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STORAGE STABILITY STUDIES OF U.S. NAVY DIESEL FUEL MARINE

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INTRODUCTION

An increasing trend in recent years is the utilization of heavier crude sources in producing middle distillate fuels. The U.S. Navy's concern about long-term (up to three years) storage stability of its diesel fuel marine (DFM) from such sources is the driving force for this study. The three major objectives of this work are: 1) to improve empirical predictive storage stability tests; 2) to better understand the chemical mechanism involved in middle distillate storage instability; and 3) to examine various commercial and experimental stabilizer additives as possible storage stability improvers suitable to Navy needs.

In this paper we will deal primarily with the first objective and also include some preliminary work and results on the second objective. Some of the problems and severe time restrictions of utilizing empirical predictive storage stability tests will be specifically addressed.

EXPERIMENTAL

Accelerated Storage Stress Test

An empirical gravimetric test which was shown to be very precise for this type of analysis ($\pm 10\%$ S. E.) of shale-derived diesel fuel marine (DFM) storage stability studies at NRL (1) was adopted for this study. It consists of filtering 300 ml of a fuel through Gelman type A/E glass fiber filters. The filtered fuel is transferred to a clean, dry, borosilicate brown glass 500 ml bottle weighed to the nearest 0.1 mg. The teflon-lined cap is placed on the bottle but not tightened. The bottles are placed in a dark oven held to constant temperatures within $\pm 0.5^\circ\text{C}$ for a specified number of days (± 0.1 days). Temperatures chosen for the accelerated tests were 43, 65, 80 and 100°C . After removal from the oven the bottles are allowed to cool to ambient temperature and relative humidity in the dark for 24 hours (± 2 hours). The fuel is filtered through a Büchner funnel with Gelman type A/E glass fiber filters weighed to the nearest 0.1 mg. The bottles and filter pads are rinsed with 3 x 50 ml of *n*-hexane aliquots to remove fuel and to ensure transfer of all non-adherent material from the bottle. The bottles and filters plus funnels are evacuated in a vacuum oven with a mechanical pump and then heated in vacuo for about 18 hours at 120°C . The vacuum oven is turned off and allowed to return to room temperature before removing the bottles and filter funnels. The bottles and filter funnels are weighed to the nearest 0.1 mg on a Mettler H315 (1000 g capacity) balance. Adherent gum is the weight difference per bottle corrected for a blank, divided by 300 and reported as mg/100 ml of fuel. Filtrable sediment is the weight difference of the filter pads corrected for a blank, divided by 300 and reported as mg/100 ml of fuel. The sum of these two values is reported as total insolubles in mg/100 ml of fuel. The mean and standard deviation of triplicate runs is generally reported. A blank determination is made for each time and temperature run. The filtrable sediment blank is a funnel and filter pad subjected to the same post stress handling a samples. All sample values reported herein have been corrected for a blank determination.

Fuels

In general, fuels used in this work were received in five-gallon metal containers and transferred to five one-gallon epoxy-lined metal containers and stored in a cold room at $+4^\circ\text{C}$ until used. Most fuels were supplied through the Navy Petroleum Office from refineries and storage depots world-wide. All fuels had conformed to military specifications for Navy DFM at time of receipt by the Navy.

Capillary GC-MS was performed on a Hewlett Packard fused silica 0.3 mm I. D. x 50 m cross-linked methyl silicone column directly inserted into the electron impact source of a Hewlett Packard 5982A mass spectrometer through a modified solids probe inlet. Flow was adjusted to one ml/min of helium and the injector split ratio was approximately 50:1.

Elemental analyses were performed on a Perkin Elmer Model 240 Elemental Analyzer for carbon, hydrogen, and nitrogen. Oxygen analysis was performed on a Coulometrics Oxygen Analyzer.

RESULTS AND DISCUSSION

Stress Tests

Four petroleum derived DFM's covering a wide range of storage stability as defined by ASTM D2774 were selected as the test matrix to determine the statistical variations of the accelerated storage stability test described above. Typical data are reported in Table I (at 80°C for 14 days) with standard errors ranging from 1 to 11% of the mean. Data for a series of triplicate tests run at 80°C for these four fuels at 7-21 days are plotted in Figure 1. All four curves are quadratic least squares best fits. Three fuels exhibit a modest acceleration in sediment formation but 82-10 exhibits a deceleration. The data are further broken down and plotted as total and filtrable sediment for two fuels (81-5 and 82-10) in Figures 2 and 3. The filtered sediment line generally follows the shape of the total sediment curve but Figure 3 shows the exception. This type of behavior underscores the importance of fuel dependence on such measurements.

TABLE I
WEIGHT OF TOTAL INSOLUBLES IN Mg/100 ML OF FUEL
STRESSED FOR 14 DAYS AT 80°C

<u>Fuel</u>	<u>Filtered Sediment</u>	<u>Adherent Gum</u>	<u>Total Insolubles</u>	<u>Mean</u>	<u>S. D.</u>
82-8	0.9	2.3	3.2	3.6	0.4
	0.9	3.0	3.9		
	0.9	2.7	3.6		
81-5	5.0	1.3	6.3	6.4	0.4
	4.6	1.6	6.2		
	4.7	2.2	6.9		
81-8	6.5	2.2	8.7	8.5	0.3
	6.4	1.8	8.2		
	6.8	1.7	8.5		
82-10	25.5	3.8	29.3	29.6	0.3
	25.5	4.3	29.8		
	24.4	5.2	29.6		

Five additional current-use Navy DFM's from petroleum were stress-tested in an effort to 1) broaden the total fuel test matrix and 2) screen for a marginal storage stability type of fuel (one which exhibits relatively high weights of total sediment during short stress tests). Table II gives selected results for four fuels which exhibit different trends in the formation of insolubles as stress temperature and time are increased. These results emphasize the fact that simultaneous, not necessarily related, reactions are proceeding, which form varying amounts of two different types of precipitate in the fuel - adherent and filtrable. The total insolubles formed by any particular fuel increase with increase in stress temperature and stress time. Data from Table II indicate that between 80 and 100°C for the five fuels studied the pseudo-Arrhenius plot of Figure 4 may be discontinuous, i. e., the rate of total sediment formation increases about two to four times faster than expected. This needs to be confirmed by running more fuels and by increasing the number of replicate samples. Figure 4 is plotted for one particular fuel, 81-5, and shows the time required at any particular temperature of stressing to form an equivalent weight of total sediment. The expected straight line relationship is not achieved. This may be indicative that accelerated storage stability tests at temperatures above 80°C may not be predicting correctly either the quantitative or the qualitative aspects of the phenomenon. This is an important consideration in future work in this area involving stabilizer additive studies.

Chemical Characterization of Sediments

Since the predominant type of sediment formed (adherent or filtrable insoluble) appears to be fuel dependent it will be necessary to carefully characterize each type in order to be able to postulate possible mechanisms of formation. In general the adherent sediment is more soluble than the filtrable sediment. This means that the adherent gum is more amenable to standard gas chromatographic and GC/MS characterization. Adherent gums formed by stressing DFM fuel samples at 100°C for 21 days were analyzed by GC/MS. Chromatograms of the adherent gum are all quite similar to those of the non-stressed fuel. The most striking feature of the chromatograms is the symmetrical appearance of *n*-alkanes ranging from C-9 to C-20 (in the adherent gum) and C-9 to C-24 (in non-stressed fuel). Preliminary work indicates that oxidized hydrocarbons are co-eluting with the higher *n*-alkanes in adherent gum samples.

TABLE II

ALL WEIGHTS ARE GIVEN IN Mg/100 ML OF FUEL. STRESS TEMPERATURES ARE GIVEN IN °C AND STRESS TIMES ARE GIVEN IN DAYS

<u>Fuel/Temp/Time</u>	<u>Filtered Sediment</u>	<u>Adherent Gum</u>	<u>Total Insolubles</u>	<u>Mean</u>	<u>S. D.</u>
82-8/43/52	0.0	0.5	0.5	0.4	0.4
	0.1	0.6	0.7		
	0.0	0.0	0.0		
82-8/20/21	0.8	4.8	5.6	5.1	1.1
	0.3	5.5	5.8		
	0.5	3.3	3.8		
81-5/43/52	0.2	1.0	1.2	1.4	0.4
	0.2	1.7	1.9		
	0.2	0.9	1.1		
81-5/80/21	5.7	2.7	8.4	9.0	0.6
	6.8	2.7	9.5		
	6.8	2.2	9.0		
82-36/80/21	1.3	1.3	2.6	2.6	0.2
	1.2	1.3	2.5		
	1.7	1.1	2.8		
82-36/100/6	1.1	6.7	7.8	8.0	0.3
	1.4	6.8	8.2		
82-32/80/21	1.5	0.9	2.4	2.3	0.1
	1.0	1.2	2.2		
82-32/100/6	1.0	7.6	8.6	8.4	0.3
	1.0	7.2	8.2		
82-33/80/21	0.5	2.3	2.8	1.3	1.3
	0.0	0.3	0.3		
	0.5	0.2	0.7		
82-33/100/6	1.3	1.6	2.9	2.9	0.0
	1.5	1.4	2.9		
82-35/80/21	1.1	0.5	1.6	1.3	0.5
	0.7	0.8	1.5		
	0.7	0.0	0.7		
82-35/100/6	1.0	2.4	3.4	2.3	1.6
	0.7	0.5	1.2		

TABLE III

ELEMENTAL ANALYSIS OF FILTRABLE SEDIMENT FROM NRL FUEL 82-10 STRESSED FOR 21 DAYS AT 80°C. ALL VALUES IN WEIGHT PERCENT

<u>Element</u>	<u>Weight %</u>
Carbon	62
Hydrogen	5
Nitrogen	3
Oxygen	25
Sulfur	2
Ash	<u>2</u>
Total	99

The filtrable insoluble sediment is much more difficult to solubilize and is not amenable to standard techniques of MS identification. Preliminary VPO measurements indicate that the filtrable

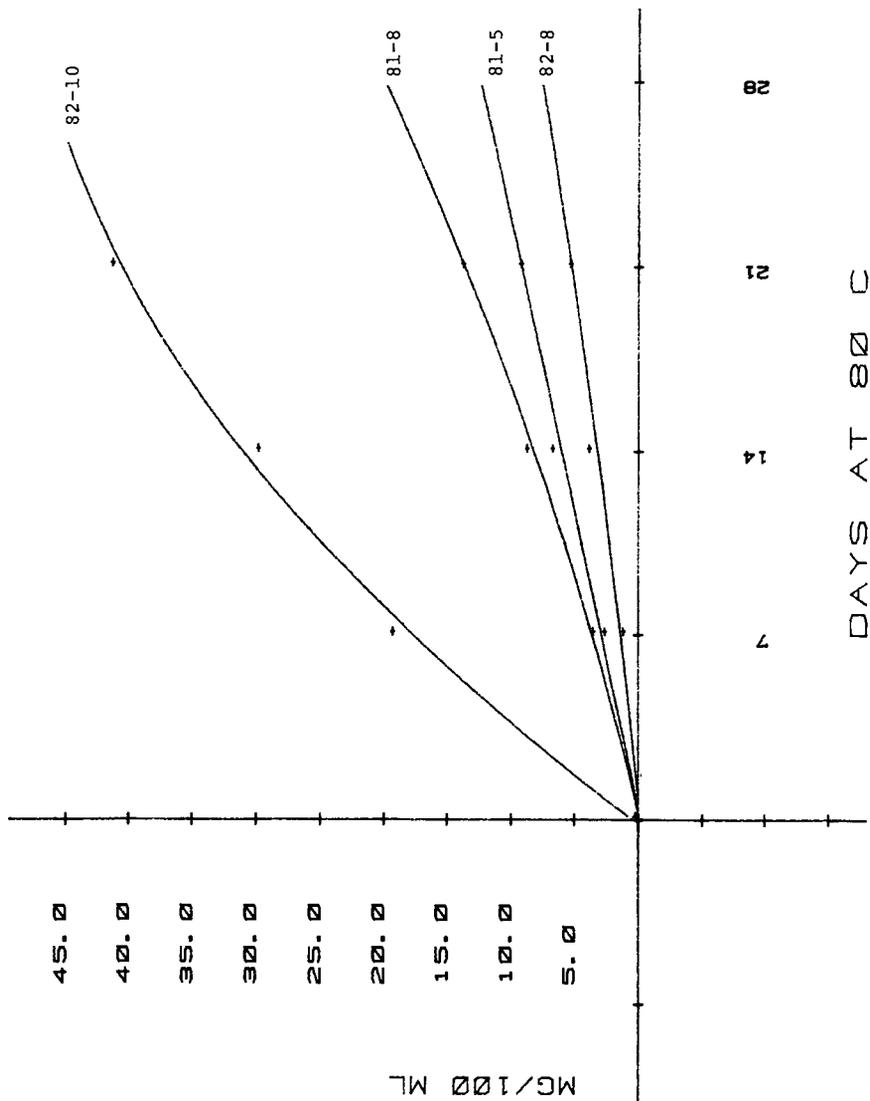


Figure 1. Total insolubles formed for four different DFM fuels stressed at 80°C for 7, 14, and 21 days each. Curves are computer generated quadratic least squares best fits.

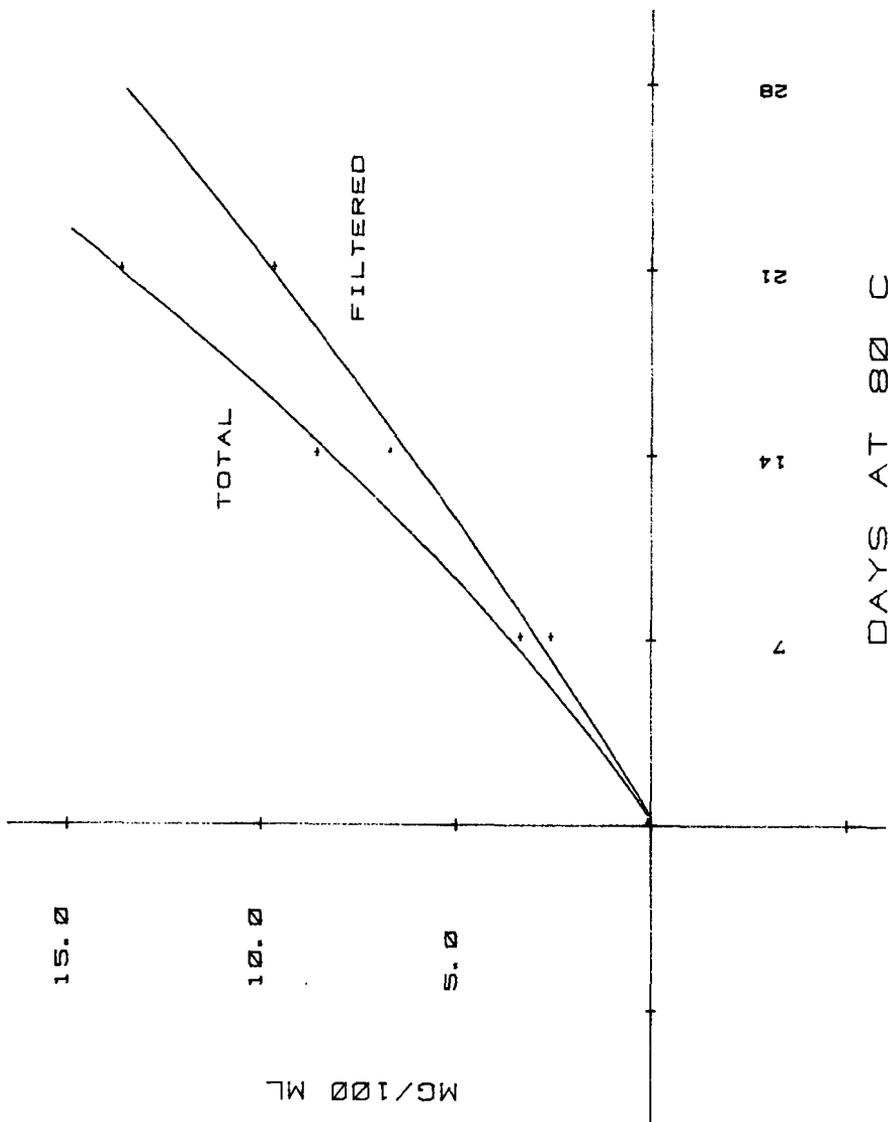


Figure 2. Breakdown of total insolubles into filtered sediment and adherent gum for fuel 81-8 stressed at 80°C for 7, 14 and 21 days. Curves are least squares best fits.

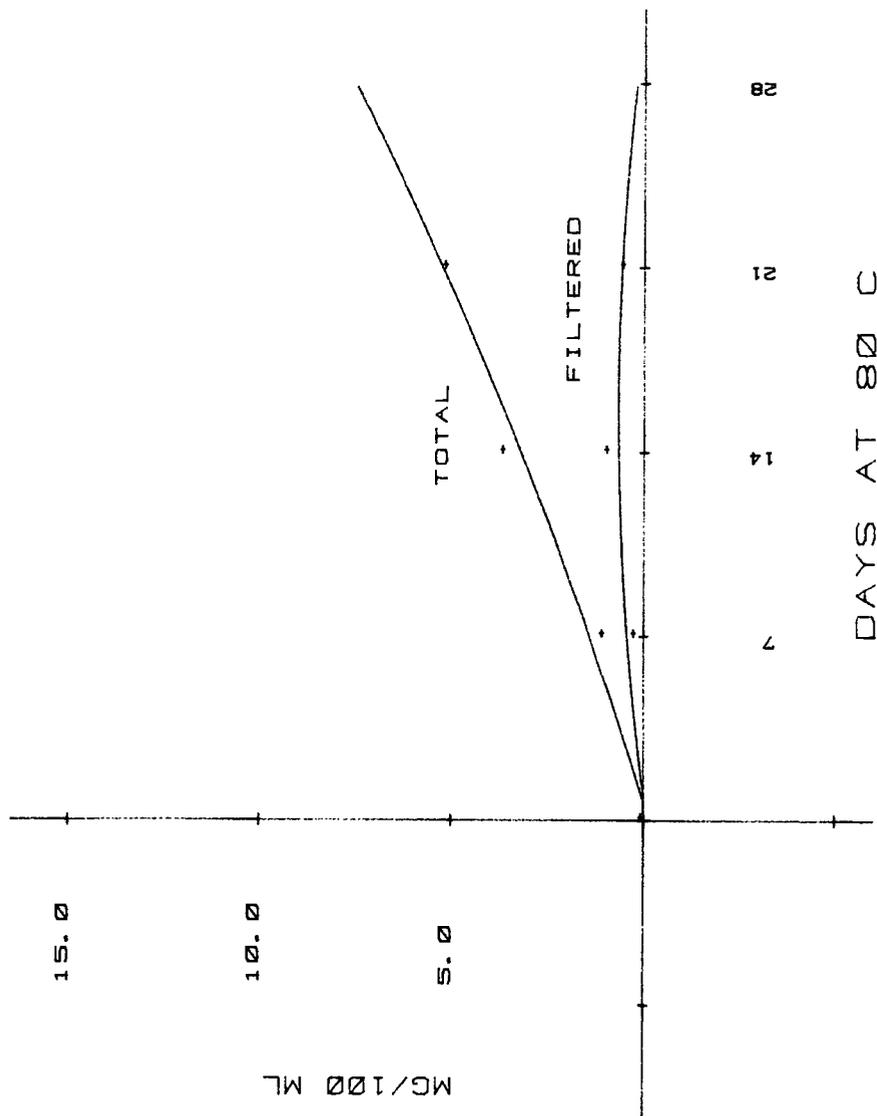


Figure 3. Breakdown of total insolubles into filtered sediment and adherent gum for fuel 82-8 stressed at 80°C for 7, 14, and 21 days. Curves are least squares best fits.

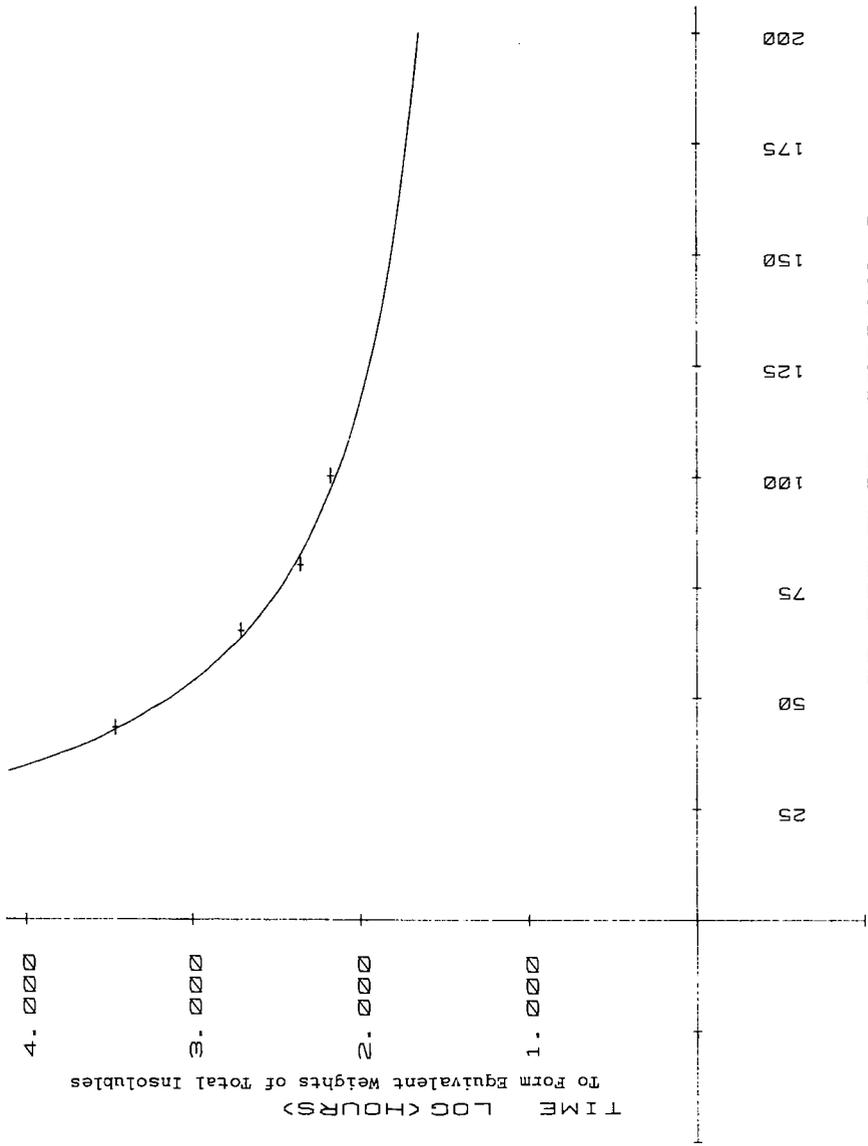


Figure 4. Plot of stress temperature of fuel 81-5 from 48°C to 100°C vs time necessary to form equivalent amount of total insolubles. The curve is a least squares best fit.

insoluble sediment is of higher molecular weight (up to 1500 amu). A typical elemental analysis for filtrable sediment of 82-10 (a particularly unstable DFM) is given in Table III. Oxygen has been directly determined by coulometric measurements. The high heteroatom content is typical for this type of sediment (2). Six major components of a filtered sediment extract in hot THF have been isolated by gas chromatography. Filtered sediments are usually insoluble in most organic solvents. Further analysis of the major fuel degradation components will establish the identity of the reactive species in fuels.

LITERATURE CITED

- (1) Hazlett, R. N., Cooney, J. V., and Beal, E. J., First Annual Report, Sept. 15, 1981-Sept. 30, 1982, NRL, Washington, D. C., to be published by USDOE under contract DE-AI-19-81BC10525.
- (2) Nixon, A. C., "Autoxidation and Antioxidants of Petroleum", Chapter 17 in "Autoxidation and Antioxidants", W. O. Lundberg, Ed., John Wiley, New York, 1962.