioxidant. Table 7 summarizes the results of these tests along with hydroperoxide concentrations measured. The data show that SMORS levels increases under ASTM D4625 test conditions. Fuels A and B which contained the highest sulfur contents developed the most SMORS.

The color of the fuels measured by ASTM D1500 did not darken during the ASTM D4625 stability tests, which indicates that the SMORS formed were not very dark. This is in contrast to what occurs in high sulfur diesel fuels where the SMORS tend to contribute to color formation during aging.

The susceptibility of the fuels to form hydroperoxides as a function of hydrotreating and accelerated storage conditions is also shown in Table 7. Initial storage conditions (1 year at ambient temperatures) show that the susceptibility of the fuel to form peroxides reduces as the sulfur content of the fuel is reduced by hydrotreating. The peroxide levels were high enough in

Fuels A and B to exceed the Navy's use limit of 16 ppm (2 meq/kg) with the exception of peroxides that formed in the oxygen overpressure test for Fuel A. Fuel D (ULSD) proved to be the least susceptible to peroxide formation as the storage stability testing increased in severity. In addition, the rate of measurable hydroperoxide formation and decomposition in Fuel D was nearly equal under all testing conditions.

Table 6. Chemical and Physical Properties of Hydrotreated No. 2 Diesel Fuels.

Property	ASTM Method	Fuel A	Fuel B	Fuel C	Fuel D
Sulfur, ppm	D4294	222	86	39	11
Total Nitrogen, ppm (wt)	D4629	75	8	4	<1
Basic Nitrogen, ppm (wt)	D2896	12	<5	<5	<5
SMORS, mg/100 mL	-	2.5	0.4	0.4	0.2
Phenalenones, ppm (wt)	ND	ND	ND	ND	ND
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
Initial Color	D1500	<1.5	-6*	-16*	<1.0
Cloud Point, °F	D2500	11	8	10	8
Pour Point, °F	D97	5	5	0	5

ND = not detected

* Saybolt color

Phenylene diamine was an approved aryl amine fuel antioxidant until studies showed that its addition to jet fuels led to thermal stability problems, due to oxidative polymerization of the additive itself [23]. Based on those studies, phenylenediamine stabilizer additives were removed from the MIL-T-5624 specification in the 1990's [24]. In addition, later studies showed these additives decreased the storage stability when added to high sulfur diesel fuels by increasing the amount of sediment formed [25]. Table 8 shows the addition of PDA to the fuels caused minor increases in the total insolubles under ASTM D4625 and the Amoco 40-hour stability test. These increases appeared only in the higher sulfur containing fuels, Fuels A and B. However, the increase in total insolubles was well within the recommended limits of 1.5 mg/100 mL in the 13 week ASTM D4625 storage stability test.

The results in Table 8 show that the PDA, in general, decreased the final hydroperoxide levels in the fuels under the milder test conditions in D4625 and CRC at 65 °C. However, the antioxidant increased the peroxide levels under the most severe storage testing conditions in the oxygen overpressure method at 100°C. Perhaps the most significant increase observed under oxygen overpressure test conditions occurred in the ULSD fuel (Fuel D). The rate of measurable

hydroperoxide formation in the fuel was increased by a factor of seven, bringing the hydroperoxide level well above the aviation use limit of 16 ppm (2 meq/kg).

Table 7. Stability of Hydrotreated No. 2 Diesel Fuels.

Property and Method	Fuel A	Fuel B	Fuel C	Fuel D
Sulfur, ppm	222	86	39	11
Initial Color, ASTM D1500	<1.5	-6*	-16*	<1.0
Stability, ASTM D2274 (16 hrs, 95°C)				
Total Insolubles mg/100 mL	0.2	0.1	0.0	0.0
Final Color, ASTM D1500	<2.0	<0.5	<0.5	<1.0
40-Hour Stability, Amoco Oil (40 hrs, 80°C)				
Total Insolubles mg/100 mL	0.4	0.1	0.0	0.0
Final Color, ASTM D1500	<1.5	-6*	-16*	<1.0
Stability, ASTM D4625 (13 weeks, 43°C)				
Total Insolubles mg/100 mL	0.3	0.2	0.2	0.2
Final Color, ASTM D1500	<2.0	<0.5	0.5	<1.0
SMORS, mg/100 mL				
Initial	2.5	0.4	0.2	0.2
After ASTM D4625 (13 weeks, 43°C)	11.0	1.0	0.4	0.3
Hydroperoxide Potential, meq /kg **				
Initial (1 yr, ambient)	7.6	1.7	0.4	0.5
After ASTM D4625 (13 weeks, 43°C)	193	24	1.4	0.5
CRC Report No. 559 (4 weeks, 65°C)	26	28	2.0	0.4
Oxygen Overpressure Method (24 hrs, 100 °C, 100 psi O ₂)	1.3	21	199	0.7

* Saybolt color

** 1 meq/kg ROOH = 8 ppm

Amoco concluded from their study that the storage stability remained excellent as the No. 2 diesel fuels were hydrotreated to lower sulfur levels. They also concluded that hydrotreatment of fuel to ULSD specification levels, should cause further decreases in hydroperoxide susceptibility. The addition of PDA to the fuels did not have any significant effect on the insolubles produced in storage stability testing, although it did cause a noticeable increase in hydroperoxide concentrations in ULSD fuel under the most severe storage conditions.

3.3 BDM Petroleum Technologies

BDM Petroleum Technologies published a study on the effects of moderate to severe hydrotreating on diesel fuel properties and performance in 1997 [26]. Depending on the refinery configuration, individual diesel blending streams or combinations of streams can be hydrotreated. One objective of the study was to look at the quality of these different streams as a function of hydrotreatment severity. The other was to determine the relationship between hydrotreatment severity of the fuel and individual fuel properties. Tables 9-12 show the feed/product properties of a straight run distillate (SR), a light cycle oil (LCO), a 75/25% SR/LCO blend, and a 75/17/8% SR/LCO/coker blend, as a function of hydrotreating severity.

In general, the properties of the fuels follow the expected trends with increasing hydrotreating severity.

Table 8. Stability of Hydrotreated No. 2 Diesel Fuels with the Addition of 50 ppm PDA.

Property and Method	Fuel A	Fuel B	Fuel C	Fuel D
Sulfur, ppm	222	86	39	11
Initial Color, ASTM D1500	<0.5	<1.5	<1	<0.5
Stability, ASTM D2274 (16 hrs, 95°C)				
Total Insolubles mg/100 mL	0.1	0.2	0.0	0.1
Final Color, ASTM D1500	<0.5	<2.0	<1.0	0.5
40-Hour Stability, Amoco Oil (40 hrs, 80°C)				
Total Insolubles mg/100 mL	0.1	2.5	0.0	0.1
Final Color, ASTM D1500	<0.5	<1.5	<1.0	<0.5
Stability, ASTM D4625 (13 weeks, 43°C)				
Total Insolubles mg/100 mL	0.8	0.9	0.2	0.1
Final Color, ASTM D1500	<0.5	<2.0	1.0	<0.5
SMORS, mg/100 mL				
After ASTM D4625 (13 weeks, 43°C)	0.5	ND/E	ND/E	ND/E
Hydroperoxide Potential, meq /kg				
After ASTM D4625 (13 weeks, 43°C)	4.2	0.4	0.4	0.5
CRC Report No. 559 (4 weeks, 65°C)	5.9	36	0.5	0.6
Oxygen Overpressure Method (24 hrs, 100 °C, 100 psi O ₂)	13	220	41	4.8

ND/E represents not detected due to emulsion formation

Table 9. Properties of Feed and Hydrotreated Straight Run Distillate (SR).

Property	Feed	Hydrotreated Product Stream				
Sulfur, ppm	5800	61	54	40	73	6
Nitrogen, ppm	177	3.3	8.1	<1	<1	<1
Total Aromatics by High Resolution Mass Spectrometry (HRMS), wt%	32	27	26	19	13	9.0
Stability, ASTM D5304 run 96 hours Total Insolubles mg/100 mL	-	12	45	34	13	9
Hydroperoxides (ppm)	-	<100	>1500	>750	-	>400

Table 10. Properties of Feed and Hydrotreated Light Cycle Oil (LCO).

Property	Feed	Hydrotreated Product Stream		
Sulfur, ppm	13000	114	172	3
Nitrogen, ppm	1100	<1	<1	<1
Total Aromatics by High Resolution Mass Spectrometry (HRMS), wt%	79	25	13	1.2
Stability, ASTM D5304 run 96 hours Total Insolubles mg/100 mL	98	2	3	18
Hydroperoxides (ppm)	-	<100	<100	>1250

Table 11. Properties of Feed and Hydrotreated SR/LCO Blend (75/25%).

Property	Feed	Hydrotreated Product Stream			
Sulfur, ppm	7000	104	50	50	52
Nitrogen, ppm	514	62	9	<1	<1
Total Aromatics by HRMS, wt%	44	39	30	18	12
Stability, ASTM D5304 run 96 hours Total Insolubles mg/100 mL	38	4	2	2	1
Hydroperoxides (ppm)	-	<100	<100	<100	<100

Table 12. Properties of Feed and Hydrotreated SR/LCO/Coker Blend (75/17/8%).

Property	Feed	Hydrotreated Product Stream			
Sulfur, ppm	8900	93	57	29	26
Nitrogen, ppm	469	38	7	<1	<1
Total Aromatics by HRMS, wt%	44	31	28	17	10
Stability, ASTM D5304 run 96 hours Total Insolubles mg/100 mL	32	4	2	1	1
Hydroperoxides (ppm)	-	<100	<100	<100	<100

In that study, most of the fuels were not hydrotreated to the sulfur specification set for U.S. ULSD (<15 ppm) but many met the ULSD specification for Europe (<50 ppm). From tables 9-12 it is evident that under extreme storage stability test conditions ASTM D5304, 90°C, even mild hydrotreating improved the stability of both the SR/LCO blend (75/25%) and the SR/LCO/coker blend (75/17/8%). These blends are even more stable than the straight run fuels.

In contrast severe hydrotreating of LCO (3 ppm sulfur) reduced its storage stability compared to mild hydrotreating.

From the studies shown only large measurable hydroperoxides formations in the fuels during ASTM D5304 test conditions may be deciphered. The largest peroxide formation was found in the straight run fuels and the severely hydrotreated LCO samples.

BDM Petroleum Technologies concluded that mild hydrotreating improved the storage stability of LCO by removing heteroatomic species that are believed to cause sediment formation in raw LCO. However, as the hydroprocessing became more severe, the diesel storage stability worsened due to the formation of hydrocarbon species prone to peroxide formation and the removal of polar species that act as antioxidants. While mild hydrotreating of neat SR caused storage stability to worsen, it significantly improved the stability of blends containing LCO. Thus the reduction in polar compounds as a result of hydrotreating fuel blends has less effect on storage stability than on individual refining streams are treated separately.

3.4 Fortum Oil and Gas Oy

Fortum Oil and Gas Oy from Finland published a study in 2000 on the storage and thermal stability of ULSD fuels [21]. One of the objectives of the study was to determine if there was a correlation between the severity of the hydrotreatment process and storage stability. The other was to determine if thermal stability of the fuel would be affected by the addition of the cetane improver, 2-ethylhexyl nitrate. The fuels tested included straight run distillates, cracked components, moderately and severely hydrotreated components, alone and in various combinations. Table 13 provides a summary of the stability tests performed and the results. In this study, the ULSD met the ULSD specification for Europe (< 50 ppm).

Fortum Oil and Gas Oy found that citydiesel fuel was very stable as shown in Table 13 (sample numbers 1-6, 10, 14, 21-22). The catalytically cracked samples (sample numbers 11-12, 15) and the straight run sample (sample number 13) were not as severely hydrotreated and contained more sulfur. These samples contained higher concentrations of polar compounds and produced the most sediment. These samples also underwent the most change in color by ASTM D1500. The fuel samples that were severely hydrotreated appeared to be the most stable.

Reformulated diesel fuel “Citydiesel” has a sulfur content <50 ppm and total aromatic content <20 vol%, and has been used commercially in Finland since 1993. Fortum Oil and Gas Oy also reported that no stability problems had occurred with citydiesel fuels in operation. They believe the degree of hydrotreatment in Finnish city diesel fuels is sufficient to prevent instability reactions that occur with partially saturated multi-ring aromatics. They also report that 2-ethyl hexyl nitrate remains stable under conditions of use, where the fuel is exposed to temperatures in excess of 100 °C in the fuel injection system.

Table 13. Results of the Fortum Oil and Gas Oy Stability Studies of Diesel with < 50 ppm Sulfur.

Sample Number	Sample	Du Pont F-8 modified 0,6,13 weeks, 50°C, mg/100 mL	ASTM D2274 16 hrs, 95°C, mg/100 mL	MeOH-extraction 0,6,13 weeks, mg/100 mL	Du Pont F-8 type filtration 6,12 month RT mg/100 mL	MeOH-extraction 6,12 month RT mg/100 mL	Color ASTM D1500 6,12 months RT
1	Citydiesel, summergrade-98* (S<50 ppm)	0.2, 0.2, 0.2	0.1	-	-	-	-
2	Citydiesel, wintergrade-98 (S<50 ppm)	0.1, 0.1, 0.2	0.4	-	-	-	
3	MK1 Citydiesel component 29.1.98 (S<50 ppm)	0.1, 0.2, 0.2	0.1	-	0.2, < 0.1	<0.1, <0.1	0, 0
4	Citydiesel component-97 (S<50 ppm)	0.6, 0.6, 0.6	0.1	-	-	-	
5	Citydiesel, component -97 (S<50 ppm) containing severely hydrated gasoil from EHVI-unit	0.1, 0.1, 0.1	0.1	-	-	-	
6	MK1 Citydiesel component (S<50ppm) 28.1.98	0.2, 0.2, 0.2	0.3	-	-	-	
7	EHVI-unit gasoil; 1 23.3.98	0.1, 0.1, 0.1	<0.1	0.1, 0.2, 0.3	<0.1, <0.1	0.2, <0.1	0,0
8	EHVI-unit gasoil; 2 23.3.98	0.1, 0.1, 0.1	<0.1	-	<0.1, <0.1	0.2, <0.1	0,0
9	EHVI-unit gasoil; 29.1.98	-	-	-	<0.1, <0.1	0.2, <0.1	0,0
10	Citydiesel, component (S<50 ppm) 24.3.98	0.1, 0.1, 0.1	<0.1	-	<0.1, <0.2	0.2, <0.1	
11	Cracked gasoil 24.3.98	0.1, 0.2, 0.4	0.1	0.4, 3.2, 9.7	0.3, 0.6	0.8, <0.1	3.5, 3.0
12	Cracked gasoil 6.8.98	<0.1, 0.2, 0.3	-	0.2, 1.9, 3.2	0.3, 0.4	1.2, 1.4	4.0, 4.0
13	Straight run gasoil 24.3.98	0.1, 0.1, 0.1	0.1	0.9, 0.7, 1.2	0.4, 0.5	0.2, 0.2	1.5, 1.5
14	Citydiesel component (S<50 ppm) 24.3.98	<0.1, 0.1, 0.1	0.2	0, 0.5, 0.5	<0.1, <0.1	0.2, 0.2	
15	Cracked gasoil (petrol) 24.3.98	0.1, 0.3, 0.3	0.2	0, 0.1, 0.1	0.2, 0.4	0.3, 0.2	1.5, 1.5
16	EHVI-unit gasoil 23.3.98 + Cracked gasoil 6.8.98 50%/50%	<0.1, 0.1, 0.1	2.1	0.3, 1.1, 1.5	-	-	
17	EHVI-unit gasoil 623.3.98 + Straight run gasoil 6.8.98 50%/50%	0.1, 0.1, 0.2	0.1	0, 0.1, 0.1	-	-	
18	Straight run gasoil 6.8.98 + Cracked gasoil 6.8.98 50%/50%	<0.1, 0.2, 0.5	0.6	0.8, 1.5, 2.1	-	-	
19	EHVI-unit gasoil 23.11.98 (naphthenic crude)	<0.1, 0.2, 0.2	-	0.2, 0.2, 0.2	<0.1, <0.1	0.2, 0.1	0, 0
20	Cracked gasoil 23.11.98 (naphthenic crude)	<0.1, 0.32, 0.4	-	0.2, 0.7, 1.9	<0.1, <0.1	0.1, <0.1	0, 0
21	MK1 Citydiesel component (S<50ppm) 23.11.98 (naphthenic crude)	<0.1, 0.1, 0.2	-	0, 0.1, 0.1			
22	Citydiesel component (S<50 ppm) 23.11.98 (naphthenic crude)	<0.1, 0.1, 0.1	-	0, <0.1, 0.1			
23	Straight run gasoil 23.11.98 (naphthenic crude)	<0.1, 0.1, 0.1	-	0.1, 0.1, 0.1			

3.5 Fisher-Tropsch Synthetic Fuels

The Naval Air Systems Command conducted a study to evaluate Fischer-Tropsch (FT) synthetic fuels for U.S. Naval applications [27]. They tested two synthetic fuels that met almost all the requirements of the JP-5 specification (MIL-DTL-5624). The largest difference was found in the synthetic aromatic content of the fuels. FT-1 contained no synthetic aromatics while FT-2 contained 14 vol% aromatics. As expected from the FT process, these fuels contained no sulfur compounds. Tables 14 and 15 summarize the storage stability test results of FT-1 and FT-2. Table 16 shows initial stability test results for two synthetic diesel fuels. The Navy Low Pressure Reactor (LPR) test method described previously was used to measure the storage stability of the test fuels.

Table 14. Stability testing of Fischer-Tropsch Jet Fuel FT-1.

Fuel, FT-1	Peroxide Formation, ppm	Gums, mg/100 mL	Saybolt Color
Initial	0	0	30
Stability, CRC Report No. 614 Run 24 hours (9 months)	>240	0	29
Stability, CRC Report No. 614 Run 48 hours (18 months)	>240	0.1	24
Stability, CRC Report No. 614 run 72 hours (27 months)	>240	1.0	19
Stability, CRC Report No. 614 run 96 hours (3 years)	>240	8.0	22
Fuel, FT-1 with 24 ppm 2,6-di-tert-butylphenol	Peroxide Formation, ppm	Gums, mg/100 mL	Saybolt Color
Initial	0	0.4	30
Stability, CRC Report No. 614 run 24 hours (9 months)	0	0.3	30
Stability, CRC Report No. 614 run 48 hours (18 months)	0	0.4	30
Stability, CRC Report No. 614 run 72 hours (27 months)	0	0.5	30
Stability, CRC Report No. 614 run 96 hours (3 years)	0	1.3	30
Fuel, 50/50 Blend FT-1 and JP5	Peroxide Formation, ppm	Gums, mg/100 mL	Saybolt Color
Initial	0	0.7	19
Stability, CRC Report No. 614 Run 24 hours (9 months)	0	0.9	18
Stability, CRC Report No. 614 Run 48 hours (18 months)	0.4	0.5	17
Stability, CRC Report No. 614 run 72 hours (27 months)	3.0	1.5	15
Stability, CRC Report No. 614 run 96 hours (3 years)	3.5	2.1	15

Table 15. Stability testing of Fischer-Tropsch Jet Fuel FT-2.

Fuel, FT-2	Peroxide Formation, ppm	Gums, mg/100 mL	Saybolt Color
Initial	0	0.2	30
Stability, CRC Report No. 614 run 24 hours (9 months)	6.0	0.4	30
Stability, CRC Report No. 614 run 48 hours (18 months)	16	0.7	30
Stability, CRC Report No. 614 run 72 hours (27 months)	68	1.0	26
Stability, CRC Report No. 614 run 96 hours (3 years)	>240	5.2	13
Fuel, FT-2 with 24 ppm 2,6-di-tert-butylphenol	Peroxide Formation, ppm	Gums, mg/100 mL	Saybolt Color
Initial	0	0.2	30
Stability, CRC Report No. 614 run 24 hours (9 months)	0	0.3	30
Stability, CRC Report No. 614 run 48 hours (18 months)	0	0.4	30
Stability, CRC Report No. 614 run 72 hours (27 months)	0	0.4	30
Stability, CRC Report No. 614 run 96 hours (3 years)	0	1.1	30
Fuel, 50/50 Blend FT-2 and JP5	Peroxide Formation, ppm	Gums, mg/100 mL	Saybolt Color
Initial	0.3	0.4	18
Stability, CRC Report No. 614 Run 24 hours (9 months)	0	0.1	17
Stability, CRC Report No. 614 Run 48 hours (18 months)	0.2	0.7	18
Stability, CRC Report No. 614 run 72 hours (27 months)	0.9	0.6	16
Stability, CRC Report No. 614 run 96 hours (3 years)	2.2	2.3	14

Table 16. Stability of Fischer-Tropsch Diesel Fuels.

Fuel, FT Diesel-1	Peroxide Formation, ppm	Gums, mg/100 mL	Saybolt Color
Initial	0	5686	30
Stability, CRC Report No. 614 run 24 hours (9 months)	0	5197	30
Stability, CRC Report No. 614 run 48 hours (18 months)	0.6	5675	30
Stability, CRC Report No. 614 run 72 hours (27 months)	8.3	5372	30
Stability, CRC Report No. 614 run 96 hours (3 years)	102	4236	22
Fuel, FT Diesel-2	Peroxide Formation, ppm	Gums, mg/100 mL	Saybolt Color
Initial	70	6	30
Stability, CRC Report No. 614 run 24 hours (9 months)	>350	55	24
Stability, CRC Report No. 614 run 48 hours (18 months)	>350	71	24
Stability, CRC Report No. 614 run 72 hours (27 months)	>350	197	23
Stability, CRC Report No. 614 run 96 hours (3 years)	>350	98	22

The results indicated that all the FT-fuels produced very high levels of hydroperoxides and gum during long-term storage stability testing. The approved antioxidant was effective when added to FT-1 and FT-2 to increase the long term storage stability of those fuels. When FT-1 and FT-2 were blended (50/50 mixture) with a stable petroleum jet containing an antioxidant, the overall long term storage stability of the FT fuels was improved. The FT-jet study along with preliminary results on FT diesels from The Naval Air Systems Command serve to demonstrate the potential stability issues that may arise for the Navy and the potential of currently used antioxidants to mitigate the problem.

3.6 American Society of Testing and Materials (ASTM)

There is now concern that climate will have a significant impact on peroxide formation in ULSD. Fuels stored in climates and regions where the temperatures exceed 35 °C for several months are believed to be more susceptible to hydroperoxide formation. Currently ULSD refiners are not required to add antioxidants to the fuels to hinder peroxide formation, because it has not been officially established that such a problem exists or could occur. To address these issues, the ASTM Subcommittee E2 on Burner, Diesel, Non-Aviation Gas Turbine, and Marine Fuels is currently formulating a stability program scheduled to begin in 2007. The program will take ten five gallon fuel samples of number 1 ULSD and ten five gallon samples of number 2 ULSD as produced. The first test series will run 500 mL of each sample at 65 °C with the cap off and the samples exposed to air for two weeks. Two weeks corresponds to 2 to 3 month fuel storage for field use. After the test, each sample will be measured for peroxide formation using ASTM

D3703. Phase 2 of the program will involve four week aging studies under the same experimental conditions. The test results from Phase 1 and 2 will determine the recommended course of action the program will take. Presently most commercial diesel fuels are burned within a few months of receiving. Therefore unless the peroxide formation considerably exceeds 8 ppm within the 2 week test period, the addition of antioxidants may not be necessary. However, peroxide formation during the four week test series, could indicate problems for military strategic storage of the fuel. If peroxide formation is considered a problem in ULSD, the program will move to begin evaluating the addition of hindered phenols to the fuels to inhibit peroxide formation.

4.0 CONCLUSIONS

This report summarizes five studies that evaluate the stability properties of ULSD fuels. These studies employed a wide range of stability test methods to classify the storage stability with respect to the formation of insolubles and hydroperoxides. In general, the differences in stability test methods used, complicated the direct comparison of the results from each study. However, it is clear from the different studies in this report and different test methods used in the literature to evaluate ULSD fuels, that the rate and potential for hydroperoxide and insoluble formation in these fuels is not very well understood. The studies seem to indicate that ULSD fuels containing sulfur contents between 10-15 ppm would meet commercial storage requirements. Commercial fuels are typically consumed between 6 to 12 months after purchase. ULSD fuels having little or no sulfur content readily peroxidized along with straight run distillates. Addition of approved antioxidants were shown to show potential in remediating this situation in limited laboratory testing.

Ethyl Petroleum Additives Inc. showed hydroperoxide formation above the Navy use limit of 16 ppm in three of the five stability tests performed on the fuel that had the lowest sulfur content (1 ppm). Amoco Petroleum Products found that storage stability was not affected by hydrotreating the fuels to decrease sulfur levels to 11 ppm. They also concluded that severe hydrotreatment of the fuels lowered their susceptibility to form hydroperoxides. Amoco also found that while PDA had little effect on storage stability in ULSD it did cause a noticeable increase in hydroperoxide formation under severe storage conditions. BDM Petroleum Technologies evaluated different refinery stocks and their blends. They found large increases in peroxide formation for straight run distillates and severely hydrotreated LCO distillates, to 3 ppm sulfur. Fortum Oil and Gas Oy concluded, on the basis of insoluble produced, that the commercially available ULSD fuel in Finland, that is produced with 50 ppm sulfur or less, was extremely stable. Finally, the FT fuels study performed by the Naval Air Systems Command showed that synthetic middle distillates containing no sulfur compounds readily develop hydroperoxides and gums. The addition of an antioxidant to the fuels showed promise in extending the long-term storage stability of the fuels.

5.0 RECOMMENDATIONS

Due to the U.S Navy's long term storage requirements it is recommend that ULSD fuels be evaluated with Navy specific test methods, such as the current Low Pressure Reactor (LPR) test method and ASTM D5304 to determine risks associated with using ULSD fuels in Navy operations. Additionally, the test results shown in this report indicate the Navy should focus its

studies on ULSD distillates varying in aromatic and sulfur content, properties that are dependent on the hydroprocessing of the fuels. The sulfur content of these fuels should range from 0 to 15 ppm sulfur. While Amoco, BDM, and Fortum studied the formation of insolubles in these fuels, no studies were found that actually measured soluble gum formation in ULSD fuels. The Navy specified test for gum formation is ASTM D381 [28]. While in depth kinetic studies of hydroperoxide formation led to approved antioxidant formulations designed to control peroxide formation in jet fuels, Amoco studies showed an increase in instability during long term storage using the antioxidant PDA. Thus based on the results of Navy conducted kinetic studies of hydroperoxide formation in FT-fuels containing no sulfur compounds, addition of current approved antioxidant formulations to ULSD fuels should be evaluated for their effect on controlling and mitigating peroxide formation under long term storage requirements.

The ASTM Subcommittee E2 is currently formulating a stability program that will begin evaluating ULSD fuels for commercial use in the 2007 fiscal year. They propose to evaluate ten five gallon samples of number 1 and ten five gallon samples of number 2 diesel as produced. It is further recommended that the Navy participates in this ASTM study in order to obtain the same sample set to determine if these fuels meet the Navy's long term storage requirements.

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