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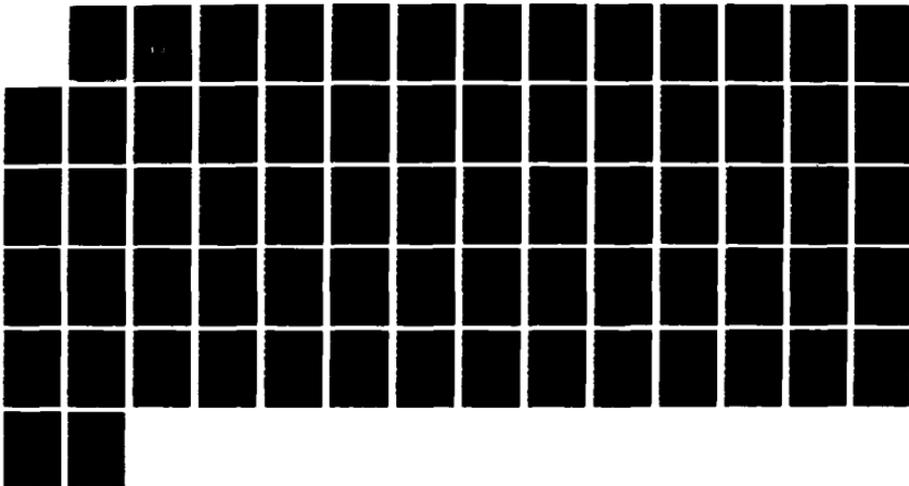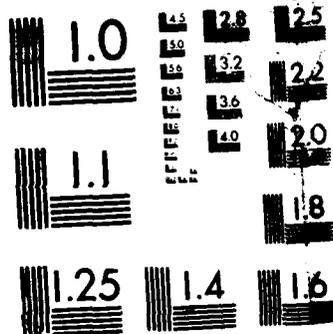
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SECOND TOPICAL REPORT

**STABILITY, COMPATIBILITY, AND
RELATED PROBLEMS OF ADDITIVES IN NAVAL
DISTILLATE FUELS DERIVED FROM LOWER
QUALITY FEEDSTOCKS**

by
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Stability testing and fuel characterizations performed at four different laboratories were used to evaluate the additives. Each laboratory used a different type of stability test. The characterization studies were performed to ensure that the base fuel blends tested were within the range allowed by MIL-F-16884H and to determine whether any of the additives would make the fuels unacceptable for Navy use.

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Because of the high degree of stability of several of the control (additive-free) fuels, it was difficult to differentiate additive effectiveness in these fuels. Some studies were performed to see if controlled aging techniques prior to actual stability testing could increase the amount of sediment in the fuel. Results indicated that this would increase sediment in some cases and would have no effect in others.

Sample collection techniques at the refineries were also investigated. Both lined and unlined cans were used in these studies. Samples were blanketed with argon, sparged with air, or left with an air blanket. Water was added to some samples to determine the effect that the moisture would have on stability. In studies on the West Coast fuel, the unlined cans increased sediment formation considerably. However, the type of cans had virtually no effect on the stability of fuel from the Gulf Coast.

In cases where control fuels exhibited instability, it was possible to demonstrate the relative effectiveness of the 12 stabilizer additives. Five of the additives (2, 3, 10, 11, and 12) have been shown to be superior to the remaining seven. However, all 12 will continue to be tested during the remainder of this study.

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STABILITY, COMPATIBILITY, AND RELATED PROBLEMS
OF ADDITIVES IN NAVAL DISTILLATE FUELS DERIVED
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SUMMARY

This report describes the first two years of a study co-sponsored by DOE and the U.S. Navy to determine which antioxidant additives are most effective in delaying fuel degradation in a variety of middle distillate straight run/ light cycle oil blends. In this study, straight-run middle distillate and catalytically cracked product were mixed at ratios of 85:15, 70:30, and 60:40, respectively. All of these blended fuels were immediately treated with commercially available additives. Usual dosages were 12 and 24 ppm (volume/ volume).

Stability testing and fuel characterizations performed at four different laboratories were used to evaluate the additives. Each laboratory used a different type of stability test. The characterization studies were performed to ensure that the base fuel blends tested were within the range allowed by MIL-F-16884H and to determine whether any of the additives would make the fuels unacceptable for Navy use.

Because of the high degree of stability of several of the control (additive-free) fuels, it was difficult to differentiate additive effectiveness in these fuels. Some studies were performed to see if controlled aging techniques prior to actual stability testing could increase the amount of sediment in the fuel. Results indicated that this would increase sediment in some cases and would have no effect in others.

Sample collection techniques at the refineries were also investigated. Both lined and unlined cans were used in these studies. Samples were blanketed with argon, sparged with air, or left with an air blanket. Water was added to some samples to determine the effect that the moisture would have on stability. In studies on the West Coast fuel, the unlined cans increased sediment formation considerably. However, the type of cans had virtually no effect on the stability of fuel from the Gulf Coast.

In cases where control fuels exhibited instability, it was possible to demonstrate the relative effectiveness of the 12 stabilizer additives. Five of the additives (2, 3, 10, 11, and 12) have been shown to be superior to the remaining seven. However, all 12 will continue to be tested during the remainder of this study.

INTRODUCTION

This report describes the first two years of a study performed for the Naval Research Laboratory (NRL) and the U.S. Department of Energy to determine which antioxidant additives are most effective in delaying fuel degradation in a variety of middle distillate straight run/light cycle oil blends. In addition to NRL, DOE, and NIPER, the other participants are David Taylor Naval Ship Research and Development Center (DTNSRDC) and the ARTECH Corporation.

In the first year of this project, NIPER personnel visited refineries in Texas and California. In both locations, we obtained several barrels each of straight-run middle distillate product (straight-run diesel fuel) and cata- lytically cracked product (light cycle oil), which were blended in ratios of 85:15, 70:30, and 60:40, respectively, to generate three fuels per refinery. All sampling and blending were done under argon and were completed as rapidly as possible to control degradation. The report summarizing the first year's efforts is listed as reference 2.

All six blended fuels were immediately treated with either 12 or 24 ppm (v/v) of one of 12 additive treatments, so that a total of 144 additive test samples was generated. The physical and chemical property analyses and the storage stability testing were then completed by NRL, DTNSRDC, ARTECH, and NIPER. Four of the fuel additive blends were more stable than expected, and no definitive conclusions could be drawn from most of the data for these fuels. During the second year, a variety of sample collection techniques which might increase the amounts of sediment in the fuels were investigated. The same two refineries provided fuel for these tests. Since the sample collection techniques were of prime importance, only an additive-free 30% (volume/volume) LCO blend and three additive blends [at a concentration of 24 ppm (v/v)] were used in this matrix.

BACKGROUND

Maintenance of the fuel supply within the military is a very complex problem. Fuels are procured around the world from a wide variety of suppliers. These products are often blended together and stored for months or years. This is in contrast to the rapid turnaround experienced in the commercial sector. Because of the high dollar value of fuels such as the Navy's F-76 (marine diesel fuel), especially in strategic storage locations,

the issue of premature stock rotation has become highly visible and logistically vital.

While petroleum fuels supplied to the military have undergone significant changes over the years as new processes and lower quality feedstocks have been incorporated, the additives permitted by military specifications have not changed. The additives permitted in jet fuel are basically the same as those previously permitted in gasoline. This status was acceptable as long as the fuels were generated from sweet crudes. Stability of the products and compatibility between product batches were not a concern.

Such complacency has been replaced by concern and scientific study over the last decade. Increasing use of catalytic cracking in refineries is just one of many potential sources of problems. One of the approaches to solving compatibility/stability problems is through the use of additives. These chemicals are usually blended at low levels with the fuel stream as it is generated in a refinery.

The chemistry explaining the role of additives can be fairly straight-forward. For example, if oxidation through a free radical pathway is a problem, a free radical scavenger, such as a hindered phenol, is introduced. The art of additive development is to find a compound or mixture of compounds that will produce the desired effect and possibly provide other benefits at as low a concentration as possible while averting detrimental side effects. Unfortunately, many additives on the current Qualified Products List tend to make fuels worse.

To date, the military's approach for dealing with fuel changes has been to grant waivers as new additives are proposed. This piecemeal, and often unverified, approach has yielded few problems. However, the trends to lower quality fuels dictate a firmer scientific basis for selecting additives most appropriate to military applications and requirements. This project is an attempt at an independent, methodical evaluation of a variety of fuels and additives.

EXPERIMENTAL

There are two separate phases of the experimental work for this project. The first involves collecting and blending samples, while the second involves testing these fuels. The testing included both specification property determinations and storage stability analyses. The procedures and equipment used in both sample preparation and stability testing are described below.

SAMPLE PREPARATION
Test Fuel Selection

Two refineries which market Navy Distillate Fuel (also known as NATO F-76) were selected to furnish the test fuels for this project. The refineries were located on the Gulf Coast and the West Coast. These refineries were chosen because they both provide fuel to the Navy and have distinctly different crude slates being charged to their distillation columns and catalytic cracking units. The Gulf Coast refinery uses a wide variety of crude oils. Jn the first sampling trip to the Gulf Coast, the refinery was being charged with a blend of over 40 different crudes. Of these, approximately 60% were Gulf Coast crudes, 30% were West Texas crudes, and 10% were foreign crude oils. A mixture of crudes was also being used on the second sampling trip to the Gulf Coast. The West Coast refinery has a steady source of North Slope Alaskan crude.

For the first phase of this work, each refinery provided NIPER with seven barrels of straight-run middle distillate from their main distillation column and three barrels of light cycle oil (LCO) from their catalytic cracking unit. In both cases, these were blended at 15, 30, and 40% light cycle oil to 85, 70, and 60% straight-run middle distillate, respectively (all volume/volume). These blends are higher in percentage of LCO than most refinery fuels. These blending proportions were selected because they represent worst case fuels as far as storage stability is concerned, and therefore should provide a real challenge to the effectiveness of the additives.

During the second year of this project, several sample collection techniques were evaluated. The West Coast refinery visited in the first year provided three barrels of LCO and five barrels of straight-run middle distillate, while the Gulf Coast refinery (also previously visited) provided two barrels of LCO and five barrels of straight-run middle distillate. All

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fuels were blended at a ratio of 30% LCO to 70% straight-run middle distillate (volume/volume). The same two refineries were chosen to provide fuel because of the extensive reference data available for them from the previous analyses.

Selection of Additives

This test program was designed to evaluate antioxidants. The NRL required that the additives meet all of the criteria specified in MIL-F-16884H. Additive packages containing dispersants, corrosion inhibitors, and/or phenylene diamines were not solicited.

Nine different additive manufacturers provided additives that were used in the test fuels. A tenth additive treatment was made of an equal blend of two of the additives to study possible incompatibility problems or synergistic enhancement. In the first phase of this project, all of these additives were blended into the test fuels at 12 and 24 ppm (volume/volume) based on the whole composition of the additive package (including diluents). The amount of active ingredients (antioxidants) in these additive packages varied from 15 to 100%. The manufacturers of the additives and their products are listed alphabetically below. The test results in this report are not in this order, but are listed in a random fashion, and are designated with an arbitrary number code throughout the text and in the data tables.

Additive Manufacturer	Product
Amoco Petroleum Additives Co.	PC5-005
ANGUS Chemical Co.	17-9-22
Chevron Chemical Co.	OFA 424
E. I. du Pont de Nemours & Co., Inc.	FOA-3
Ethyl Petroleum Additives Division	EDA-40
Nalco Chemical Co. Oilfield Services	5300
Nutmeg Chemical Co.	USN-FP#3
Petrolite Industrial Chemicals Group	XF-1300
UOP Process Division	POLYFLO 121

In a cooperative agreement with NRL, the U.S. Army provided two additional additives for this study. The Army was interested in the use of both biocides and antioxidants and included both in their additives. They also wanted their additives blended at higher levels than the NRL samples. One of these additives was blended at levels of 100 and 300 ppm (v/v), while the other was blended at 67 and 200 ppm (v/v). These values are based on the whole additive

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package. The high levels are the recommended treatment levels for field use by the Army, while the low levels provide a similar concentration of antioxidant to those for the other packages evaluated.

The visit to the Gulf Coast refinery to collect fuels for testing sample collection techniques was different from the trip to the West Coast refinery because many of the test conditions were eliminated due to storage stability results on the West Coast fuels. Also, all of the additives were used in one of the sampling techniques. The data for these tests will be presented in the next report.

Test Fuel Generation

Two refineries were visited in the first year of this study. The first test fuels were generated at a Gulf Coast refinery the week of March 18, 1985. Stability tests were started on these fuels before the West Coast samples were blended. Therefore, samples were not collected at the West Coast refinery until the week of May 13, 1985.

In order to assure good quality control of these samples, a strict experimental protocol was followed. This protocol attempted to limit all sources of fuel contamination or exposure to oxygen prior to complete additive treatment.

The first step in quality control was in obtaining proper containers for the sample fuels. All containers used for the fuel additive study had closed heads and were epoxy lined unless otherwise noted. The cans and barrels conformed to the following specifications:

Container	Gauge	DOT classification	Opening(s)
55-gallon drum	20x18	17EDOT	2" and 3/4"
5-gallon cans	24	17EDOT	2-1/3"
1-gallon cans	24	17EDOT	1-3/4"

Prior to visiting the refiners, the cans and drums needed for the additive testing were carefully prepared. They were rinsed with toluene, permitted to soak overnight with toluene, and drained thoroughly. They were then rinsed with acetone to remove all traces of toluene. This was followed by a second

acetone rinse and drying. The dried containers were filled with argon and sealed. The argon filling minimized the contact the oil had with air at each step of the sampling procedure since the fuel was displacing argon as each container was filled.

The test fuels were blended using 15, 30, and 40% (volume/volume) light cycle oil (LCO). Because of physical constraints, it was impossible to complete all blending within 24 hours. Since LCO is known to be relatively unstable, it was critical to have it exposed to the additives before any oxidation took place. Therefore, the test fuels were blended on two different days. The additives were added to appropriate portions of straight-run middle distillate on the first day, leaving the second day for the blending of the LCO. In this way, the LCO was in contact with the additive at the earliest possible time.

On the first day of sampling, seven 55-gallon drums were filled with straight-run middle distillate. At both refineries, the fuel was obtained directly after the dryer so that water was removed from the sample. After the drums were filled with fuel, they were blanketed with argon for further protection of the fuel until it was used. Later that day, the straight-run middle distillate was poured into the 5-gallon cans using weight as the basis for measuring the amount of fuel needed to make up the 85, 70, or 60% (volume/volume) straight-run middle distillate portion of the fuel.

The specific gravity of each barrel of fuel was measured with a hydrometer. This was used to calculate the weight of fuel needed to account for a given volume of the straight-run middle distillate or light cycle oil. Then, the appropriate volume was obtained by weighing the fuel. After the first trip to the Gulf Coast refinery, where all weighing was done with a Model 2881 Toledo Scale which was accurate to 0.11 kg, all scales were rented on location. They were all digital and were accurate to ±0.05 kg.

The additives were added to the straight-run middle distillate at levels of 12 and 24 ppm (v/v) using an SMI P5068-2000 adjustable, digital Micro/ Petter with disposable tips. Since the fuel was blended by volume, the additives were added by volume. The volume of additive needed for 12 and 24 ppm (v/v) of additive in five gallons of fuel was calculated, and the same volume was used for all test fuels. The volume of the Micro/Petter was sufficiently accurate (±0.02 μl) that weight measurements were not used. The

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only blending done on the first day was mixing caused by the movement of the cans.

On the second day of sampling, three 55-gallon drums were filled with LCO. The LCO was obtained directly from a tap leaving the catalytic cracking unit at both refineries. The cracked stock was added to the straight-run middle distillate/additive mixtures using the weight of fuel needed to account for the 15, 30, and 40% LCO in this blend.

As soon as the cracked stock was added to the mixture, it was blended vigorously with a mechanical stirrer powered by an air-driven motor for approximately two minutes. At that point, a 1-gallon can was filled with the blend from the five-gallon can. Both the 5-gallon cans and the 1-gallon cans were then blanketed with argon and sealed. All cans were labeled with a four-digit number that did not indicate their origin. While the samples are sequential and follow a pattern as far as the percentage of LCO and the parts per million of additive, the additives are in no particular order. They were primarily listed in the order they were received at NIPER and are not in alphabetical order.

The 5-gallon cans containing four gallons of fuel were shipped to DTNSRDC for distribution to their own labs, NRL, and ARTECH Corporation. The 1-gallon cans were shipped to NIPER for testing. The cans were kept in cold storage before distribution. DTNSRDC and NRL used 4° C storage, while the storage at NIPER was 15° C. ARTECH did not store the fuel for any length of time before testing, so cold storage was not used.

During the second year of testing, the focus was on investigating sample collection techniques which might artificially stabilize the fuels. There-fore, fuel was blended using several different protocols. At the West Coast refinery, which was visited the week of February 3, 1986, eight different sets of parameters were used in the sample collection process. All fuels were blended at 70% straight-run middle distillate to 30% LCO (volume/volume). Each set of fuels contained an additive-free sample and three additive blends. The additives were blended into the fuel at a concentration of 24 ppm (v/v).

Due to safety considerations at the refinery, the blending was performed in a different order than in the past. The LCO was obtained first and could

not be moved immediately because of the high temperature of the fuel. However, the additives were blended into the LCO within 24 hours. The straight-run middle distillate was then blended into the LCO/additive mixture.

A control set of samples was collected using the same sample collection procedure that was used during the first year. A second set was generated by blending in 5-gallon epoxy-lined cans, but the samples were sparged with air for 30 minutes at a rate of 1 l/min. Bottled air with an in-line filter was used for the air supply. This was hooked to a manifold that had six delivery points. Each port was controlled by an Ideal metering needle valve that was calibrated with a rotameter. A Teflon tube connected the valve with a gas dispersion tube (Pyrex 39533, coarse).

The third set of samples was also collected in epoxy-lined cans and blanketed with argon. However, just prior to blending, 10 ml of HPLC grade water was added to the sample using a 10-ml syringe. The fourth set of samples was collected in epoxy-lined cans which were infused with 10 ml of water and sparged with air for 30 minutes.

The remainder of the samples was blended in unlined steel cans. These cans were carefully checked for any signs of rust before they were cleaned and dried. However, these samples were all collected in duplicate in case one of the cans had rust which was not detected. The samples collected in these cans were 1) argon blanketed, 2) air sparged, 3) injected with water and argon blanketed, and 4) injected with water and sparged with air. In other words, these were an exact parallel set to those obtained in lined cans. Two samples [the control (additive-free) fuel and an additive blend] were collected in unlined cans and were left with an air blanket.

The visit to the Gulf Coast refinery to test sample collection techniques took place the week of June 9, 1986. These samples were collected at the same points where they were drawn on the previous visit.

Because of the storage stability results from the sample collection techniques from the West Coast fuels, the test matrix for this trip could be reduced considerably. Four sets of samples were collected in epoxy-lined cans. Of these, one was sparged with air for 30 minutes at 1 l/min, a second was blanketed with argon, and a third had 10 ml of water added to each sample before being air sparged.

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One set of samples was drawn in the lined cans at this refinery which was not drawn at the West Coast refinery. Steel wool was placed in these cans to provide a metallic contact without the risk of hidden rust in an unlined can. The amount of steel wool used in each sample, in those tests where it was used, was based on the metallic surface area which would come in contact with the fuel in an unlined can. The surface area of the steel wool was estimated using the following method:

1. The diameters of fifteen 4-inch strands of steel wool were measured with a micrometer.

2. The total surface area of each of the strands was calculated.

3. The area of all of the strands was totaled.

4. The weight of all the strands of steel wool was measured on a Mettler balance. The weight divided by the surface area gave an estimate of the weight needed for a given surface area.

After the steel wool was weighed, it was cleaned with toluene and acetone. It was then dried for an hour at 100° C and stored in a closed plastic bag until it was used. The steel wool was introduced into the sample after the blending was completed.

The remaining samples were blended in unlined steel cans. Water was added to one set of samples which were then sparged with air for 30 minutes at 1 l/min. The remaining set was blended and left with an air blanket.

Besides the samples gathered to test sample collection techniques, a set of fuels was obtained in unlined cans in which all of the additives were blended at a concentration of 24 ppm (v/v). These samples were left with an air blanket.

Testing of Additive Blends

In order to evaluate the additives in this test matrix, both storage stability and bulk property tests were run on the fuels blended during both phases of this program. The storage stability studies covered a wide range of temperatures and were conducted at four different laboratories. The specification tests were primarily aimed at ensuring that the base fuels conformed to Naval specifications. However, tests such as the demulsification tests [modified ASTM D1401 using synthetic sea water (ASTM D665)] at a test

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temperature of 25° ±1.1° C were aimed at ensuring the additive did not make the fuel unusable for Naval use.

Stability Testing. Samples were subjected to accelerated aging at temperatures of 43°, 65°, 80°, and 95° C. Except for the 95° C test (ASTM D2274), none of these tests have a standardized protocol. Therefore, a detailed description of the tests will be included below. Four different types of stability tests were used in this study. First, there are the bottle tests which were conducted at 43°, 65°, and 80° C. Second is the ASTM D2274 accelerated storage test that was modified for some of the stability studies. The third test used was a small-scale Teflon cup method, and the fourth was a method using an oxygen pressurized glass bomb.

Since the bottle tests are very similar, they will be discussed as a group. Where necessary, different techniques used by one lab or another will be pointed out. Both DTNSRDC and NRL performed 43° C storage stability tests on the fuel additive blends. Duplication was performed at this temperature because it is generally agreed that results at this temperature are indicative of what will happen to a fuel in long-term ambient storage. ARTECH did bottle studies at 65° C, while NRL conducted a second set at 80° C.

The bottle tests were performed on 300 ml samples in 500 ml-borosilicate glass bottles with Teflon-lined screw caps. In order to allow oxygen to come into contact with the sample, holes were drilled into the bottle caps to accommodate 6-mm glass tubing. After a glass wool plug was inserted into the tubing, it was fitted into the hole in the cap. The glass wool plug elimi-nated the possibility of contamination of the fuel by particles in the air. The bottles are shown in figure 1.

The bottles were initially cleaned with a gum solvent (an equal parts mixture of ethanol, acetone, and toluene). They were then scrubbed with a slightly alkaline cleaning solution and rinsed thoroughly with tap water and distilled water. The bottles were then soaked in distilled water for at least 8 hours. After this, they were rinsed with acetone and put in a 110° C drying oven for an 8-hour period. At NRL, these bottles were weighed after cooling overnight. The other laboratories did not weigh the bottles at this point.

After being cleaned (and weighed at NRL), the bottles were rinsed with approximately 50 ml of the sample fuel. They were then filled with 300 ml of

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Glass wool plug

Cap

Borosilicate glass tube

PTFE insert for cap

500 mL Borosilicate glass bottle
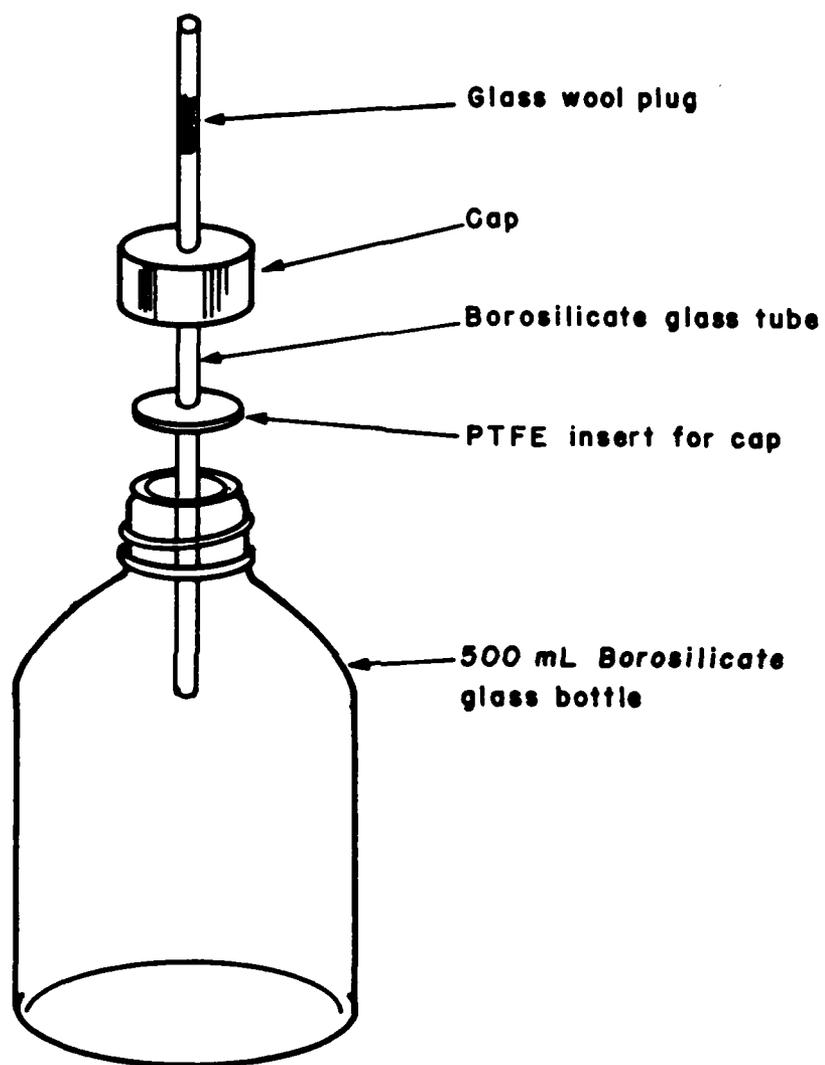
FIGURE 1.   Flasks used in accelerated storage stability bottle tests.

the test fuel which had been filtered through Gelman A-E glass fiber filters. These bottles were stored in the dark at an accurately maintained temperature for the predetermined test period. When the test period was over, the bottles were removed from the oven and allowed to cool in a dark place for 24 hours.

After cooling, the samples were filtered for sediment. Two Gelman glass fiber filters (type A-E, 47 mm) were cut down to a 45-mm diameter and placed in a #0 Buchner filter funnel. These filters were wetted with heptane and several ml of fuel. This blend was discarded, and the remainder of the fuel was filtered. Some of this fuel was saved for ASTM D1500 color determination. The bottles were rinsed with three 50-ml portions of heptane. These rinses were also filtered through the glass fiber filter, followed by a heptane rinse of the filter cake.

At NRL, the bottles and funnels were placed in a vacuum oven which was evacuated from an initial 27 inches Hg to 30 inches of Hg. The oven was heated to 120° C, and the contents were maintained at that temperature and pressure for 12 hours. The oven was then cooled to room temperature before the vacuum was relieved. The bottles and funnels were allowed to equilibrate for several hours after which final weights were determined. The filterable sediment was determined by the change in weight of the filter and filter holder, while the adherent gum was determined by the weight change of the 500-ml flask. Both the filterable sediment and adherent gum were corrected using appropriate blanks. The blanks were empty bottles treated the same way that the fuel samples were treated.

DTNSRDC and ARTECH followed the same protocol for filterable sediment but used a different technique for obtaining adherent gum. Both of these laboratories rinsed the 500-ml bottles with a gum solvent to remove all adherent gums. They then evaporated the solvent in a preweighed 200-ml beaker using the apparatus and procedure described in ASTM D381 (Existent Gum in Fuels by Jet Evaporation). After the beakers were allowed to equilibrate, they were accurately weighed on an analytical balance to determine the amount of adherent gum. Blanks were used to ensure accurate values for the gum.

The following tests were performed using this basic bottle method of accelerated storage stability:

Temperature, °C	Laboratory
43	NRL
43	DTNSRDC
65	ARTECH
80	NRL

A new Teflon cup stability test that was developed in an attempt to gener-
ate useful fuel degradation data without requiring large amounts of sample
fuel or oven volume was used by NIPER. In standard procedures such as those
just described, fuel that has been stored at elevated temperatures for a
period of time is filtered through a glass fiber filter, and the weight
increase of the filter is reported as filterable sediment. Adherent gum is
determined from the weight gain of the storage container. Since the adherent
gum often represents a weight change of only a few milligrams in a bottle
weighing many grams, it can be difficult to determine accurately. In
addition, most methods of determining stability require a relatively large
volume of sample and a large number of storage containers, since each sample
and each storage time requires a separate container. In the Teflon cup
method, the sediment is collected in small Teflon weighing cups. Since the
cups weigh only about 50 mg, the weight of sediment can be determined to the
nearest 0.01 mg on an electronic microbalance. Several cups can be placed in
each storage container with one cup being removed at the end of each
designated time period. Consequently, only one container of fuel is required
for testing a fuel over an entire series of times (see figure 2).

The storage containers used in the Teflon cup tests were 480 ml boro-
silicate glass jars measuring 121 mm in diameter by 97 mm high (Pyrex 6946).
The polystyrene screw caps on the jars were fitted with a layer of Teflon FEP
film backed by a layer of aluminum (Cole-Parmer 6804-30). This was cut so
that it was approximately 5 mm larger on all sides than the lid. The con-
tainers were thoroughly cleaned before the storage period. They were
initially cleaned with 5% detergent solution and rinsed with tap water to
remove all traces of the detergent. This was followed by sequential rinses
with deionized water, acetone, and pentane. The storage jars were then dried
at 100° C for one hour to ensure they were completely dry.

The Teflon FEP weighing cups (Cahn Instrument 2034) used in this set of
tests were approximately 18 mm in diameter by 10 mm deep with a volume of
2 ml. Five holes were punched in the bottom of each cup with a No.19 syringe

needle so that the fuel could be drained from the cups. These cups were cleaned by the same procedure that was used for the storage jars, except that they were dried at 40° C under vacuum.

Teflon (polytetrafluoroethylene) cup holders were constructed at NIPER to hold the test cups (see figure 2). These holders are disks 13-mm thick by 985 mm in diameter. Ten flat-bottomed holes 9-mm deep and 18 mm in diameter were machined into each disk in a distinctive pattern such that a cup could be identified by the hole it occupied. The position of each test cup is identified in figure 2. The holders were cleaned with the same technique used for the storage containers and then allowed to equilibrate overnight.

The Teflon cups were fitted with nylon filters (Schleicher & Schnell 13 mm diameter, 1.2 μm pore size) that covered the inside of the bottom of the cup (figure 2). The cups with the filters were weighed on a microbalance. They were then placed in the Teflon cup holder in the storage jars. Three hundred ml of fuel was vacuum filtered through a Gooch crucible fitted with two 934-AH Whatman glass microfiber filters. Then this filtered fuel was carefully poured into the storage jars which subsequently were transferred to a Despatch laboratory oven set at 65° C. The oven temperature was monitored by a thermocouple immersed in a bottle of oil and connected to a digital pyrometer.

For these tests, two Teflon cups were removed from storage at two, four, eight, and twelve weeks. At the end of each time period, the jars of fuel were removed from the oven and were allowed to cool in darkness for four hours. Two preweighed, mixed esters of cellulose filters (Millipore RAWP04700, 1.2-μm pore size and 47-mm diameter) were placed on a vacuum filter apparatus, and the vacuum was started (figure 3). (One of these filters was used as a blank, and the other was used to collect the sediment. Blanks were needed for each sample because repeatability was unacceptable using a single blank for a set of filters.) A Teflon cup full of fuel was carefully removed from the storage jar with a pair of Teflon tweezers. The cup and filter were placed on the Millipore filters with the vacuum on and rinsed thoroughly with iso-octane. The vacuum was turned off after the iso-octane had been pulled through the filters and they appeared dry. The two filters and the Teflon cup fitted with a filter were placed in a vacuum oven (National Appliance Co. Model 5831) and dried overnight at 40° C and 9.5×10^4 N/m^2. The next morning, they were allowed to cool in the oven and then were exposed to the
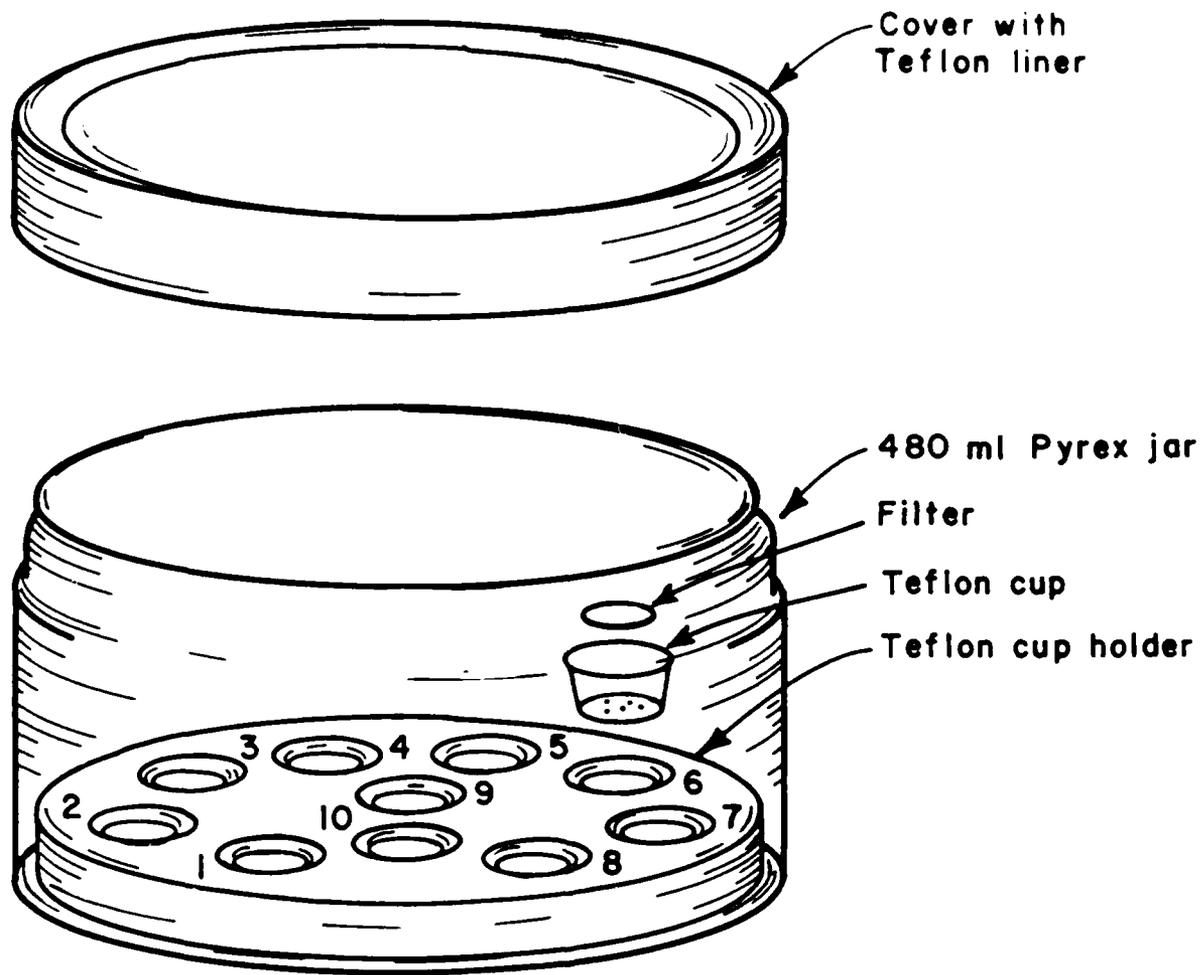
FIGURE 2. - Apparatus for Teflon cup stability storage test method.

Teflon cup

Filters (2)

Membrane filter holder

Rubber stopper

To vacuum

1000 ml. Vacuum flask
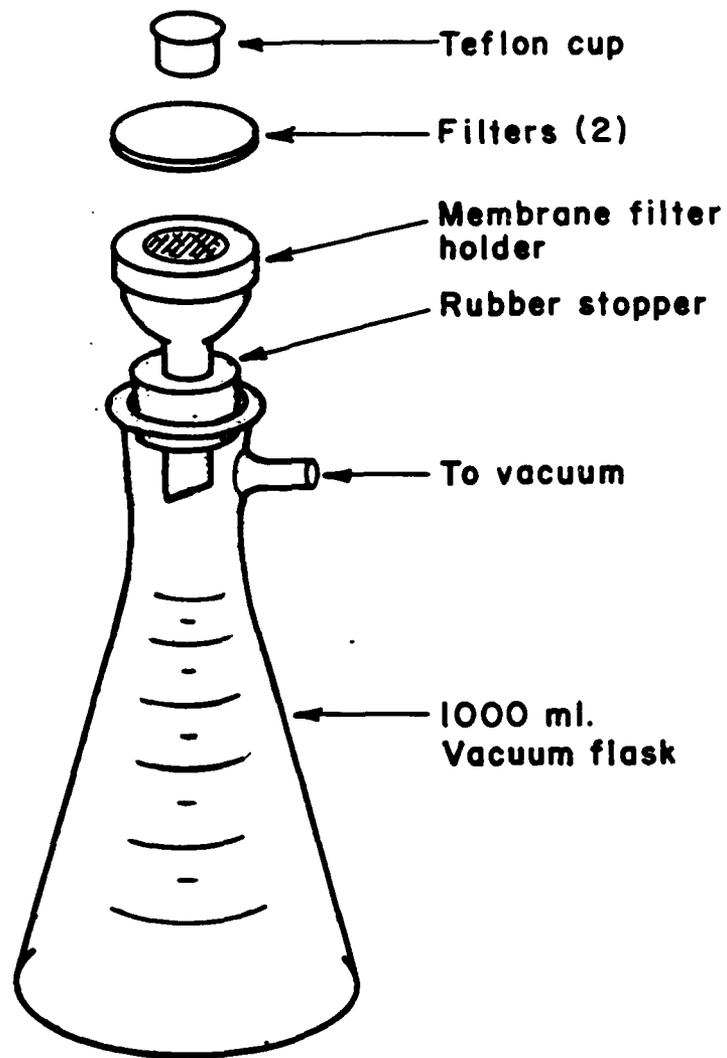
FIGURE 3. - Filtering apparatus used in the Teflon cup stability test.

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atmosphere of the room for one hour before weighing. A Cahn Model 4700 Automatic Electrobalance was used for weighing all filters and Teflon cups to the nearest 0.01 mg. The total amount of sediment was the weight increase of the filter-fitted Teflon cup added to the weight increase of the top filter.

DTNSRDC performed a modified version of the ASTM D2274 accelerated storage stability test on many of the fuel blends. The test procedure that was used is generally the same as that found in the ASTM manual, but three significant changes were made in the test protocol.

The first change in procedure was in the cleaning process. In order to ensure that no chromium ions were added to the fuel, and to protect laboratory personnel, no chromic acid was used. Instead, the oxidation cells were initially cleaned with 50-ml aliquots of gum solvent until the discard was colorless. This glassware was then scrubbed with a mildly alkaline detergent and thoroughly rinsed with deionized water. The oxidation cells were soaked in deionized water overnight and then dried at 100° C for 4 hours. They were then cooled to room temperature for 4 hours.

Another variance from D2274 was the use of blanks in the weighing of crucibles and beakers. Specifically, a blank crucible was carried through the test from the initial weighing, to the filtering of heptane, to the drying, to the final weighing. The blank beakers were weighed, filled with an amount of gum solvent equivalent to that in the sample beakers, dried by jet evaporation, equilibrated, and reweighed.

The ASTM D2274 accelerated storage stability tests are run for 16 hours. However, some of the test fuels were so stable that the time was extended for carrying out these tests. Some were run at 24 hours, while others were stressed as long as 40 hours. All other steps were carried out as described in the ASTM D2274 test procedure. It was only in the cleaning, the use of blanks, and the duration time that the DTNSRDC varied from the written test procedure.

NRL and DTNSRDC both did work with pressurized ASTM D525 bombs. In these tests, the glass liners in the bombs were washed in detergent and rinsed with deionized water. They then were rinsed with gum solvent and dried prior to testing.

The fuel samples were filtered through nominal 1.2-μm glass fiber filters (Gelman A-E). One hundred ml of the filtered fuel was poured into the glass liner, which was inserted into the bomb. The bomb was sealed and attached to a manifold connected to a source of 99% pure oxygen. The gauge measuring the oxygen pressure was capable of measuring 0.1 psig increments. The bomb was pressurized to 100 psi and flushed three times. When the bomb was filled for the fourth time, the gauge was used to adjust the pressure to 100 ± 0.1 psi. The isolation valve then was closed, and the bomb was placed in the oven for the duration of the test.

After the bomb was stored for the appropriate time period, it was removed from the oven and quenched in cold tap water for several hours. The pressure was measured and relieved, and the bomb was allowed to equilibrate for several more hours. After equilibration, the fuel was filtered through a 1.2-μm glass fiber filter with a slight suction. Both the filter and glass liner were washed with small amounts of hexane to rinse away any fuel. The liner was then carefully rinsed with gum solvent (approximately 25 ml). The gum solvent was allowed to evaporate on a hot plate in an aluminum weighing dish. Both the filters and weighing dishes were then placed in a 100° C oven for several hours. Blank filters and weighing dishes were treated the same as the test filters and weighing dishes. The filters and weighing dishes were removed from the oven and weighed on an analytical balance. The initial weights were subtracted from the final weights and were corrected for the blanks. Duplicate analyses were performed for all samples.

Fuel Characterization

Military specifications require that the fuel used in Naval distillate meet certain bulk property requirements. Therefore, the control fuels used in these studies were analyzed for all of the tests specified in Military Specification MIL-F-16884H. Because an additive could have an effect on the demulsibility [ASTM D1401 Using Synthetic Sea Water(ASTM D665) at 25° C], the copper corrosion (ASTM D130), and the flash point (ASTM D93), a blend containing each of these additives was also subjected to these tests.

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DISCUSSION OF RESULTS

There are four laboratories involved in testing fuels for this additive study. All four laboratories have conducted accelerated storage stability studies as well as necessary fuel characterization tests. As has been mentioned previously, the first year of this study was spent on analyzing additive blends from two refineries. Storage stability studies were conducted at 43°, 65°, 80°, and 95° C on the 30% LCO/70% straight-run middle distillate additive blends from the Gulf Coast and on the 40% LCO/60% straight-run middle distillate additive blends from the Gulf and West Coast refineries. Fuel characterization studies were carried out on all of the control fuels to ensure that they met military specifications. In addition, some of the additive blends were tested for copper corrosion, demulsibility, and flash point to ensure that there was nothing in the additives that would make them unacceptable for use by the Navy.

The initial phase of this project brought mixed results as to the efficacy of the additives. Some of the control (additive-free) fuels proved to be so stable that no definitive statements could be made. However, the least stable fuel did produce some variation in the additives. Therefore, the decision was made to do some experimental work to increase sediment levels produced by the fuels. The results showed that this technique was not uniformly effective in increasing sediment from fuel to fuel, so new sample collection techniques were proposed.

The second year of this study was primarily concerned with testing a variety of sampling collection techniques. This was done because it was theorized that the careful collection of the samples had resulted in stabilization of the fuels. In this phase of the study, only the additive-free 30% LCO/70% straight-run middle distillate blend and three of the additive blends were tested. The samples for the sample collection techniques were stored at 43°, 65°, 80°, and 95° C. Very few fuel characterization studies were done on these fuels.

ADDITIVE EVALUATION

Test Fuel Characterization

The straight-run middle distillate and LCO streams from each of the refineries have been characterized by David Taylor Naval Ship Research and Development Center (DTNSRDC). Their results are shown in table 1. Also shown is the test method used by DTNSRDC and the Naval requirement for each of the tests. These tests indicate that the West Coast fuel is higher in aromatics, nitrogen compounds, unsaturated compounds, and sulfur than the Gulf Coast fuel. It is also darker in color than the Gulf Coast fuel. All of these results imply that the West Coast fuel would be less stable than that obtained on the Gulf Coast.

The additive-free LCO from the West Coast is darker in color than allowed, but the percentage of LCO in the diesel fuel is small enough that the blended color would be acceptable. The cetane index for the additive-free LCO from both refineries is lower than the accepted minimum, but this would also be alleviated when the two streams were blended. Thus, specification fuels can be made from these streams.

NIPER did several characterization tests on the fuels blended for these studies. The results can be found in table 2. All of these fuels were within the tolerances required by Military Specification MIL-F-16884H. Therefore, if a blend with additive does not meet one of these standards, the failing result can be attributed to the additive.

Selected fuel characterization studies were run on all of the West Coast 40% LCO/60% straight-run middle distillate fuel additive blends which were treated at 24 ppm (v/v). These results are shown in table 3. The results show that the acid number, ash content, copper corrosion, and flash point were not affected by the additives. However, some of the additives did affect the demulsibility tests. Additive number 4 did not pass this test even after several repeats, and additive 12 showed an increase in demulsification time over the control fuel. All other additive blends seemed to separate more easily than the control fuel itself. The Navy allows 0.2 weight percent of carbon residue on 10% of the bottoms. It appears that additives 6 and 10 caused the fuel to develop more carbon residue than is allowed. Both the demulsibility and carbon residue will have to be checked in future samples to see if these additives should be disallowed.

A wide range of fuel additive blends were tested for both demulsibility and flash point. None of the additives had any impact on the flash point of these blends (table 4). The major factor in determining the flash point was the percentage of LCO in the blend rather than the presence of additives. The additives did have an affect on the demulsibility of the fuels (table 5). Fuels 4, 5, 7, 11, and 12 did not pass the demulsibility specification of 10 minutes in some of the blends. However, only additives 11 and 12 failed the test in more than one case.

Accelerated Storage Stability

Three of the six blended streams were analyzed for storage stability at 43°, 65°, 80°, and 95° C. The streams chosen for analysis were the 30% LCO/70% straight-run middle distillate from the Gulf Coast refinery and the 40% LCO/60% straight-run middle distillate from both the Gulf Coast and West Coast.

95° C Studies

The 95° C accelerated storage stability test (ASTM D2274) was carried out by DTNSRDC personnel. This test is required by Military Specification MIL-F-16884H, which has a maximum of 1.5 mg/100 ml sediment. The test is normally run for 16-hour time periods. However, since these fuels were so stable under the standard 16-hour condition, the 30% LCO fuel blends from the Gulf Coast were run for 40 hours, and the 40% LCO fuel blends from the West Coast were aged for 24 hours.

The fuel additive blends containing 40% LCO from the Gulf Coast were stored for the normal 16 hours. They ranged from 0.1 to 0.8 mg/100 ml sediment (see table 6) with the 100% LCO generating 4.3 mg/100 ml. With the exception of the LCO, these fuel additive blends meet the military specification of ≤1.5 mg/100 ml. While the values of the additive blends range from 0.1 to 0.8, no real conclusions can be made about the additives because the control fuel (additive-free) was apparently quite stable under D2274 conditions. Thirteen of these 40% LCO blends with additives appear to be better than the straight-run middle distillate, indicating that this is a poor test for evaluating the additives in freshly refined fuels.

The color data for these samples are given in table 6. All of the samples had a color of <1.0 when the tests were started. At the end of the 16-hour period, the color had changed to between 2.0 and 3.0. The color for samples with additives 1 and 4 deteriorated the least at this condition.

The Gulf Coast 30% LCO samples were in the 95° C temperature bath for 40 hours. Table 7 shows that sediment values ranged from a low of 0.3 mg/100 ml to a high of 2.6 mg/100 ml. The control fuel contained 2.2 mg/100 ml of sediment. While there was only one additive that appeared to be worse than the control fuel, there were several that were within experimental error of having no effect on the control fuel. A few additives did seem to delay sediment formation.

The colors from the 30% LCO blends initially ranged from 1.0 to <4.0 with most being in the range from 2.0 to 2.5 (table 7). After aging, almost all were between 4.0 and 5.0. Samples with additives 2 and 11 at 24 ppm (v/v) gave the least color formation. Both of these samples also appeared to delay sediment formation, although the correlation between color and sediment formation does not always hold.

The fuel additive blends from the West Coast containing 40% LCO were stored at 95° C for 24 hours (table 8). These studies showed that the sediment in the fuels varied from 0.1 to 3.6 mg/100 ml. The interesting thing about these studies is that both fuels 7 and 8 at concentrations of 12 and 24 ppm (v/v) were considerably worse than the LCO. Many of the additives were better than the control fuel; but, since the control fuel only produced 0.5 mg/100 ml of sediment, these results are inconclusive in regard to additive efficacy.

All of the colors for the 40% LCO blends from the West Coast were initially <2.5 on the color scale (table 8). This value is an approximation because the fuel has a red tint, which is not on the ASTM D1500 color wheel. After 24 hours, most of the samples developed a color between 3.5 and 4. Fuels with additives 2 and 10 had the least color degradation with a final color of 3.0. These fuels also generated little sediment (0.1 mg/100 ml).

Fuels with additives 2, 10, 11, and 12 generally produce the least amount of sediment in the fuels tested at 95° C. Fuels with additives 7, 8, and 9 seem to have the least benefit to the fuels. However, the control fuels did not produce enough sediment to draw any definitive conclusions.

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80° C Studies

NRL completed 80° C bottle tests on the same three fuels studed by DTNSRDC. The 80° C bottle tests are generally run for two weeks but were stored for longer periods in this study in hopes of generating enough sediment to show some differentiation between the additives. The 40% LCO fuel additive blends from the Gulf Coast were stored for two weeks, while the 30% LCO fuel additive blends from the Gulf Coast were in storage for four weeks, and the 40% LCO blend from the West Coast were stored for three weeks.

In the 80° C, two-week studies of the 40% LCO blends from the Gulf Coast, the fuels generated from 1.8 to 5.0 mg/100 ml sediment (table 9). The control fuel had 3.4 mg/100 ml sediment, while 10 of the additive blends produced less, and 14 had as much or more. It appears that some of the blends did reduce sediment formation while others actually increased sedimentation. Several appeared to have very little impact on the storage stability of the fuel.

The color results for these fuels (table 9) indicated that the additives had no real effect on the color of these fuels. The initial colors varied from 1.0 to 3.0 for the additive blends, but there was little variation in the final colors. All of these were between 5.0 and 5.5.

The 30% LCO fuel additive blends from the Gulf Coast were aged twice as long as the 40% LCO blends but developed little additional sediment or color (tables 10). It is interesting to note that the samples with 24 ppm (v/v) of additives 2 and 3 only developed a color of 5.0 while generating a relatively small amount of sediment. On the other hand, the samples with 12 ppm (v/v) of additives 8 and 9 were the darkest of this group with a color of 6.0. These samples also produced much more sediment than the control fuel.

The West Coast fuels tended to generate more sediment than those from the Gulf Coast. NRL tested the straight-run middle distillate and the LCO as well as the 40% fuel blends for three weeks. They found between 0.6 and 9.6 mg/100 ml of sediment in the samples (table 11). The rankings for this set of fuels show that only four additive blends generated significantly more sediment than the control fuel. These were additives 6 and 8 at a concentration of 12 ppm (v/v) and additives 7 and 8 at a concentration of 24 ppm (v/v).

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The sample of the blend containing 12 ppm (v/v) of additive 8 also showed the most color degradation from the initial to the final color (table 11). This sample changed from <3.0 to <7.5 in three weeks, while the majority of the other fuels had final colors between 6.0 and 7.0. The final color for the control fuel was 6.5. The two additives which seemed to delay color degradation to the greatest extent were 2 and 10. They were also among the best at reducing sediment formation.

After two weeks at 80° C, a fuel which has 6 mg/100 ml of sediment is approximately equivalent to 1.5 mg/100 ml of sediment using the ASTM D2274 technique (1). None of the 40% LCO fuel additive blends from the Gulf Coast developed 6 mg/100 ml, while only one of the 30% LCO blends developed that much. Therefore, none of the Gulf Coast fuels were deemed poor enough to adequately determine additive efficacy. After three weeks, several of the 40% LCO blends from the West Coast developed more than 6.0 mg/100 ml. This set of tests showed more variation among the additives than was found in the other two sets of data. The fuel with additive 2 performed well on all of these 80° C studies, while the fuels with additives 7, 8, and 9 were generally worse than the control fuel. This is the type of differentiation desired.

65° C Studies

Both ARTECH and NIPER aged the fuel additive blends at 65° C. ARTECH did bottle tests, while NIPER used a small-scale Teflon cup method. ARTECH aged the 40% LCO blend from the Gulf Coast for eight weeks while the 30% LCO Gulf Coast blends and the 40% LCO blends from the West Coast were both aged for 12 weeks. Aside from the 30% LCO blend from the Gulf Coast, which was aged for eight weeks, NIPER stored all samples for 12 weeks.

ARTECH

The fuels from the Gulf Coast which contained 40% LCO produced 0.5 to 4.3 mg/100 ml sediment after eight weeks of storage (table 12). These studies indicated that two of the additive blends were better than the straight-run fuel, and all of the blended fuels were somewhat better with additives than without.

Somewhat different results were found with the 30% LCO blends from the Gulf Coast that were aged for 12 weeks. Table 13 gives the gravimetric

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results for this set of fuels. Sediment ranged from 1.8 to 5.1 for these blends, which is slightly higher than was found in the first test fuels. These results indicate that several of the additives had little, if any, effect in delaying sediment formation.

The 40% LCO blends from the West Coast developed much more sediment than those from the Gulf Coast (table 14). For the additive blends, the sediment ranged from 3.8 to 13.7 mg/100 ml. Therefore, there was much more differentiation between the additives. In this series of tests, two additive blends [6 at 24 ppm (v/v) and 8 at 12 ppm (v/v)] produced somewhat more sediment than the control fuel. However, there were several blends which showed a significant decrease in sediment formation with the addition of an additive.

The control fuels from the Gulf Coast did not produce enough sediment to show any type of differentiation between additives. However, the West Coast fuel developed significantly more sediment. It appears that there were several blends which were virtually unaffected by the additives they contained, while several additives seemed to reduce sedimentation significantly. This trend was seen in the Gulf Coast fuels also but not so dramatically.

NIPER

Tables 15 through 20 contain the stability data (gravimetric and color) from NIPER's Teflon cup test method. The blends from the Gulf Coast were originally scheduled to be in 65° C storage for eight weeks. However, they were more stable than expected, so the 15 and 40% LCO blends were stored an additional four weeks to ensure sufficient sediment could be obtained for the evaluation of additive efficacy. The 30% LCO blends were removed at the eight-week point when it became obvious that this set of samples was not providing any additional information. The West Coast fuels were all stored for 12 weeks.

Figure 4 is a plot of the amount of sediment produced by the Gulf Coast control fuels. As expected the straight-run middle distillate has the most stability while the LCO forms the most sediment. The 15, 30, and 40% LCO blends tend to generate sediment in proportion to the amount of LCO in the blend.

25
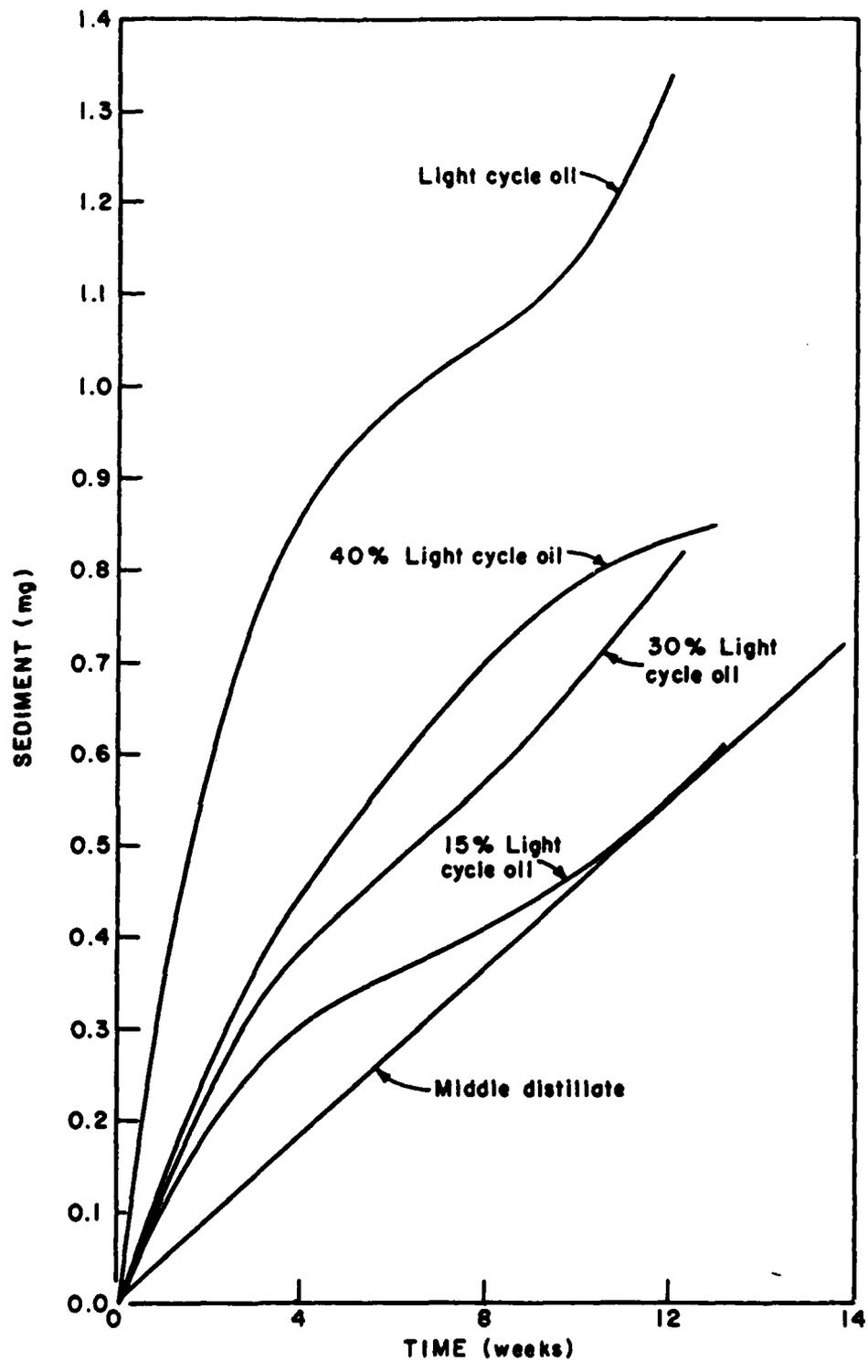
FIGURE 4. Sediment versus time for the base fuels from the
Gulf Coast using 65° C Teflon cup test method.

The control fuels from the West Coast tend to follow the same pattern as the Gulf Coast fuels. Again, the amount of sediment formed is mainly dependent on the percentage of LCO in the fuel. The West Coast fuels did produce somewhat greater quantities of sediment than those from the Gulf Coast. However, the amount of sediment is relatively small in both cases.

Data from the 15, 30, and 40% LCO additive blends from the Gulf Coast are included in tables 15 through 17. The data from these same additive blends from the West Coast can be found in tables 18-20. The units of the data from the Teflon cup stability studies are in milligrams rather than milligrams/100 milliliters, which is usually used. This is a small-scale test, and less than 3 ml of fuel is filtered through any one cup.

NIPER's data on the 15% LCO additive blends from the Gulf Coast are plotted in figure 5. The most significant aspect of this plot is that most of the additive blends fall in the same general area. This stability test method has a degree of error similar to the differences observed for many of the additives. However, especially after 12 weeks of aging at 65° C, a few additives seem to be demonstrating statistically significant improvement. Similarly, a few seem to be degrading the fuel.

The data for the 40% LCO fuel blends from the West Coast are plotted in figure 6. As has been found at the other laboratories, the West Coast fuels generally produced more sediment than those from the Gulf Coast; therefore, there is more differentiation among the additives. The 15% LCO blends from the Gulf Coast provided the least amount of differentiation among additives, while the 40% LCO blends from the West Coast supplied the most. Figure 6 indicates that only three additive blends are better than the 40% LCO blend without additives. Similar findings were confirmed by the other laboratories. The control fuels were found to be better than some of the additive blends. Also, there are cases where additive blends are worse than the 100% LCO blending stock.

As part of the stability studies, NIPER measured colors on all additive blends at each stage of the aging process. The color (ASTM D 1500) of the test fuels was read before aging and as each sample was removed. Although there were minor differences among the colors obtained for the various additive blends, these were not significant. For the most part, the colors

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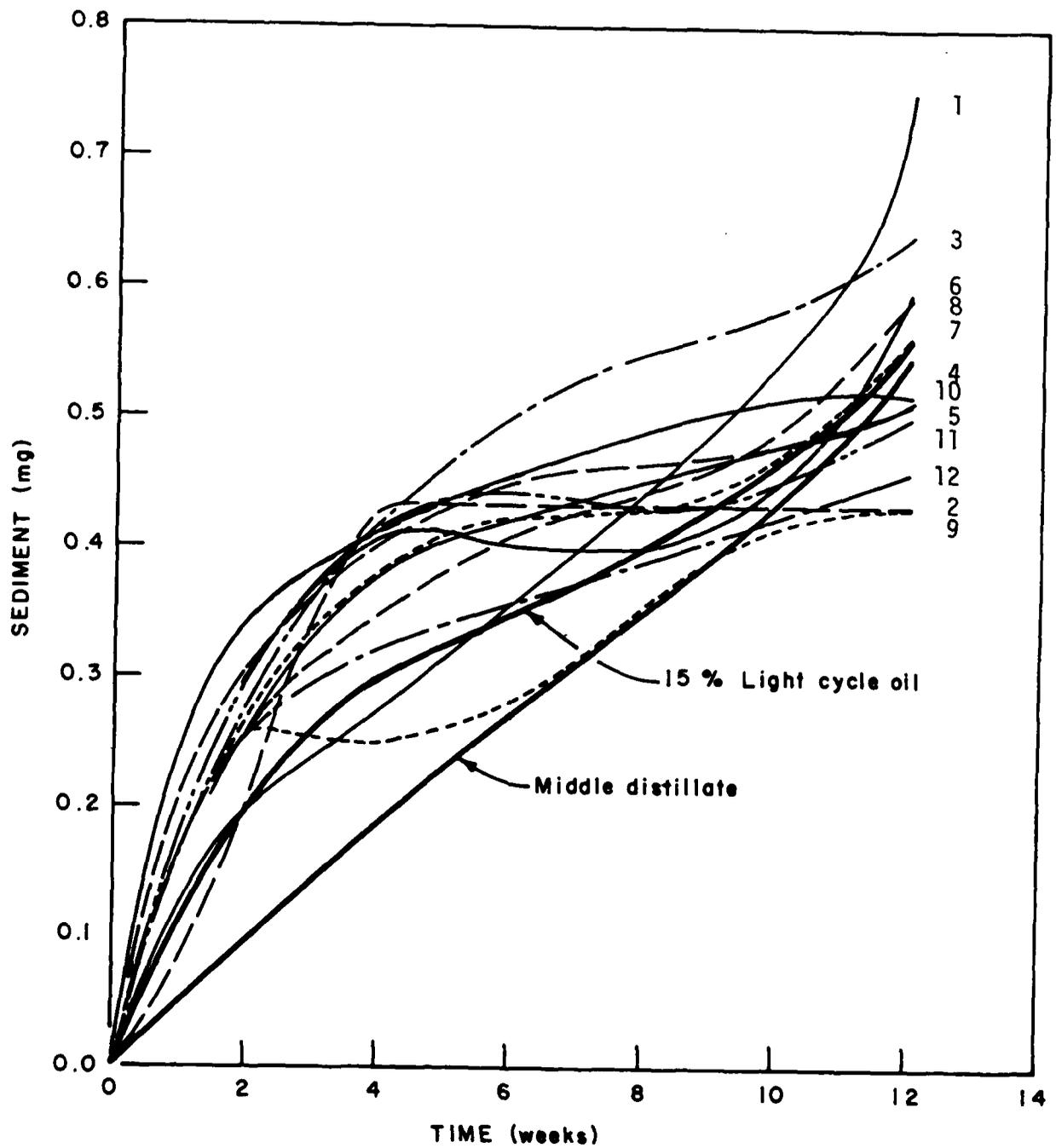
FIGURE 5. - Sediment versus time for the 15% light cycle oil blends from the Gulf Coast usinc a 65° C Teflon cup test method. These blends contain 24 ppm (v/v) of the indicated additive.

FIGURE 6. - Sediment versus time for the 40% light cycle oil blends from the West Coast using a 65° C Teflon cup test method. These blends contain 24 ppm (v/v) of the indicated additive.

were dependent on the percentage of LCO in the blends. Fuels with and without additives showed the same tendency to darken with age and generally at the same rate. No additive demonstrated any effective control over color degeneration (see tables 15-20).

43° C Studies

The 43° C accelerated storage stability tests are generally considered to be the most indicative of what can be expected of a fuel in long-term storage. Both NRL and DTNSRDC stored fuels at 43° C, but only NRL's data are included because of their longer test duration. NRL tested the 30 and 40% LCO blends from the Gulf Coast for 35 weeks. The 40% LCO blends from the West Coast were in storage for 32 weeks. The results for these studies can be found in tables 21 through 23.

The data for the 40% LCO fuel additive blends from the Gulf Coast range from a high of 6.0 mg/100 ml to a low of 0.2 mg/100 ml. The 0.2 mg/100 ml blend appears to be even more stable than the straight-run middle distillate, which generated 1.2 mg/100 ml of sediment. The additive-free 40% LCO fuel produced 4.7 mg/100 ml of sediment, and several of the fuel additive blends are no better than the fuel without the additive.

In the 30% LCO blends from the West Coast which were aged at 43° C, the control (additive-free) fuel generated 3.8 mg/100 ml of sediment. While a few of the additives appeared to be beneficial to the fuel, some were actually harmful. Fuels with additives 5 and 6 both seemed to have significantly more sediment than the control fuel. They ranged from 4.4 to 4.9 mg/100 ml sediment.

The 40% additive blends from the West Coast generated much more sediment than the Gulf Coast fuels at 43° C. The control fuel developed 11.8 mg/100 ml of sediment. In these tests, several of the additives seemed to have no impact on the control fuel. While none of the additives appeared to really hurt the fuel, several did seem effective in delaying fuel degradation.

Overall, in the 43° C studies, the fuels with additive 11 seemed to be generally good at delaying oxidation. Fuels with additive 6 were generally among those that generated the most sediment.

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The color data on the fuels which were aged at 43° C indicate there were no additives that were effective in delaying color degradation (tables 21 through 23). In fact, most colors tended to be dependent on the percentage of LCO in the fuel, and the additive blends were nearly the color of the control fuels.

Comparison of Data and Effect of Sample Treatment Before Stability Testing

All laboratories found that the 40% additive blends from the Gulf Coast did not produce significant quantities of sediment in the usual test times. Therefore, DTNSRDC did a modified D2274 test on the 40% LCO blends from the West Coast to aid in determining the amount of time other test facilities should age their fuels. They performed 95° C (modified D2274) tests on a sample of the 40% LCO fuel for 16, 20, 24, 29, 40, and 46 hours. They found that there was no significant breakdown in the fuel until it had been aged for a minimum of 24 hours, which is 1-1/2 times the normal storage period. It was decided that all laboratories would store the West Coast fuel one and 1-1/2 times longer than the normally accepted storage time for their various test procedures.

Once again, data from all laboratories show that some of the control fuels develop less sediment than those with additives. This might indicate that some additives are actually causing the degeneration of the fuels. Another indication of this is that a few of the fuels blended at 24 ppm (v/v) show more sediment than those blended at 12 ppm (v/v). However, the amount of sediment is generally so low that no definitive statement can be made.

There is a large variation in the ranking of the fuels between the various laboratories. It appears that the wide variation between laboratories could be caused by the possibility that the fuels did not undergo oxidation reactions. When the fuels were obtained, there was little contact with oxygen because they were collected in an argon atmosphere immediately upon exit from the refinery towers. The fuels were also blended under argon and blanketed with argon before shipping. The argon-saturated fuel was only exposed to air when it was filtered just before stability testing began. Therefore, the level of oxygen availability probably varied. In addition, the fuels could be exhibiting a tendency toward condensation reactions rather than oxidation.

One piece of evidence implying that oxidation did not take place in our initial laboratory testing is the observation one laboratory made that the color had degraded on a fuel that was in cold storage for several months after it had been exposed to the atmosphere. They then re-ran their stability test and obtained twice the sediment they were able to obtain with the argon-saturated fuel. Therefore, it was proposed that all laboratories prefilter the fuel and let it set at room temperature for several days in the dark before starting the stability tests.

Researchers at DTNSRDC and NRL performed studies to find out whether an exposure to oxygen and controlled waiting periods before initiation of stability testing would provide significantly more sediment. The following techniques were tested:

1. Fuel samples were sparged with oxygen at 1.8 1/hr for 24 hours at 43° C.

2. Fuel samples were evacuated to 25 inches Hg vacuum and then purged with oxygen. This was done three times before they were allowed to sit at room temperature for a period of time.

3. Fuel samples were sparged with oxygen at 1.0 1/min for 30 minutes and were then allowed to sit at room temperature.

The data indicated that significantly more sediment developed in the West Coast fuels subjected to these techniques. However, the results on the Gulf Coast fuels showed little increase in sediment with pre-aging.

Sample Collection Techniques

Since preliminary sample treatment did not enhance sediment formation as desired, it was decided that several techniques for sample collection should be tested. The theory was the same. If argon saturation was hindering oxidation, it might be necessary to eliminate some or all of the use of argon.

Two refinery visits were made to test sample collection conditions. The refineries which provided the fuel for the first phase of testing also provided the second set of test fuels. Since sample collection was of prime importance for these tests, only one fuel blend (30%) was used to test the control fuel and three additives.

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West Coast Blends

Nine different sample collection techniques were tested at the West Coast refinery. A summary of the tests done on the control fuel is in table 24. The D2274 results indicate that sample collection techniques have a strong impact on sediment formation. All of the samples in lined cans had much less sediment than those in the unlined cans. The other storage stability tests show a similar trend. However, the data are not as conclusive as they are in the case of the D2274. The unlined cans which were air blanketed and had no added water were among the top three producers of sediment in all of the stability tests. The unlined cans which were sparged with air (dry) were among the top three sediment producers in all but the 43° C tests. In the unlined cans, those that had been blanketed with argon produced the least sediment in all cases. The presence of argon also increased the stability of the fuels in the lined cans.

Gulf Coast Blends

The samples which were drawn at the Gulf Coast refinery generated much less sediment than the West Coast samples (table 25). The ASTM D2274 accelerated storage stability tests produce between two and ten times more sediment in the West Coast fuels than in those from the Gulf Coast. The sediment was 1-1/2 to 2 times greater in the West Coast fuels studied at 65° C and 80° C than the Gulf Coast fuels. There was also little difference in the various sampling techniques used to collect the fuels.

CONCLUSIONS AND RECOMMENDATIONS

In cases where the control (additive-free) fuels generated sufficient sediment, the additive blends could be evaluated at all test temperatures. Five of the additives (2, 3, 10, 11, and 12) are clearly beneficial. The remaining additive blends appear innoculous to detrimental thus far. However, further evaluation is needed before any definitive conclusions are drawn.

Two techniques were used in order to generate the additional sediment needed for the evaluation of the additives. In the first technique, fuels were exposed to oxygen and allowed to sit at room temperature for a period of time before storage stability testing. The results from the testing of the West Coast fuels demonstrated that significant amounts of additional sediment

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could be generated using this technique. However, there was little, if any, additional sediment found in the Gulf Coast samples. Since these techniques add complexity to the testing and exhibit a fuel/refinery dependence, they will not be used in future work.

The second method used to generate more sediment involved the use of several different sample collection techniques. Parameters which were varied in this testing included the type of can (epoxy lined as opposed to unlined steel), the type of atmosphere (samples were sparged with air, argon blanketed, and air blanketed), and the moisture content of the fuel (some fuels had 10 ml/5 gal of additional water introduced). Some tests were also conducted using steel wool in an epoxy-lined can to give the control of a lined can with the metallic contact of the unlined can. Since these techniques also exhibited a fuel/refinery dependence, only one collection method will be used in all future work -- epoxy-lined cans with an air blanket and dry conditions.

While both color and sediment levels are reported in many of the data tables, it would be wrong to assume a direct correlation between the two quantities. Other studies have shown that a fuel can become dark without forming solids, and similar conflicting results have been seen in this work.

Since the main goal of this project is to qualify additives for use by the Navy, it is important to get a relatively unstable fuel. Differentiation between the additives will only become apparent when a fuel is undergoing significant oxidative chemistry.

REFERENCES

1. Hardy, D. R., R. N. Hazlett, R. Giannini, and R. Strucko. Stability Measurements of Commercial Marine Fuels from a Worldwide Survey. SAE Technical Paper Series 860895, Washington, D. C., May 12-14, 1986.

2. Brinkman, D. W., K. Q. Stirling, J. W. Goetzinger, M. E. Hefner, and E. J. Zagula. Stability, Compatibility, and Related Problems of Additives in Navy Distillate Fuels Derived from Lower Quality Feedstocks. NIPER-110, November 1985, 32 pp.

TABLE 1. – Test fuel properties

Test category	Test Specification	Units	Gulf Coast		West Coast		Naval requirement
			Light cycle oil	Straight-run middle distillate	Light cycle oil	Straight-run middle distillate	
Pour point	D97	°C	-13	-17	-30	-13	20 maximum
Cloud point	D2500	°C	-9	-13	-20[1]	-3[1]	30 maximum
Viscosity	D445	cSt	3.28	3.04	2.62	3.63	1.7-4.3
Cu corrosion[2]	D130	ASTM	1B	1A	1B	1A	1B maximum
Color	D1500	ASTM	L1.0	L0.5	L3.5[3]	L1.0[3]	3 maximum
Total acid No.	D974	mg KOH/mL	0.025	0.25	0.059	0.050	0.3 maximum
Surface tension	D971	dynes/cm	32.9	28.0	32.4	28.9	
Nitrogen[4]	--	mg N/L	61	25	428	96	
Salt H_2O demul.	mil spec	minutes	2	4	2	2	10 maximum
Dist H_2O demul.	D1401	minutes	1	1	3	2	
Microseparometer	D3948	msep rating	99	98	99	99.5	
Bromine number	D1159	--	0.47	0.12	1.13	0.20	
API gravity	D298	°API	26.4	37.7	17.0	33.7	record
Flash point	D93	°C	66.7	88.9	103.3	82.2	60 minimum
Neutrality	FTM 5101.6	P/F	P	P	P	P	
Aniline point	D611	°C	42.8	73.2	<-10	63.8	record
Distillation	D86						
50% point		°F	542	526	516	546	record
90% point		°F	618	606	580	626	675 maximum
End point		°F	624	640	614	630	725 maximum
Residue + loss		pct.	5	3	2.5	7.0	3 maximum
Cetane index	D976-80		37	54	23	49	45 minimum
Sulfur content	D129	wt. pct.	0.34	0.32	0.98	0.47	1.00 maximum
Accelerated storage stability	D2274	mg/100 ml	3.62	0.36	0.56		1.5 maximum

[1] Dried with sodium sulfate, filtered through 0.45 micron membrane filter prior to determination. All samples with LCO became uniformly turbid at reduced temperature, despite drying per ASTM D 2500.

[2] At 100° C.

[3] LCO = red, SR = yellow.

[4] By chemiluminescence, standardized with pyridine in toluene.

TABLE 2. Characterization of the six fuel blends used in the additive study

Test	Naval requirement	Gulf Coast			West Coast		
		15% LCO	30% LCO	40% LCO	15% LCO	30% LCO	40% LCO
Acid number, D664, mgKOH/g	max 0.3	0.18	0.16	0.13	0.05	0.05	0.06
Ash, D482, wt pct	max 0.005	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Color, D1500	max 3.0	<1.0	<1.0	<1.0	<1.0	1.0	<1.5
Copper corrosion, D130	max 1	1a	1a	1a	1b	1b	1b
Demulsibility, military specification, minutes	max 10	5	4	2	2	2	4
Elements in oil, qualitative XRF, limit of detection, approximately 15 ppm		Sulfur only	Sulfur only	Sulfur only	Sulfur only	Sulfur only	Sulfur only
Flash point, D93, °C	max 60.0	80.5	79.5	83.5	81.5	84.5	86.5
Gravity, API		35.4	33.4	32.3	30.4	27.7	26.0
Chemiluminescence nitrogen, wt pct		0.0056	0.0066	0.0078	0.0165	0.0208	0.0226
LECO sulfur, total, wt pct	max 1.0	0.227	0.228	0.270	0.607	0.593	0.892
Copper concentration by atomic absorption, ppm		0.008	0.024	0.002	0.001	0.004	0.002
Simulated distillation, D2887, °F	IBP	266	272	278	280	284	288
	10%	419	423	428	419	424	428
	50%	534	535	536	541	535	532
	90%	654	651	650	661	652	649
	FBP	764	757	753	754	748	745

TABLE 3. Characterization of the 40% LCO additive blends (blended at
24 ppm) from the West Coast

Additive sample No.	Acid number potentiometric D664 mg KOH/g	Ash content D482 wt pct	Copper corrosion D130	Demulsibility, military specification, minutes	Flash point Pensky-Marten's closed test D93, °C	Carbon residue
Neat[1]	0.06	<0.001	1b	4	86.5	0.138
1	0.06	<0.001	1b	2	84.5	0.161
2	0.03	<0.001	1b	2	85.5	0.160
3	0.02	<0.001	1b	2	86.5	0.110
4	0.05	<0.001	1b	*	86.5	0.106
5	0.04	<0.001	1b	3	86.5	0.123
6	0.03	<0.001	1b	1	86.5	0.212
7	0.04	<0.001	1b	1	86.5	0.136
8	0.02	<0.001	1b	2	88.5	0.180
9	0.03	<0.001	1b	2	85.5	0.140
10	0.03	<0.001	1b	1	85.5	0.217
11	0.02	<0.001	1b	3	85.5	0.165
12	0.04	<0.001	1b	5	86.5	0.120

* At one hour there were 37 ml of oil and 43 ml of water; there was obvious oil in the water
phase and water in the oil phase.

[1] Control (additive-free) fuel.

TABLE 4. Flash point data for fuel additive blends at a concentration of 24 ppm (v/v) additive

Additive sample	Gulf Coast Fuels			West Coast Fuels		
	15% LCO	30% LCO	40% LCO	15% LCO	30% LCO	40% LCO
Neat[1]	80.5	79.5	83.5	81.5	84.5	86.5
1	80.5	81.5	83.5	83.5	85.0	84.5
2	80.5	82.5	85.5	83.5	85.0	85.5
3	80.5	81.5	84.5	83.0	84.0	86.5
4	80.5	84.5	84.5	82.0	85.0	86.5
5	80.5	84.5	84.5	83.0	85.0	86.5
6	86.5	81.5	84.5	83.0	85.0	86.5
7	81.0	83.5	85.5	83.0	85.0	86.5
8	81.0	84.0	85.0	83.0	85.0	88.5
9	81.0	84.5	85.5	82.0	85.0	85.5
10	81.5	84.5	85.0	82.0	84.0	85.5
11	81.0	84.5	85.5	82.0	84.0	85.5
12	81.5	84.0	85.5	82.0	85.0	86.5

[1] Control (additive-free) fuel.

TABLE 5. Demulsibility data for fuel additive blends at a concentration of 24 ppm (v/v) additive

Additive sample	Gulf Coast Fuels			West Coast Fuels		
	15% LCO	30% LCO	40% LCO	15% LCO	30% LCO	40% LCO
Neat[1]	5	4	2	2	2	4
1	5	5	4	3	2	2
2	4	4	4	1	2	2
3	6	4	6	3	2	2
4	4	3	2	3	2	>10
5	5	4	>10	2	2	3
6	6	6	5	2	2	1
7	5	6	>10	3	3	1
8	3	4	3	2	2	2
9	5	8	6	2	2	2
10	8	6	4	3	2	1
11	>10	>10	>10	3	5	5
12	>10	8	8	>10	4	2

[1] Control (additive-free) fuel.

TABLE 6. Accelerated storage stability tests,[1] gravimetric and color results at 95° C, 16 hours, for the 40% LCO blends from the Gulf Coast

Sample identification[2]	Initial color	Final color	Total insolubles, mg/100 ml
12d	<1.0	2.5	0.1
11c	<1.0	<2.5	0.1
2b	<1.0	2.5	0.1
11d	<1.0	2.5	0.1
12c	<1.0	2.5	0.2
4b	<1.0	2.0	0.2
10b	<1.0	<3.0	0.2
3a	<1.0	<2.5	0.2
1a	<1.0	2.0	0.2
1b	<1.0	2.0	0.2
3b	<1.0	<2.5	0.2
4a	<1.0	2.0	0.2
10a	<1.0	<3.0	0.3
SR	---	---	0.3
2a	<1.0	2.5	0.3
6b	<1.0	<3.0	0.3
7b	<1.0	<3.0	0.4
6a	<1.0	<3.0	0.4
5a	<1.0	2.5	0.5
7a	<1.0	<3.0	0.5
5b	<1.0	3.0	0.6
9b	<1.0	3.0	0.6
8a	<1.0	<3.0	0.6
Neat[3]	<1.0	2.5-3.0	0.6
9a	<1.0	3.0	0.6
8b	<1.0	3.0	0.8
LCO	---	---	4.3

[1] Experiments performed at DTNSRDC. No statistics available.
[2] These results are in order of additive efficacy for this set of tests. SR - straight-run middle distillate, LCO - light cycle oil, neat - neat fuel blend. Numbers 1 through 12 represent additive blends: "a" - 12 ppm, "b" - 24 ppm, 11c - 100 ppm, 11d - 300 ppm, 12c - 67 ppm, and 12d - 200 ppm (ppm based on v/v).
[3] Control (additive-free) fuel.

TABLE 7. Accelerated storage stability tests,[1] gravimetric and color results at 95° C, 40 hours, for the 30% LCO blends from the Gulf Coast

Sample identification[2]	Initial color	Final color	Total insolubles, mg/100 ml
11d	2.0	<4.5	0.3
12d	<2.0	4.0	0.5
2b	<2.0	<4.0	0.7
11c	<2.0	<4.0	1.0
10b	2.5	<4.5	1.0
2a	1.5	<4.5	1.1
12c	<2.5	<4.5	1.2
4b	<1.5	4.0	1.2
3b	<1.5	4.0	1.2
6b	<2.5	<4.5	1.3
10a	<2.5	4.5	1.3
3a	<1.5	<4.5	1.4
4a	1.0	<4.5	1.6
1b	1.0	4.5	1.6
6a	<2.5	<5.0	1.6
7b	<3.0	5.0	1.8
8b	2.5	<5.0	1.8
1a	1.0	4.5	1.9
9b	3.0	<5.0	1.9
8a	2.5	5.0	2.0
7a	2.5	<5.0	2.1
5b	<2.0	5.0	2.1
Neat[3]	2.0-2.5	5.0	2.2
5a	1.5	<5.0	2.2
9a	<4.0	5.0	2.6

[1] Experiments performed at DTNSRDC. The maximum standard error for these data is 12%.

[2] These results are in order of additive efficacy for this set of tests. SR - straight-run middle distillate, LCO - light cycle oil, neat - neat fuel blend. Numbers 1 through 12 represent additive blends: "a" - 12 ppm, "b" - 24 ppm, 11c - 100 ppm, 11d - 300 ppm, 12c - 67 ppm, and 12d - 200 ppm (ppm based on v/v).

[3] Control (additive-free) fuel.

TABLE 8.   Accelerated storage stability tests,[1] gravimetric and color
            results at 95° C, 24 hours, for the 40% LCO blends from the
            West Coast

Sample identification[2]	Initial color	Final color	Total insolubles, mg/100 ml
10b	<2.5*	3.0	0.1
SR	--	--	0.1*
2a	<2.5*	3.0	0.1
12c	<2.5*	4.5	0.1
2b	<2.5*	3.0	0.1
4b	<2.5*	3.5	0.1
3a	<2.5*	<3.5	0.1
1b	<2.5*	3.5	0.2
1a	<2.5*	3.5	0.2
3b	<2.5*	<3.5	0.2
4a	<2.5*	3.5	0.2
11c	<2.5*	5.5	0.2
10a	<2.5*	--	0.3
5b	<2.5*	3.5	0.3
5a	<2.5*	3.5	0.4
12d	<2.5*	<3.5	0.4
Neat[3]	<2.5*	3.5	0.5
11d	<2.5*	3.5	0.5
9a	<2.5*	3.5	0.5
6a	<2.5*	3.5	0.5
6b	<2.5*	<4.0	0.6
9b	<2.5*	<4.0	0.6
LCO	--	--	0.7
7a	<2.5*	<4.0	1.4
7b	<2.5*	4.0	1.4
8b	<2.5*	4.0	2.2
8a	<2.5*	4.5	3.6

* 16-hour data.

[1]   Experiments performed at DTNSRDC. No statistics available.
[2]   These results are in order of additive efficacy for this set of tests. SR
      - straight-run middle distillate, LCO - light cycle oil, neat - neat fuel
      blend. Numbers 1 through 12 represent additive blends: "a" - 12 ppm,
      "b" - 24 ppm, 11c - 100 ppm, 11d - 300 ppm, 12c - 67 ppm, and
      12d - 200 ppm (ppm based on v/v).
[3]   Control (additive-free) fuel.

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TABLE 9.   Accelerated storage stability tests,[1] gravimetric and color
           results at 80° C, 2 weeks, for the 40% LCO blends from the
           Gulf Coast

Sample identification[2]	Initial color	Final color	Total insolubles, mg/100 ml
11c	1.5	5.0	1.8
SR	<0.5	<2.0	1.8
2b	3.0	<5.5	2.1
12d	<3.0	<5.5	2.2
2a	2.5	<5.5	2.4
4a	<2.0	<5.5	2.6
5a	<1.5	5.5	2.7
6b	<3.0	<5.5	2.9
9b	1.5	5.5	3.1
3a	<1.5	5.0	3.2
11d	1.5	5.0	3.3
Neat[3]	<2.0	<5.5	3.4
6a	<3.0	<5.5	3.4
10b	<3.0	5.0	3.6
10a	<3.0	<5.5	3.6
7a	<2.0	5.5	3.6
4b	<2.0	<5.5	4.0
5b	<1.5	5.0	4.0
8a	<3.0	<5.5	4.0
12c	<3.0	5.0	4.2
3b	<1.5	<5.0	4.2
9a	1.5	5.0	4.3
8b	<3.0	<5.5	4.3
7b	<2.0	5.0	4.8
1a	1.0	<5.5	4.8
1b	1.0	5.0	5.0
LCO	<2.0	>8.0	12.0

[1]   Experiments performed at NRL. The maximum standard error for these data
      is 31%.
[2]   These results are in order of additive efficacy for this set of tests. SR
      - straight-run middle distillate, LCO - light cycle oil, neat - neat fuel
      blend. Numbers 1 through 12 represent additive blends: "a" - 12 ppm,
      "b" - 24 ppm, 11c - 100 ppm, 11d - 300 ppm, 12c - 67 ppm, and
      12d - 200 ppm (ppm based on v/v).
[3]   Control (additive-free) fuel.

TABLE 10. Accelerated storage stability tests,[1] gravimetric and color results at 80° C, 4 weeks, for the 30% LCO blends from the Gulf Coast

Sample identification[2]	Initial color	Final color	Total insolubles, mg/100 ml
2b	<2.0	5.0	2.4
2a	2.0	5.5	3.1
3a	<1.5	<5.5	3.7
10b	<2.5	<5.5	3.7
3b	<2.5	5.0	3.8
10a	<2.5	5.5	4.1
4b	<2.0	5.5	4.4
Neat[3]	2.5	5.5	4.5
5a	2.0	5.5	4.6
5b	<2.5	<6.0	4.7
6b	2.5	5.5	4.7
4a	<1.5	<5.5	5.0
8b	<3.5	5.5	5.0
1b	<1.5	5.5	5.0
9b	<4.0	5.5	5.1
1a	<1.5	5.5	5.2
7b	3.0	5.5	5.2
6a	<3.0	5.5	5.2
8a	3.0	6.0	5.4
7a	<3.0	<6.0	5.5
9a	<4.0	6.0	8.2

[1] Experiments performed at NRL. The maximum standard error for these data is 24%.

[2] These results are in order of additive efficacy for this set of tests. SR - straight-run middle distillate, LCO - light cycle oil, neat - control (additive-free) fuel blend. Numbers 1 through 12 represent additive blends: "a" - 12 ppm, and "b" - 24 ppm (ppm based on v/v).

[3] Control (additive-free) fuel.

TABLE 11. Accelerated storage stability tests,[1] gravimetric and color results at 80° C, 3 weeks, for the 40% LCO blends from the West Coast

Sample identification[2]	Initial color	Final color	Total insolubles, mg/100 ml
SR	<1.0	3.5	0.6
2b	<3.5	6.0	2.0
2a	3.0	5.5	2.6
11d	<3.5	7.0	3.1
10b	<2.0	5.5	3.2
11c	<3.5	6.5	3.2
12d	<2.0	6.5	3.4
3b	<2.0	<6.0	4.1
12c	<2.0	6.5	4.1
9b	<2.0	6.5	4.6
3a	<2.0	<6.0	4.9
6b	<3.5	<6.5	5.8
5b	<2.0	6.0	6.2
10a	<2.0	6.0	6.6
LCO	<4.0	8.0	7.1
1b	<3.5	6.0	7.3
4a	<2.0	<6.5	7.3
4b	<2.0	<6.0	7.3
5a	<2.0	<6.5	7.4
1a	<3.5	6.0	7.6
Neat[3]	3.0	6.5	8.0
7a	<3.5	7.0	8.1
9a	<2.0	6.5	8.1
7b	<3.5	7.0	8.9
8b	<3.0	7.0	9.3
8a	<3.0	<7.5	9.6
6a	<2.0	<6.5	9.6

[1] Experiments performed at NRL. The maximum standard error for these data is 30%.

[2] These results are in order of additive efficacy for this set of tests. SR - straight-run middle distillate, LCO - light cycle oil, neat - neat fuel blend. Numbers 1 through 12 represent additive blends: "a" - 12 ppm, "b" - 24 ppm, 11c - 100 ppm, 11d - 300 ppm, 12c - 67 ppm, and 12d - 200 ppm (ppm based on v/v).

[3] Control (additive-free) fuel.

TABLE 12. Accelerated storage stability tests[1] at 65° C, 8 weeks, for the 40% LCO blends from the Gulf Coast

Sample identification[2]	Total insolubles, mg/100 ml
11d	0.5
12d	0.9
SR	1.1
10b	2.5
2b	2.6
10a	2.9
2a	2.9
9a	2.9
3b	3.0
11c	3.0
3a	3.1
4b	3.2
9b	3.2
7b	3.3
12c	3.3
7a	3.4
8b	3.4
6b	3.5
1b	3.6
6a	3.6
1a	3.6
5a	3.7
8a	3.7
4a	3.9
5b	4.2
Neat[3]	4.3
LCO	11.2

[1] Experiments performed at ARTECH. No statistics available.
[2] These results are in order of additive efficacy for this set of tests. SR - straight-run middle distillate, LCO - light cycle oil, neat - neat fuel blend. Numbers 1 through 12 represent additive blends: "a" - 12 ppm, "b" - 24 ppm, 11c - 100 ppm, 11d - 300 ppm, 12c - 67 ppm, and 12d - 200 ppm (ppm based on v/v).
[3] Control (additive-free) fuel.

TABLE 13. Accelerated storage stability tests[1] at 65° C, 12 weeks, for the 30% LCO blends from the Gulf Coast

Sample identification[2]	Total insolubles, mg/100 ml
11d	1.8
2b	3.2
11c	3.3
3b	3.3
10a	3.4
10b	3.5
2a	3.5
12c	3.6
3a	3.7
6b	3.9
12d	4.1
4b	4.1
5a	4.1
8a	4.1
5b	4.2
8b	4.2
4a	4.3
1b	4.4
1a	4.5
7b	4.5
9b	4.6
6a	4.7
Neat[3]	4.8
7a	4.8
9a	5.1

[1] Experiments performed at ARTECH. No statistics available.
[2] These results are in order of additive efficacy for this set of tests. SR - straight-run middle distillate, LCO - light cycle oil, neat - neat fuel blend. Numbers 1 through 12 represent additive blends: "a" - 12 ppm, "b" - 24 ppm, 11c - 100 ppm, 11d - 300 ppm, 12c - 67 ppm, and 12d - 200 ppm (ppm based on v/v).
[3] Control (additive-free) fuel.

TABLE 14. Accelerated storage stability tests[1] at 65° C, 12 weeks, for the 40% LCO blends from the West Coast

Sample identification[2]	Total insolubles, mg/100 ml
SR	0.7
11c	3.8
11d	4.6
2b	4.6
10b	5.1
2a	5.8
12c	7.0
12d	7.9
3b	8.5
3a	8.8
5a	9.0
1a	10.1
7a	10.7
8b	10.7
10a	10.7
4b	10.9
7b	11.1
5b	11.3
9b	12.2
9a	12.5
1b	12.7
6a	12.7
4a	13.3
Neat[3]	13.3
6b	13.5
8a	13.7
LCO	25.6

[1] Experiments performed at ARTECH. No statistics available.
[2] These results are in order of additive efficacy for this set of tests. SR - straight-run middle distillate, LCO - light cycle oil, neat - neat fuel blend. Numbers 1 through 12 renresent additive blends: "a" - 12 ppm, "b" - 24 ppm, 11c - 100 ppm, 11d - 300 ppm, 12c - 67 ppm, and 12d - 200 ppm (ppm based on v/v).
[3] Control (additive-free) fuel.

TABLE 15. Accelerated storage stability tests,[1] microgravimetric and color results at 65° C, 12 weeks, for the 40% LCO blends from the Gulf Coast

Sample identification[2]	Initial color	Final color	Total insolubles, mg
11c	<1.0	>5.5	0.5
SR	<0.5	<2.0	0.6
11d	<1.0	5.5	0.6
12c	<1.0	5.5	0.6
9a	<1.0	>5.5	0.7
12d	<1.0	5.5	0.7
1b	<1.0	6.0	0.7
8a	<1.0	<6.0	0.7
5b	<1.0	>5.5	0.8
7a	<1.0	<6.0	0.8
3b	<1.0	<6.0	0.8
7b	<1.0	<6.0	0.8
4b	<1.0	<6.0	0.8
3a	<1.0	<6.0	0.8
Neat[3]	<1.0	<6.0	0.8
6b	<1.0	>6.0	0.8
2b	<1.0	5.5	0.8
8b	<1.0	<6.0	0.8
5a	<1.0	<6.0	0.8
2a	<1.0	>5.5	0.9
4a	<1.0	<6.0	0.9
6a	<1.0	>5.5	0.9
1a	<1.0	6.0	0.9
10b	<1.0	<6.0	1.0
LCO	1.0	<8.0	1.3
9b	<1.0	--	--
10a	<1.0	--	--

[1] Experiments performed at NIPER. The maximum standard error for these data is 25%.

[2] These results are in order of additive efficacy for this set of tests. SR - straight-run middle distillate, LCO - light cycle oil, neat - neat fuel blend. Numbers 1 through 12 represent additive blends: "a" - 12 ppm, "b" - 24 ppm, 11c - 100 ppm, 11d - 300 ppm, 12c - 67 ppm, and 12d - 200 ppm (ppm based on v/v).

[3] Control (additive-free) fuel.

TABLE 16. Accelerated storage stability tests,[1] microgravimetric and color
results at 65° C, 8 weeks, for the 30% LCO blends from the
Gulf Coast

Sample identification[2]	Initial color	Final color	Total insolubles, mg
SR	<0.5	<2.0	0.4
2a	<1.0	<5.5	0.4
4b	>0.5	>5.0	0.5
10b	<1.0	<5.0	0.5
4a	>0.5	<5.5	0.5
9b	<1.0	5.0	0.5
8a	<1.0	<5.5	0.5
11c	<1.0	<5.0	0.5
10a	<1.0	>5.0	0.5
3b	<1.0	>5.0	0.5
9a	<1.0	>5.0	0.5
1b	<1.0	5.5	0.5
11d	<1.0	4.5	0.5
5b	>0.5	<5.5	0.6
3a	<1.0	5.0	0.6
6a	<1.0	<5.5	0.6
Neat[3]	<1.0	5.5	0.6
12d	<1.0	<5.5	0.6
12c	<1.0	>5.0	0.6
5a	>0.5	--	0.6
7a	<1.0	<5.5	0.6
6b	<1.0	<5.5	0.6
8b	<1.0	<5.5	0.6
2b	<1.0	<5.0	0.6
7b	<1.0	<5.5	0.6
1a	<1.0	<5.5	0.7
LCO	1.0	>8.0	1.1

[1] Experiments performed at NIPER. The maximum standard error for these data
is 20%

[2] These results are in order of additive efficacy for this set of tests. SR
- straight-run middle distillate, LCO - light cycle oil, neat - neat fuel
blend. Numbers 1 through 12 represent additive blends: "a" - 12 ppm,
"b" - 24 ppm, 11c - 100 ppm, 11d - 300 ppm, 12c - 67 ppm, and
12d - 200 ppm (ppm based on v/v).

[3] Control (additive-free) fuel.

TABLE 17. Accelerated storage stability tests,[1] microgravimetric and color
results at 65° C, 12 weeks, for the 15% LCO blends from the
Gulf Coast

Sample identification[2]	Initial color	Final color	Total insolubles, mg
2b	0.5		0.4
10b	<1.0	<4.5	0.4
10a	<1.0	<4.5	0.4
8a	<1.0	>4.0	0.5
9a	<1.0	<4.5	0.5
11d	<1.0	>3.5	0.5
2a	0.5		0.5
11c	<1.0	>4.0	0.5
5b	<1.0	<4.5	0.5
12d	1.0	4.0	0.5
4b	0.5	4.0	0.5
9b	1.0	4.5	0.5
7a	<1.0	<4.5	0.5
SR	<0.5	<2.0	0.6
Neat[3]	>0.5	<4.5	0.6
7b	<1.0	<4.5	0.6
6a	<1.0	>4.0	0.6
8b	<1.0	>4.0	0.6
6b	<1.0	>4.0	0.6
5a	<1.0	>4.0	0.6
3b	0.5	>4.0	0.6
4a	0.5	<4.5	0.6
12c	<1.0	4.0	0.7
3a	0.5	<4.5	0.7
1b	0.5	<4.5	0.8
1a	0.5	<4.5	0.8
LCO	1.0	<8.0	1.3

[1] Experiments performed at NIPER by Teflon cup method. The maximum standard
error for these data is 13%.
[2] These results are in order of additive efficacy for this set of tests. SR
- straight-run middle distillate, LCO - light cycle oil, neat - neat fuel
blend. Numbers 1 through 12 represent additive blends: "a" - 12 ppm,
"b" - 24 ppm, 11c - 100 ppm, 11d - 300 ppm, 12c - 67 ppm, and
12d - 200 ppm (ppm based on v/v).
[3] Control (additive-free) fuel.

TABLE 18. Accelerated storage stability tests,[1] microgravimetric and color results at 65° C, 12 weeks, for the 40% LCO blends from the West Coast

Sample identification[2]	Initial color[3]	Final color	Total insolubles, mg
SR	<1.0	3.5	0.7
2b	1.0[3]	<7.5	0.9
2a	1.0[3]	<7.5	1.0
3b	1.0[3]	>5.0	1.0
11c	1.0[3]	<7.5	1.0
3a	1.0[3]	<8.0	1.0
10b	1.0[3]	>7.5	1.2
10a	1.0[3]	<8.0	1.2
12c	1.0[3]	<8.0	1.2
8a	1.0[3]	8.0	1.2
9a	1.0[3]	<8.0	1.3
4a	1.0[3]	<8.0	1.3
7a	1.0[3]	<8.0	1.3
5a	1.0[3]	<8.0	1.3
11d	1.0[3]	<8.0	1.4
Neat[4]	>1.0	<8.0	1.4
12d	1.0[3]	>8.0	1.4
8b	1.0[3]	>8.0	1.4
LCO	<3.5	>8.0	1.5
1a	1.0[3]	>8.0	1.5
4b	<1.5[3]	>8.0	1.5
5b	1.0[3]	<8.0	1.5
6b	1.0[3]	8.0	1.5
1b	1.0[3]	8.0	1.6
7b	1.0[3]	8.0	1.6
9b	1.0[3]	>8.0	1.6
6a	1.0[3]	<8.0	1.8

[1] Experiments performed at NIPER. The maximum standard error for these data is 22%.
[2] These results are in order of additive efficacy for this set of tests. SR - straight-run middle distillate, LCO - light cycle oil, neat - neat fuel blend. Numbers 1 through 12 represent additive blends: "a" - 12 ppm, "b" - 24 ppm, 11c - 100 ppm, 11d - 300 ppm, 12c - 67 ppm, and 12d - 200 ppm (ppm based on v/v).
[3] There is a red tint to the fuel so that it did not match any of the colors in the ASTM D1500 apparatus. This estimate is based on light intensity.
[4] Control (additive-free) fuel.

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TABLE 19. Accelerated storage stability tests,[1] microgravimetric and color
results at 65° C, 12 weeks, for the 30% LCO blends from the
West Coast

Sample identification[2]	Initial color[3]	Final color	Total insolubles, mg
SR	<1.0	3.5	0.7
2a	1.0[3]	<6.5	0.7
2b	1.0[3]	<6.5	0.7
10b	1.0[3]	<7.0	0.7
3b	1.0[3]	6.5	0.8
Neat[4]	1.0[3]	>7.0	0.8
3a	1.0[3]	>7.0	0.8
11d	1.0[3]	<7.0	0.8
5b	1.0[3]	<7.0	0.8
4b	1.0[3]	<7.5	0.9
6a	1.0[3]	<7.0	0.9
5a	1.0[3]	<7.5	0.9
8a	1.0[3]	<7.0	0.9
9b	1.0[3]	<7.5	1.0
4a	1.0[3]	<7.0	1.0
6b	1.0[3]	<7.0	1.0
1a	1.0[3]	<7.5	1.0
8b	1.0[3]	>6.5	1.0
10a	1.0[3]	<7.0	1.0
12d	1.0[3]	<8.0	1.0
1b	1.0[3]	<7.0	1.0
7b	1.0[3]	>7.0	1.1
7a	1.0[3]	<7.0	1.1
11c	1.0[3]	<7.0	1.1
12c	1.0[3]	>7.0	1.1
9a	1.0[3]	<7.5	1.3
LCO	<3.5	>8.0	1.5

[1] Experiments performed at NIPER. The maximum standard error for these data is 24%.
[2] These results are in order of additive efficacy for this set of tests. SR - straight-run middle distillate, LCO - light cycle oil, neat - neat fuel blend. Numbers 1 through 12 represent additive blends: "a" - 12 ppm, "b" - 24 ppm, 11c - 100 ppm, 11d - 300 ppm, 12c - 67 ppm, and 12d - 200 ppm (ppm based on v/v).
[3] There is a red tint to the fuel so that it did not match any of the colors in the ASTM D1500 apparatus. This estimate is based on light intensity.
[4] Control (additive-free) fuel.

TABLE 20. Accelerated storage stability tests,[1] microgravimetric and color results at 65° C, 12 weeks, for the 15% LCO blends from the West Coast

Sample identification[2]	Initial color[3]	Final color	Total insolubles, mg
Neat[4]	<1.0[3]	5.5	0.4
2a	<1.5[3]	<5.5	0.5
12d	<1.5[3]	7.0	0.5
10a	<1.5[3]	>5.5	0.5
2b	<1.5[3]	<5.5	0.5
5b	<1.5	<6.5	0.5
8b	<1.5[3]	>5.5	0.6
4b	<1.5[3]	>6.0	0.6
5a	<1.5	<6.0	0.6
1a	<1.5[3]	6.0	0.6
4a	<1.5[3]	<6.0	0.6
7b	<1.5	<6.0	0.6
3b	<1.5[3]	<5.5	0.6
8a	<1.5[3]	>5.5	0.6
6a	<1.5	>6.0	0.6
3a	<1.5[3]	6.0	0.6
9a	<1.5	>5.5	0.6
10b	<1.5	6.0	0.7
7a	<1.5	7.0	0.7
6b	<1.5	<6.0	0.7
12c	<1.5[3]	5.5	0.7
SR	<1.0	3.5	0.7
11d	<1.5	>6.0	0.7
9b	<2.0	>6.0	0.7
11c	<1.5	>5.5	0.7
1b	1.0[3]	<6.0	0.8
LCO	<3.5	>8.0	1.5

[1] Experiments performed at NIPER. The maximum standard error for these data is 26%.
[2] These results are in order of additive efficacy for this set of tests. SR - straight-run middle distillate, LCO - light cycle oil, neat - neat fuel blend. Numbers 1 through 12 represent additive blends: "a" - 12 ppm, "b" - 24 ppm, 11c - 100 ppm, 11d - 300 ppm, 12c - 67 ppm, and 12d - 200 ppm (ppm based on v/v).
[3] There is a red tint to the fuel so that it did not match any of the colors in the ASTM D1500 apparatus. This estimate is based on light intensity.
[4] Control (additive-free) fuel.

TABLE 21. Accelerated storage stability tests,[1] gravimetric and color
results at 43° C, 35 weeks, for the 40% LCO blends from the
Gulf Coast

Sample identification[2]	Initial color	Final color	Total insolubles, mg/100 ml
11d	1.5	6.5	0.2
SR	<0.5	<2.0	1.2
7a	<2.0	6.5	3.0
3a	<1.5	6.5	3.1
11c	1.5	6.0	3.3
5b	<1.5	6.5	3.7
5a	<1.5	6.5	3.7
12d	<3.0	<7.0	3.7
3b	<1.5	6.5	4.0
2b	3.0	6.0	4.1
1a	1.0	7.0	4.1
1b	1.0	7.0	4.1
9b	1.5	6.5	4.2
4a	<2.0	<6.0	4.4
Neat[3]	<2.0	<6.5	4.7
4b	<2.0	<6.0	4.7
2a	2.5	6.0	4.9
10b	<3.0	6.0	5.0
10a	<3.0	6.0	5.4
7b	<2.0	6.5	5.4
9a	1.5	<6.5	5.5
12c	2.5	6.0	5.7
8a	2.5	<6.5	5.7
8b	<3.0	6.0	5.7
6b	<3.0	<6.5	6.0
6a	<3.0	<6.5	6.0
LCO	<2.0	<8.0	11.0

[1] Experiments performed at NRL. The maximum standard error for these data
is 32%.
[2] These results are in order of additive efficacy for this set of tests. SR
- straight-run middle distillate, LCO - light cycle oil, neat - neat fuel
blend. Numbers 1 through 12 represent additive blends: "a" - 12 ppm,
"b" - 24 ppm, 11c - 100 ppm, 11d - 300 ppm, 12c - 67 ppm, and
12d - 200 ppm (ppm based on v/v).
[3] Control (additive-free) fuel.

TABLE 22. Accelerated storage stability tests,[1] gravimetric and color
results at 43° C, 35 weeks, for the 30% LCO blends from the
Gulf Coast

Sample identification[2]	Initial color	Final color	Total insolubles, mg/100 ml
11d	<1.5	5.5	1.1
SR	<0.5	2.0	1.2
10a	1.5	5.5	2.0
10b	1.5	5.5	2.1
3b	<1.0	<5.5	2.4
9b	2.0	5.5	2.5
12d	1.5	5.5	2.5
11c	<1.5	5.5	2.9
8b	<2.0	<6.0	3.1
12c	<1.5	5.5	3.4
1b	<1.0	<6.0	3.4
8a	<1.5	6.0	3.4
7a	<2.0	5.5	3.5
2a	<1.5	5.5	3.5
2b	<1.5	5.0	3.5
1a	<1.0	<6.0	3.6
Neat[3]	1.0	<6.0	3.8
7b	<1.5	6.0	3.9
4b	<1.0	<5.5	3.9
9a	<2.5	6.0	4.0
4a	<1.0	<6.0	4.2
3a	<1.0	5.5	4.3
5b	1.0	<6.0	4.4
6b	<1.0	<6.0	4.7
6a	1.0	<6.0	4.7
5a	<1.0	<6.0	4.9
LCO	<2.0	<8.0	11.0

[1] Experiments performed at NRL. The maximum standard error for these data
is 22%.
[2] These results are in order of additive efficacy for this set of tests. SR
- straight-run middle distillate, LCO - light cycle oil, neat - neat fuel
blend. Numbers 1 through 12 represent additive blends: "a" - 12 ppm,
"b" - 24 ppm, 11c - 100 ppm, 11d - 300 ppm, 12c - 67 ppm, and
12d - 200 ppm (ppm based on v/v).
[3] Control (additive-free) fuel.

TABLE 23. Accelerated storage stability tests,[1] gravimetric and color results at 43° C, 32 weeks, for the 40% LCO blends from the West Coast

Sample identification[2]	Initial color	Final color	Total insolubles, mg/100 ml
SR	<1.0	<3.0	0.3
11c	<3.5	<7.5	6.4
11d	<3.5	<7.5	6.9
9a	<2.0	7.0	7.2
2b	<3.5	7.5	7.4
3b	<2.0	7.0	7.5
5a	<2.0	<7.5	7.8
3a	<3.0	<7.0	8.0
9b	<2.0	<7.5	8.2
2a	<3.5	<7.5	8.2
5b	<2.0	<7.5	8.3
4a	<2.0	7.0	9.1
4b	<2.0	<7.5	10.2
1a	<3.5	7.5	10.3
1b	<3.5	7.5	10.3
8b	<3.0	<7.5	10.7
7b	<3.5	<7.5	10.7
10a	<2.0	<7.5	10.8
12c	<2.0	<7.5	10.9
7a	<3.5	<7.5	11.0
6b	<3.5	<7.5	11.5
10b	<2.0	<7.0	11.6
Neat[3]	<3.5	7.5	11.8
12d	<2.0	<7.5	11.9
6a	<2.0	<7.0	12.1
8a	<3.0	<7.5	12.4
LCO	<4.0	8.0	23.8

[1] Experiments performed at NRL. The maximum standard error for these data is 33%.

[2] These results are in order of additive efficacy for this set of tests. SR - straight-run middle distillate, LCO - light cycle oil, neat - neat fuel blend. Numbers 1 through 12 represent additive blends: "a" - 12 ppm, "b" - 24 ppm, 11c - 100 ppm, 11d - 300 ppm, 12c - 67 ppm, and 12d - 200 ppm (ppm based on v/v).

[3] Control (additive-free) fuel.

TABLE 24. Summary of stability studies done on several sample collection techniques on a 30% LCO fuel blend from the West Coast refinery[1]

Sample condition[2]	Sediment developed using the following stability test techniques					
	D2274	80° C 2 weeks	80° C 64 hrs 100 psi O_2	65° C 8 weeks	43° C 17 weeks	43° C 18 weeks
	(DTNSRDC)	(NRL)	(NRL)	(ARTECH)	(NRL)	(DTNSRDC)
	Total sediment, mg/100 ml					
Lined can, argon blanket, dry	0.5	4.0	8.3	4.7	4.4	4.4
Lined can, air sparge, dry	0.6	3.7	8.7	4.4	4.3	4.7
Lined can, argon blanket, wet	0.1	4.5	9.0	3.3	5.7	4.7
Lined can, air sparge, wet	0.5	5.2	9.4	5.4	6.2	5.3
Unlined can, argon blanket, dry	3.1	4.6	10.0	5.7	9.6	8.8
Unlined can, air sparge, dry	3.8	6.5	10.3	7.9	7.8	8.2
Unlined can, argon blanket, wet	2.7	3.9	6.0	5.9	7.1	6.6
Unlined can, air sparge, wet	3.5	6.9	9.4	6.9	7.5	8.8
Unlined can, air blanket, dry	4.4	6.7	11.3	10.0	8.3	10.2

[1] No statistics available.

[2] Lined - epoxy; unlined - rust-free steel; argon blanket -layer of argon; air blanket - untreated; sparge - air bubbling for 30 minutes at a rate of 1 liter/minute; wet - 10 ml of water added; dry - no water added (possible moisture in fuel because of the location of the sampling point of the LCO).

TABLE 25. Summary of accelerated storage stability tests on several sample
handling techniques on a 30% LCO fuel blend from the Gulf Coast[1]

Sample condition[2]	D2274 (DTNSRDC)	80° C 2 weeks (NRL)	65° C 8 weeks (ARTECH)
Lined can, argon blanket, dry	0.3	4.2	4.4
Lined can, air blanket, dry	0.3	3.9	4.4
Lined can, air sparge, wet	0.4	3.6	4.4
Lined can, air blanket, dry 100 g steel wool added	0.4	3.2	4.8
Unlined can, air sparge, wet	0.3	3.6	4.6
Unlined can, air blanket, dry	0.4	3.6	4.3

[1] The maximum standard error for these data is 28%.

[2] Lined - epoxy; unlined - rust-free steel; argon blanket -layer of argon;
air blanket - untreated; sparge - air bubbling for 30 minutes at a rate of
1 liter/minute; wet - 10 ml of water added; dry - no water added (possible
moisture in fuel because of the location of the sampling point of the
LCO).

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