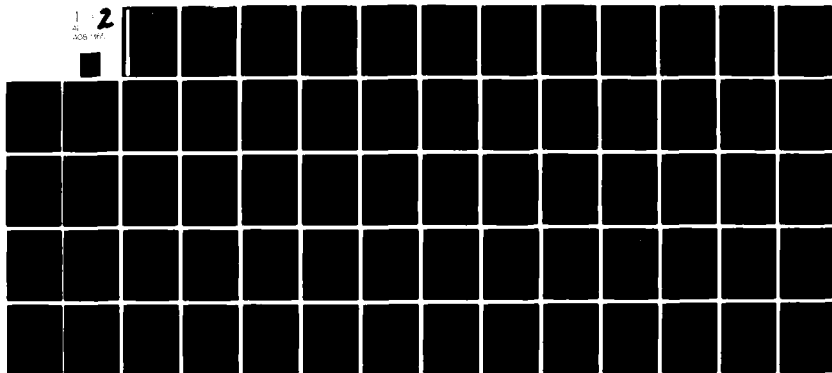


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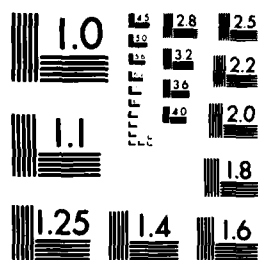
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FINAL REPORT ON ASSESSMENT OF CRUDE OIL AND REFINED PETROLEUM PRODUCT QUALITY DURING LONG-TERM STORAGE

AFLRL REPORT No. 121

by

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20. ABSTRACT

the state-of-the-art in crude and petroleum product storage. The second task investigated the effect of storage on the quality of finished products. The third task developed a DOE/SPRO computer-based search capability for crude oil characterization data. The fourth and final program task consisted of an overall assessment of long-term fuel storage, including recommendations for product specifications intended for storage, and test methodology for monitoring selected product quality.

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FOREWORD

This document is the final report of a 4-task program, which was conducted at the U.S. Army Fuels and Lubricants Research Laboratory (USAFLRL) at Southwest Research Institute, San Antonio, Texas under Contracts DAAK70-78-C-0001 and DAAK70-80-C-0001, during the period June 1978 through December 1979. The work was funded through Interagency Agreement EL-78-A-01-2815 between the Department of Energy and the Department of Defense. The contract monitor was Mr. F.W. Schaekel of the Energy and Water Resources Laboratory, U.S. Army Mobility Equipment Research and Development Command, DRDME-GL, Ft. Belvoir, VA.

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TABLE OF CONTENTS

	<u>Page</u>
I. INTRODUCTION.....	5
II. APPROACH.....	6
Task 1: State-of-the-Art Review and Assessment.....	6
Task 2: Experimental Study of the Effect of Storage on the Quality of Finished Products.....	7
Task 3: Update and Expand Data Base for Crude Oil Characteristic Programs.....	7
Task 4: Overall Assessment and Report.....	7
III. RESULTS AND DISCUSSION.....	8
Task 1: State-of-the-Art Review and Assessment.....	8
A. Data Base Sources.....	8
B. Questionnaires.....	9
C. Consultations.....	9
D. Summary of State-of-the-Art Review and Assessment.....	9
E. Summary of Work Recently Completed in West Germany.....	11
Task 2: Experimental Study of the Effects of Storage on the Quality of Finished Products.....	13
A. Proposed Product Specification.....	13
B. Industry Recommendation.....	16
C. Evaluation of Samples for Storage Characteristics.....	17
1. Sedimentation Tendencies of Burner Fuels.....	22
2. Water Shedding Tendencies of Burner Fuel Oils.....	24
3. Free Wax in Burner Fuel Oils.....	25
D. Microbiological Growth in Stored Fuels at Hydrocarbon- Water Interface.....	27
Task 3: Update and Expand Data Base for Crude Oil Characteristic Program.....	30
Task 4: Overall Assessment.....	32
A. Summary of Crude and Product Storage: State-of-the-Art Review and Assessment.....	33
1. Crude Oil Storage.....	33
2. Gasoline Storage.....	33
3. Jet Fuels.....	34
4. Distillate Fuels.....	34
5. Heavy or Residual Fuel Oils.....	36

TABLE OF CONTENTS (Cont'd)

	<u>Page</u>
B. Selection of Products for Storage.....	37
C. Assessment of Residual Fuel Storage Stability.....	39
D. Procurement Specifications.....	41
E. Periodic Monitoring of Stored Fuels.....	42
LIST OF REFERENCES.....	43
 APPENDICES	
A. Tentative Method for Measuring the Sedimentation Tendencies of Burner Fuel Oils.....	47
B. Method for Quantitatively Determining Particulate and Asphaltene-Like Contamination of Fuel Oil.....	51
C. Method for Quantitatively Determining Free Wax in Residual Fuel Oils by Filtration.....	59

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1 SPRO-Proposed Specification for Hydrotreated Vacuum Gas Oil.....	15
2 Tentative Specifications for Products Considered for Storage in a Regional Reserve.....	17
3 Analytical Data for Refinery Samples.....	18
4 Weight Percent Sediment in Burner Fuel Oils Following Various Time Intervals at 7500 rpm.....	23
5 Weight Percent Sediment in Burner Fuel Oils Following Various Time Intervals at 15,000 rpm.....	24
6 Data for Emulsion Test (Modified ASTM D 1401).....	26
7 Fuel Oil Filtering and Free Wax Filtering Procedure Results.....	28
8 Current SPRO Crude Oil Specifications.....	31
9 SPRO Search File Organization.....	32
10 Planning Assumption Limits for Residual Fuel Oil for Storage in a Regional Reserve.....	39

I. INTRODUCTION

The Energy Policy and Conservation Act (EPCA), Public Law 94-163, which was signed into law on December 22, 1975, provided the legislative authorization for the creation of a Strategic Petroleum Reserve (SPR). The Strategic Petroleum Reserve Office was to provide for the storage of up to one billion barrels of petroleum in order to diminish United States vulnerability to the effects of a severe petroleum supply interruption.^{(1)*} On May 25, 1977, SPR Plan Amendment No. 1 was transmitted to Congress as Energy Action No. 12, and became effective on June 20, 1977. The purpose of this amendment was to accelerate the development schedule so as to have 500 million barrels of oil in storage by the end of 1980.

A second amendment, Energy Action DOE No. 2, was submitted to Congress in April 1978 and became effective on June 13, 1978. This amendment provides for the expansion of the reserve size from 500 million barrels to 1000 million barrels, and provides implementation for the third 250 million barrels.⁽²⁾ Decisions have not been made regarding the extent of Government and industry involvement in developing the final increments of the SPR.

A further proposed amendment to the SPR Plan would remove the discretionary language regarding regional and noncontiguous storage. Upon enactment of the windfall profits tax and the establishment of the Energy Security Fund proposed by the President, this amendment would:

- Provide for storage of residual fuel oil, or alternative refined petroleum products or crude oil, for the U.S. Northeast Coast;
- Provide for crude oil and refined petroleum product storage (commercial jet fuel) in the State of Hawaii; and
- Provide for crude oil and unfinished oil (i.e., naphtha) storage in the Commonwealth of Puerto Rico.

* Superscript numbers in parentheses refer to the list of references at the end of this report.

These changes would amend Chapter V of the SPR Plan and are the result of a continuing reassessment of the SPR program to ensure maximum energy supply protection for the United States, consonant with the President's National Energy plan.⁽³⁾

If regional petroleum product storage is implemented, it will be imperative that the stability of the stored products be known. An investigative program was initiated to develop information to help ensure that products being considered for storage in a regional petroleum reserve would be of a quality to be immediately usable, and to identify appropriate quality assurance procedures. An interagency agreement between the Department of Energy (DOE) and the Department of Defense (DOD) provided funding for this program.

II. APPROACH

A work directive was prepared under contract DAAK70-78-C-0001 between the U.S. Army Mobility and Equipment Research and Development Command (MERADCOM) and Southwest Research Institute (SwRI) to implement the interagency agreement. The four tasks detailed in the work directive were performed at the U.S. Army Fuels and Lubricants Research Laboratory (AFLRL) located at SwRI and can be briefly described as follows:

Task 1: State-of-the-Art Review and Assessment

The objective of this task was to compile comprehensive information on the known effects of storage on the quality of crude oil and refined petroleum products and to detail the experience of other countries in maintaining strategic petroleum reserves. Input to this task included a review of information in the technical literature and consultation with selected experts in the various areas of interest. From this information, an assessment was made of: (1) the current state-of-the-art in estimating the effects of strategic storage; and (2) detailed conditions and analytical inspections to be employed in the petroleum product accelerated aging experimental program.

Task 2: Experimental Study of the Effect of Storage on the Quality of Finished Products

The purpose of this task was to perform accelerated aging tests on samples of finished products using conditions designed to simulate the actual environment to be encountered in (1) salt dome storage, (2) rock cavern storage, and (3) steel tank storage. In conjunction with DOE, a series of finished product samples, including such diverse oils as No. 2 burner fuel and residual fuel oil, was selected.

Task 3: Update and Expand Data Base for Crude Oil Characteristic Program

The purpose of this task was to develop a computer transformation program which would permit SPRO to access the more than 9000 crude oil analyses which are stored in the computer facility at DOE's Bartlesville Energy Technology Center (BETC). These analyses, spanning over 60 years, were performed using what is popularly known as the "Bureau of Mines Routine Method." The format of this method is not compatible with current SPRO crude oil "type" specifications, and, consequently, the data cannot be directly searched to identify crude oils potentially meeting SPRO requirements.

Task 4: Overall Assessment and Report

This task integrates and reports the work products from the previous tasks and provides an assessment for the SPR program in the following areas:

- Expected changes in the composition and properties of petroleum products as a result of salt dome, rock cavern, and steel tank storage.
- Impact of finished product changes, such as need for reblending of stored fuels before use; criteria for the choice of finished products for storage and the choice of storage methods; need for improved storage techniques; and estimates of turnover frequencies needed to maintain specification product in storage.

- Recommendations of various finished product specifications appropriate to each different storage mode.
- Recommendations for a schedule of inspection and test procedures to monitor petroleum products in storage.
- Potential for maximizing crude oil supply options by blending "off-spec" crudes.

III. RESULTS AND DISCUSSION

Task 1: State-of-the-Art Review and Assessment

The state-of-the-art review and assessment of storage effects on crude and product quality was undertaken through: (1) a search of the literature utilizing selected data bases; (2) questionnaires submitted to various companies and foreign organizations having experience in long-term and underground storage of petroleum products and crude oil, and (3) consultations with individuals knowledgeable in the area of petroleum storage stability. This work resulted in two reports^(4,5); one published through the Department of the Army, MERADCOM and the other through the Department of Energy, Bartlesville Energy Technology Center.

A. Data Base Sources

A literature search was undertaken by computer, accessing the following selected data base sources as follows: APILIT, TULSA, ENERGYLINE, CONDENS/CASIA, NTIS, and SSIE. These data base sources covered references from 1961 to the present and are described in detail in the report on this task.⁽⁴⁾ The data bases yielded a total of 1400 citations, 300 of which were considered to be directly applicable to the stability and storage of petroleum products and crude oil. Many of these references were trade journal notices and short articles announcing various phases of the SPR program and other underground storage activities, and were not considered sufficiently technical to be included in a comprehensive bibliography of the subject. References to underground storage of natural gas and gaseous hydrocarbons were quite

numerous, but also were not included in the bibliography. In addition, several environmental impact statements for various sites being considered for inclusion in the SPR program were not referenced in the report.

B. Questionnaires

Questionnaires of three types were prepared and sent to individuals in various companies having experience in storage of crude oil, storage of refined products, or manufacture of additives for refined products. In this task, seven companies (including three in the United States, two in West Germany, and one each in Finland and The Netherlands) were contacted regarding their experience in the underground storage of crude oil and/or refined products. Responses were received from six of the seven. In addition, eight companies in the U.S. were contacted regarding their experience and/or recommendations in the use of additives for increasing the storage life of refined products. Only three of the eight responded.

C. Consultations

Personal consultations were held with individuals in several companies regarding their experiences in the underground storage of refined products or crude oil. Individuals in two companies which manufacture additives were also contacted regarding their experience and recommendations in the use of additives for improving the storage stability of refined products.

D. Summary of State-of-the-Art Review and Assessment

The practice of storing petroleum products and crudes underground began in 1915 with the successful storage of natural gas in old gas wells in Welland County, Ontario, Canada. Since then, two modes of underground storage have been commonly used in various parts of the world. These are porous media and open cavities. Porous media storage includes depleted gas or oil fields, and water-bearing sands or aquifers, and have been utilized primarily for storage of normally gaseous materials such as natural gas, butane, propane, butylene, ethylene, propylene, and air. The open cavities may be abandoned mines; specially mined cavities in granite, rock salt or other suitable

ble rock formations; and solution-mined cavities in salt. A variety of petroleum products, including LPG, gasoline, distillates and crude oil, have been stored in salt cavities and in specially mined cavities. Abandoned mines have been used for both crude oil and distillate storage.

Until recently, long-term storage of crude oil had taken place only in a few instances in Europe and in South Africa. Based on what is known for this limited number of cases, it appears that the refinability of crude oil will not be affected by prolonged storage. Most crudes will likely deposit a "sludge" during storage which may interfere with withdrawal pumping when submerged type pumps are used. It is speculated that this sludge is composed of micro-crystalline wax, sand, clay, water and possibly asphaltenes. Emulsions at the water-oil interface have been reported after prolonged storage, and these have been attributed to the action of centrifugal pumps used to remove accumulated seepage water. It is possible that these emulsions resulted from biological activity, although the only such activity noted was reported to be anaerobic (a process that produces hydrogen sulfide). However, no detection of hydrogen sulfide was noted. The bitumen sediment and water inherently present in crude may contribute to this layer by settling out during quiescent storage.

Underground storage of products, including natural gas, LPG, gasoline, diesel fuel, burner fuel, gas oil, and jet fuel has become common practice in Europe. The lighter products, natural gas through gasoline, and, in a few instances, diesel fuel, have been stored in salt cavities and mines in the U.S. for varying periods of time since about 1943. There are no reports of deterioration, although these are mostly short-term storage programs (one year or less) as opposed to long-term strategic reserve storage programs.

Several governments, notably West Germany, France, and other European Community countries, have imposed regulations requiring that reserves of products be kept by various oil companies to ensure against petroleum shortages. Salt dome cavities and mined rock caverns are typically utilized for this product storage, and even though storage temperatures range from a low of approximately 5°C in mined rock caverns to a high of 50°C in some of the salt dome caverns, none of the stored products was reported to be unstable even after a number of years. One instance of a relatively high sodium con-

tent in a gas oil (equivalent to an ASTM No. 2 burner fuel oil*) stored in West Germany was observed. However, by blending with fresh refinery product at a 2-to-1 ratio, this fuel was utilized with no problem.

In general, the technical report reviews and the personal contacts indicated that long-term underground storage of refined distillate products has been accomplished through proper selection of products to be stored by means of specification requirements; judicious use of additives to control any potential oxidation, sediment formation, biological activity, etc.; and quality control/surveillance.

No experience with extended storage of heavy or residual fuels has been reported in the literature, although correspondence related to this study indicates the Scandinavian countries have had experience in this area. The main concern with storage of this fuel is wax and sludge separation, which may be controlled by continuous heating and circulation of the fuel. Fuel temperature should be maintained above the wax appearance point, and circulation should be performed in order to reduce particulate matter sedimentation.

While considerable information was gained on the effects of prolonged storage of crude oils and products, no specific guidelines were identified for purchase specifications, quality control/surveillance measures or handling of jet or residual burner fuels. Considerable information, however, was identified for use in programs relating to the effect of storage on the quality of these finished products, some of which are summarized in a later section of this report under "Task 4: Overall Assessment."

E. Summary of Work Recently Completed in West Germany

Kavernen Bau-und Betriebs-GmbH (KBB), working under contract to the Strategic Petroleum Reserve Office, Department of Energy, recently completed

* ASTM refers to the American Society for Testing and Material. No. 2 fuel oil is described in the ASTM Annual Book of Standards, Part 23, Designation D 396. Subsequent references to ASTM methods in this report can also be found in the ASTM Annual Book of Standards.

studies on the effect of storage in salt dome solution caverns on the properties of petroleum.⁽⁶⁾ The following paragraphs summarize this work on "Evaluation of the Effects of Long-Term Storage in Salt Caverns on the Physical and Chemical Properties of Certain Crude Oils and Distillate Fuel Oils."

During the course of these studies, a series of samples was collected from three West German salt dome solution-mined caverns. One of these caverns contains a diverse mixture of light and heavy Middle East crude oil; another of the caverns contains a single generic Middle East crude oil; and the third cavern contains distillate heating oil. These samples were subsequently analyzed, using a number of standard petroleum test methods, to ascertain if any physical or chemical changes which would affect the refining or marketability of the oils had occurred.

Analytical results for the samples collected from the cavern containing the mixture of crudes indicate that a nearly total mixing has taken place during the two to three years of storage. The mixing is apparently caused primarily by thermal convection within the cavity configuration. It was judged that no changes had occurred which would prevent the crude mixture from being processed using existing refining technology.

For the samples collected from the cavern containing only a single generic crude oil, the analytical results indicate that it is moderately homogeneous in quality and does not exhibit any significant deviations from what is expected, based on historical data. The crude oil had not undergone any deleterious changes in quality during the more than six years it had been in storage.

In both of these caverns, a viscous layer containing significant quantities of water, sediment, and salt, and enriched in trace metals and the acidic components of crude oil (such as mercaptans and asphaltenes) had developed at the oil/brine interface. Studies revealed that this layer also contained normal alkane waxes in greater amounts than present in the crude oil. This layer comprised about 0.5 percent of the volume of hydrocarbons stored in each of the caverns. It is likely that this layer formed as a result of natural processes, involving the settling of flocculated petroleum resins and concurrently precipitated trace metals, as well as inherent sediment and water. This layer apparently forms, with time, in all crude oil storage caverns, whether they

contain a single generic crude or a mixture of crudes. No evidence suggested that this layer resulted from crude oil incompatibility with other crude oils or the environment in which it was stored. These studies have provided the most compelling evidence, to date, that crude oil stored in large underground chambers in salt over brine will not undergo any deleterious changes in quality.

Analytical results for the samples collected from the cavern containing distillate fuel oil indicate that the product is marketable and still conforms to its original specifications. No viscous layer was found at the oil/brine interface in this cavern, and such a layer would not be expected to form because distillate fuel oils of the ASTM No. 2 type do not typically contain surfactants, asphaltenes, or water in sufficient quantity to promote its formation.

The results of ancillary studies of the brine existing below the oil/brine interface level in the three caverns studied indicate that the brine has not become contaminated to a measurable degree, through solution or dispersion, with oil or other organic substances. Sampling of liquid at the cavern floor has been done, but not yet reported.

Task 2: Experimental Study of the Effects of Storage on the Quality of Finished Products

The work directive description for Task 2 stated that accelerated aging tests would be carried out with samples of finished products selected from types such as No. 2 and residual heating oils and jet fuels. The experimental work was focused on residual heating oils or likely substitutes because this was the major product being considered for storage along the Northeast United States. The storage characteristics and practices for these fuels are less well known than those for No. 2 and jet fuels.

A. Proposed Product Specification

Investigations by DOE/SPRO resulted in a preliminary recommendation that a hydrotreated vacuum gas oil be considered for storage in the regional product storage program for supplying Northeast U.S. residual fuel oil consumers.

This product would have viscosity and other specifications comparable to an ASTM No. 4 burner fuel oil. The main reasons for the recommendation were related to potential:

- (1) availability,
- (2) chemical stability, and
- (3) flexibility of use and handling.

Within U.S. refineries, this type of product is internally available as:

- (1) hydrotreated catalytic cracker feedstock,
- (2) first stage product from hydrocracking, and
- (3) hydrotreated lube oil basestocks.

The aggregate of the above supply sources was projected to exceed two million barrels per day.

Vacuum gas oil desulfurization is widely practiced in the Caribbean refineries as the major process to produce low-sulfur residual fuel oils. Total processing capacity in this area (including Venezuela) is about one million barrels per day. If the Strategic Petroleum Reserve Office purchased at a rate of about 50,000 barrels per day and stayed out-of-phase with seasonal variations, a clearly ample supply was projected to be available from both domestic and foreign refineries without significantly impacting cost or availability.

A hydrotreated vacuum gas oil would be expected to exhibit better stability qualities than products that contain residual or untreated cracked components. The proposed specifications for this product appear in Table 1.

A recent study sponsored by SPRO indicated that a large percentage of No. 6 fuel oil users could readily switch to a lighter grade fuel oil with little difficulty.⁽⁷⁾ The major problem encountered would be loss of pumping capacity. This loss is caused by the fact that, in the gear pumps used to move residual fuel oils, shear increases as viscosity decreases. Switching to a No. 4 grade fuel oil would create considerably less impact than using a No. 2 grade. Thus, the recommended hydrotreated vacuum gas oil product would

TABLE 1. SPRO PROPOSED SPECIFICATION FOR
HYDROTREATED VACUUM GAS OIL

	<u>Values</u>
Grade (ASTM)	4
Saybolt Viscosity, SUS at 37.8°C (100°F)	45-125
Kinematic Viscosity, cSt at 37.8°C (100°F)	5.8-26.3
Flash Point, °C(°F), min	54(130)
Pour Point, °C(°F), max	-7(20)
Ash, wt%, max	0.1
Water and Sediment, vol%, max	0.5
Sulfur, wt%, max	0.3
Compatibility with Standard*	Yes
Cracked Stocks, vol%, max	20
Residual Stocks, vol%, max	0
Ramsbottom Carbon Residue, wt%, max	0.3
Additives, lb/1,000 bbl	
Oxidation Inhibitor, amine type	10-20
Metal Deactivator	0.5-1
Corrosion Inhibitor	0.5-1
Dispersant	Open
Pour Depressant	Open
* Can be mixed with a preselected standard fuel oil or a hydrocarbon solvent without precipitation of asphaltenes.	

be of a quality acceptable by most No. 6 fuel consumers. Moreover, the cleaner fuel would result in reduced maintenance costs.

In addition, the recommended fuel for storage could also be readily used as a refinery feedstock in the event an interruption occurs during a period in which shortages of light products (gasoline and No. 2 diesel fuel) are more critical than heavy fuel oil. Hydrotreated vacuum gas oil makes an excellent conversion feedstock for increasing refinery yields of gasoline and light distillate products.

From a distribution standpoint, it might be possible to ship hydrotreated vacuum gas oil through terminals and pipelines which cannot handle heavy residual products (Nos. 5 and 6 burner fuel oils).

B. Industry Recommendation

While attempting to obtain samples of No. 4 burner fuel meeting the proposed specification shown in Table 1, it was learned that hydrotreated vacuum gas oil is not as generally available as initially indicated by the SPRO preliminary studies. Some suppliers suggested that No. 6 fuel should be the product considered for storage. Following these contacts, a meeting was held in Washington, D.C. at the American Petroleum Institute offices. Representatives of the petroleum industry, boiler manufacturers, SPRO, and the Army were present. It was recommended at this meeting that a low-pour/high-sulfur No. 6 burner fuel (considered more widely available) be selected as the product for storage. Because of concern over the high sulfur level with respect to environmental considerations, specifications for the low-pour/high-sulfur fuel as well as an alternate low-pour/low-sulfur fuel were suggested. Table 2 compares the proposed specification for these fuels with the hydro-treated vacuum gas oil specification.

C. Evaluation of Samples for Storage Characteristics

A decision was made to evaluate both No. 4 and No. 6 fuels for their respective storage characteristics. Following requests for candidate test fuels, seventeen samples from nine suppliers, including some foreign suppliers, were received. These samples represented refinery process feedstocks, hydro-treated distillates, desulfurized gas oil, No. 4, No. 6, and Bunker C fuel oils. A No. 2 fuel received from the United Kingdom was included in the evaluation. Table 3 contains a listing of these samples along with their description and physical/chemical properties.

None of the No. 4 fuels listed in Table 3 meet all the SPRO requirements for a hydrotreated vacuum gas oil. Sample AL-776-F fails only the 0.30 wt% sulfur limit with a value of 0.32 wt%, while Sample AL-7753-F failed only the carbon residue limit. Samples AL-7680-F and AL-8012-F failed both sulfur and carbon residue limits. Sample AL-7679-F, described as a hydrotreated distillate, has a viscosity within the No. 4 fuel oil range; however, the pour point and sulfur content are above the prescribed limits. Sample AL-7756-F meets all the requirements shown in Table 2 for a low-pour/low-sulfur No. 6

TABLE 2. TENTATIVE SPECIFICATIONS FOR PRODUCTS CONSIDERED FOR STORAGE
IN A REGIONAL RESERVE

	SPRO Specs for Hydrotreated Vacuum Gas Oil	Recommended Low-Pour/ High-Sulfur Fuel Oil	Recommended Low-Pour/ Low-Sulfur Fuel Oil
Grade (ASTM)	4	6	6
Specific Gravity, 15.6°/15.6°C	---	0.910-0.993	0.887-0.930
Gravity, °API	---	11-24	20-28
Saybolt Viscosity, at 37.8°C (100°F), SUS	45-125	---	150-225
Kinematic Viscosity at 37.8°C (100°F), cSt	5.8-26.3	---	31.9-48.4
Furol Viscosity at 50°C (122°F), SSF	---	50-250	---
Kinematic Viscosity at 50°C, cSt	---	103-530	---
Flash Point, °C(°F), min	54(130)	66(150)	66(150)
Pour Point, °C(°F), max	-7(20) ^a	7(45)	13(55)
Ash, wt%, max	0.1	0.1	0.1
Water & Sediment, vol%, max	0.50	---	---
Water, vol% (D 95), max	---	1	1
Sediment by Extraction, wt% (D 473), max	---	0.1	0.1
Sulfur, wt%, max.	0.3 ^a	2.5	0.3
Compatibility With Standard	Yes ^b	---	---
Compatibility Rating (D 2781), max	---	2	2
Cracked Stocks, vol%, max	20	---	---
Residual Stocks, vol%, max	0	---	---
Ramsbottom Carbon Residue, wt%, max	0.3	15	15
Additives, mg/l (1b/1000 bbl)			
Oxidation Inhibitor, amine ^c	28.5-57 (10-20)	None	None
Metal Deactivator	1.45-2.9 (0.5-1)	None	None
Corrosion Inhibitor	1.45-2.9 (0.5-1)	None	None
Dispersant	Open	None	None
Pour Depressant	---	Open	Open

a - Subject to revision.

b - Can be mixed with a preselected standard batch of fuel oil or a hydrocarbon solvent without precipitation of asphaltenes.

c - FOA-3 or comparable product.

TABLE 3. ANALYTICAL DATA FOR REFINERY SAMPLES

AFLRL Code (AL- -F)	7660	7661	7662	7680	7679	7753	7756	7757
Supplier Code	A	A	A	B	B	E	E	E
Description	H-FCC Feed	IsomaxII Feed	Crude II FCC Feed	No. 4 Fuel Oil	Hydro-treated Distillate	No. 4 Fuel Oil	No. 6 Fuel Oil	Desulfurized Gas Oil
Appearance	Brown Opaque Waxy Liquid	0.5 Color Liquid	Brown Opaque Liquid	Black Liquid	Brown Opaque Waxy Liquid	Black Liquid	Black Liquid	8.0 Color Liquid
API Gravity, D 287	22.2	42.2	23.7	23.4	26.2	26.2	22.9	24.0
Viscosity, D 445, 38°C(100.4°F)								
cSt	72.3	2.8	(a)	17.5	26.0	19.5	33.5	50.9
SUS	335	35.4	(a)	87.5	123.5	95.6	157	237
Viscosity, D 445, 50°C(122°F)								
cSt	---	---	---	16.3	10.6	12.3	19.8	28.4
SUS	---	---	---	82.6	61.4	67.3	97.0	134.4
Pour Point, D 97, °F(°C)	100(38)	30(-1)	100(38)	10(-12)	95(35)	10(-12)	0(-18)	70(21)
Sulfur, wt%, XRF	1.70	0.01	0.50	0.86	0.54	0.28	0.27	0.16
Insolubles, D 893, Pentane, wt%	0.04	0.01	0.02	2.92	0.01	0.46	0.42	0.03
Benzene, wt%	0.01	0.01	0.01	0.15	0.01	0.06	0.04	0.03
Ramsbottom Carbon, D 524, wt%	---	---	---	1.73	0.14	0.56	0.52	0.15
Flash Point, D 93, °F(°C)	---	---	---	161(72)	191(88)	222(106)	278(136)	262(128)
Water & Sediment, D 1796, vol%	---	---	---	0.60	0.06 ^(d)	0.04 ^(d)	0.4 ^(d)	3.4 ^(e)
Ash, D 482, wt%	---	---	---	---	---	0.004	0.007	0.001
Spot Test, D 2781 ^(h)	---	---	---	3-4	1-1	2-3	3-4	2-2

a - Sample is not fluid at 38°C

b - This value represents repeated washings to give a constant weight. The value after one washing was 2.7 wt%.

c - Results for procedure as run according to D 893. After 10 additional benzene washes, the value was 0.18%.

d - Sediment, not water.

e - Predominately wax.

f - Water = 0.01 vol%.

g - No water or sediment detected.

h - Cat 1-H reference fuel (DF-2), Method A-Method B

i - No spot detected by either Method A or Method B

<u>7776</u>	<u>7798</u>	<u>7966</u>	<u>8012</u>	<u>8100</u>	<u>8171</u>	<u>8281</u>	<u>8508</u>	<u>8513</u>
C	C	C	C	F	G	H	I	J
No. 4 Fuel Oil	No. 6 Fuel Oil	No. 6 Fuel Oil	No. 4 Fuel Oil	No. 2 Fuel Oil from UK	Burner Fuel Oil from Italy	Bunker C Fuel Oil	Heavy No. 6 Fuel Oil	Heavy No. 6 Fuel Oil
Black Liquid	Black Liquid	Black Liquid	Black Liquid	0.5 Color Liquid	Black Liquid	Black Liquid Asphalt- like	Black Liquid Asphalt- like	Black Liquid Asphalt- like
28.8	23.2	16.6	24.0	38.1	22.4	6.7	13.8	10.1
14.7 76.2	65.2 303	939 4348	15.2 78.1	2.79 35.3	57.6 268	765 3543	587 2721	1446 6697
9.7 57.9	36.3 170	389 1808	9.5 57.3	2.22 33.4	35.3 166	314 1458	249 1154	573 2659
-15(-26)	70(21)	10(-12)	5(-15)	5(-15)	40(4)	45(7)	40(4)	40(4)
0.32	0.30	2.2	0.50	0.50	2.4	1.40	1.85	2.4
0.72	0.95	14.3	0.63	0.02	4.7	14.29	5.61	7.15
0.02	0.04	0.02 ^(b)	0.03	0.02	1.2	8.11 ^(c)	0.22	0.20
0.63	1.65	2.6	0.88	0.01	2.56	4.30	4.34	4.76
201(94)	229(109)	171(77)	211(99)	155(68)	172(78)	223(106)	229(109)	204(96)
0.16 ^(d)	0.20 ^(d)	0.05 ^(f)	0.6 ^(d)	(g)	trace ^(d)	0.08 ^(d)	0.05 ^(g)	(g)
0.005	0.008	0.009	0.16	0.005	0.013	9.3	4.1	7.5
3-3	2-3	1-1	2-3	(1)	1-1	2-4	1-1	1-1

fuel, and Samples AL-7966-F and AL-8171-F meet the requirements suggested for a low-pour/high-sulfur No. 6 fuel. Samples AL-8281-F, AL-8505-F, and AL-8513-F, all No. 6 or Bunker C type fuels, have excessively high ash content.

In February of 1979, a meeting attended by representatives of SPRO/DOE, AFLRL, and representatives of a major petroleum company was held to discuss properties and availability of certain fuel oils. The proposed specifications shown in Table 2 and the properties of many of the fuel samples in Table 3 were discussed, resulting in the following comments:

- Sample AL-7756-F, while described as a No. 6 burner fuel oil, is actually a No. 5 light which would typically have a pour point of 30° to 35°F (-1° to 2°C) as opposed to the reported 0°F (-18°C).
- The availability of a fuel such as AL-7756-F would be low. For a buy of 20 million barrels under present circumstances, delivery would possibly take 20 years.
- No. 6 fuel oils generally are shipped at 100° to 135°F (38° to 57°C), depending on viscosity and pour point. They are not generally stored in large volume due to heating requirements (nor are they put into pipelines).
- Gas oil such as AL-7757-F has low availability since it is a feed stock for gasoline manufacture.
- It was generally felt that storage of typical No. 6 fuel oil would be prohibitively expensive due to heat input requirements. On the other hand, it was believed that procurement of a fuel not requiring heating but having a viscosity greater than 150 SUS at 100°F would be difficult if not impossible.
- With regard to the "Proposed Specifications for Products Intended for Storage:"

Low-Pour/High-Sulfur fuel:

- (a) would normally be shipped at 130°-135°F (54° to 57°C).
- (b) would be very expensive for long-term storage due to heating requirements.
- (c) sediment by extraction would probably be 0.5 rather than 0.1 wt%.

Low-Pour/Low-Sulfur fuel:

- (a) would not be readily available,
- (b) would be costly to store as it would require heating to maintain pumpability,
- (c) would probably range upward to 1000 SUS at 100°F (38°C) as opposed to the stated value of 225 SUS,
- (d) would not contain pour depressant since this oil company uses none in its Nos. 4 or 6 fuel oils. European fuels may be pour depressed since this oil company has noted increases in pour of fuels purchased in Europe upon delivery to the United States. Pour depressants could form emulsions since most are water soluble.

Generally accepted storage or accelerated aging tests for gasolines, jet fuels, and middle distillates such as No. 2 diesel and burner fuels are fairly well established (for short-term storage) in the petroleum industry. However, these tests generally cannot be applied directly to heavy distillate and residual fuels, either in purchase specifications or quality monitoring. A recent article on the subject of trends in marine fuels suggests that liquid fuels will continue to supply the bulk of marine bunker demand well into the 1990s.⁽⁸⁾ The increased demand of lighter products, gasoline, and distillates is being met by increased cracking and (visbreaking) of available crude oil, and these processes tend to increase the sediment and carbon residue content of residual fuels such as Bunker C. It is believed that, in order to successfully burn the residual fuels of the future, on-board purification processes will be needed and injection timing must be readily adjustable. The U.S. Navy has indicated its concern about this trend in lower quality of residual fuels. Therefore, tests to evaluate characteristics of heavy fuels that could affect their performance during and after prolonged storage were selected and developed under this task. Specifically, the characteristics of interest were: sedimentation tendencies, water-shedding characteristics, and wax content.

1. Sedimentation Tendencies of Burner Fuels

It is known that certain fuel oils are incompatible when commingled, resulting in precipitation of asphaltenes and sludge and, possibly, separation of wax. This incompatibility is even more marked when distillate fuel oils, such as ASTM grade No. 2 are used as "cutter stock" to reduce the viscosity of the heavier fuel oils. During quiescent storage, entrained water and sediment in the fuel oil can settle out under gravity and produce a sludge layer. This sludge can cause excessive wear in transfer pumps, strainer fouling, and burner flame instability.

To evaluate the sedimentation tendencies of burner fuels, a procedure was developed which consists of high-speed centrifugation of the test fuels for 15, 30, 60, 120, or 240 minutes, followed by measurement of any sediment deposited.⁽⁹⁾ Centrifugation was conducted at 7,500 and 15,000 rpm, which, based on the radius of the centrifuge rotor used in this program, corresponds to relative centrifugal forces (RCF) of 6773 and 27091 gravities, respectively.

Table 4 summarizes the sediment levels for selected test fuels at given centrifuge time intervals at 7500 rpm, RCF = 6773 gravities. For some of the fuels, these data do not follow a pattern of increasing sediment with time, particularly for samples AL-8012-F and AL-8513-F. In some cases, there seems to be only one erratically low or high point, and, in some cases, more than one.

Table 5 gives data for centrifugation of the fuels at 15,000 rpm, RCF = 27091 gravities. Since the calculations show that only one-fourth the amount of spinning time is required at 15,000 as compared to 7500 rpm to achieve the same results, only four time periods were chosen for the higher speed. Discrepancies exist between the corresponding data at the two time periods, and the exact reason is uncertain. The fact that the fuel has a high amount of sediment after the heptane wash compared to a low amount after the toluene wash indicates that the fuel is high in asphaltic sediment.

TABLE 4. WEIGHT PERCENT SEDIMENT IN BURNER FUEL OILS FOLLOWING
VARIOUS TIME INTERVALS AT 7500 RPM

		Centrifuge Test Time Interval(min)	AL-7680-F	AL-7753-F	AL-7756-F	AL-7776-F	AL-7798-F
Description			No. 4 Fuel Oil	No. 4 Fuel Oil	No. 6 Fuel Oil	No. 4 Fuel Oil	No. 6 Fuel Oil
n-heptane wash	15		1.49	0.067	0.421	0.212	0.069
	30		1.88	0.083	0.417	0.214	0.084
	60		1.62	0.081	0.438	0.220	0.113
	120		1.54	0.039	0.535	0.229	0.145
	240		1.66	0.083	0.696	0.223	0.193
toluene wash	15		1.09	0.043	0.082	0.020	0.022
	30		1.43	0.075	0.085	0.019	0.030
	60		1.19	0.070	0.082	0.019	0.039
	120		1.17	0.034	0.085	0.025	0.058
	240		1.24	0.071	0.087	0.021	0.071
		Centrifuge Test Time Interval(min)	AL-7966-F	AL-8012-F	AL-8508-F	AL-8513-F	
Description			No. 6 Fuel Oil	No. 4 Fuel Oil	Heavy No. 6 Fuel Oil	Heavy No. 6 Fuel Oil	
n-heptane wash	15		2.23	0.161	0.678	3.17	
	30		2.61	0.299	0.686	1.24	
	60		2.95	0.300	0.424	0.547	
	120		2.58	0.540	1.039	0.921	
	240		2.94	0.668	a	a	
toluene wash	15		0.013	0.102	0.012	0.033	
	30		0.015	0.199	0.001	0.036	
	60		0.014	0.221	0.001	0.035	
	120		0.013	0.373	0.001	0.045	
	240		0.015	0.405	a	a	
a = Test not performed							

**TABLE 5. WEIGHT PERCENT SEDIMENT IN BURNER FUEL OILS FOLLOWING
TIME INTERVALS AT 15,000 RPM**

Description	Centrifuge Test Time Interval (min)	AL-7680-F	50% AL-7680-F 50% AL-8100-F	AL-7798-F	50% AL-7798-F 50% AL-8100-F	AL-8012-F	50% AL-8012-F 50% AL-8100-F
		No. 4 Fuel Oil	No. 4 & No. 2 Fuel Oils	No. 6 Fuel Oil	No. 6 & No. 2 Fuel Oils	No. 4 Fuel Oil	No. 4 & No. 2 Fuel Oils
n-heptane wash	15	1.58	0.66	1.89	0.06	2.72	0.39
	30	1.62	0.73	2.74	0.10	3.61	0.32
	60	1.73	0.70	2.11	0.10	3.54	0.36
	120	1.55	a	2.45	a	3.84	0.36
toluene wash	15	1.23	0.40	0.26	0.01	0.48	0.17
	30	1.23	0.46	0.37	0.02	0.71	0.17
	60	1.24	0.49	0.37	0.03	0.61	0.18
	120	1.24	a	0.37	a	0.81	0.19
Spot Test, D 2781, (Method A - Method B)			3-4	a	2-3	a	2-3
(a) Test not performed.							

Centrifugation data are also given in Table 5 for some 1:1 mixtures of fuels. These were the results of an evaluation of the high-speed centrifugation technique for fuel compatibility testing. Compatibility of test fuels with No. 2 fuel was evaluated by blending equal parts of the test fuel and No. 2 fuel and centrifuging at 15,000 rpm. The quantitatively low sedimentation results seem to indicate satisfactory compatibility; however, spot tests conducted by ASTM Method D 2781 (a qualitative rather than quantitative method) indicated poor compatibility with the No. 2 fuel as shown in Table 3.

The procedure for quantitative sedimentation tendencies (described in Appendix A) appears to be a useful technique; however, some test details and significance of results need to be further developed. This method could be used in specifications to prevent purchase of undesirable fuels for storage and in preventing undesirable commingling effects.

2. Water-Shedding Tendencies of Burner Fuel Oils

Fuel oil stored in a solution-mined or a conventionally-mined cavern will likely have a waterbed to some extent due to seepage. Therefore, there is a need to know the tendencies of the fuel to shed water entrained or emulsified as a result of turbulence during fill/withdrawal.

Eight methods for measuring water-shedding tendencies were evaluated.⁽¹⁰⁾ Of the methods investigated, a modification of the procedure for "Emulsion Characteristics of Petroleum Oils and Synthetic Fluids," ASTM Standard D 1401, was the most effective for measuring water-shedding tendencies of the heavier burner fuels. In this procedure, equal parts of fuel and water were stirred for 5 minutes at 54°C in a graduated cylinder. The time required for the separation of the emulsion thus formed was recorded. Table 6 contains the results for two fuels evaluated by this procedure and the same fuels including a dispersant.

3. Free Wax in Burner Fuel Oils

Free wax in stored fuel oil can form with time and thus accumulate on the fuel surface and container wall, and also contribute to the sludge layer. Consequently, it is imperative that fuel oils considered for storage be evaluated for their free-wax content.

A method was developed for determining the filterable free wax in burner fuel oils at a given temperature.⁽¹¹⁾ During the course of this work, nineteen procedures found in the literature for measuring wax content of oils were examined for possible use. The investigation resulted in the development of a procedure which essentially consists of two separate steps. The first, entitled "Method for Quantitatively Determining Particulate and Asphaltene-Like Contamination of Fuel Oil," involves the filtration of a solvent-diluted fuel oil sample through a preweighed filter. This procedure is included as Appendix B. The residue is rinsed with toluene, and the soluble portion is determined as asphaltenes. Toluene-insoluble material remaining on the filter is measured as particulates. In the second step, "Method for Quantitatively Determining Free Wax in Residual Fuel Oils by Filtration" (Appendix C), the solvent is removed from the filtered fuel-solvent mixture (obtained for the fuel sample in the first step) by rotary flash evaporation and additional vacuum to remove the last traces of solvent. A known amount of the fuel is then filtered through a jacketed filter funnel with a coarse porosity fritted glass filter at a specified temperature. The filter funnel is then cooled to 0°C. The funnel is rinsed with a fuel solvent also maintained at 0°C to remove any fuel remnants and leave behind the filterable free wax. The filter funnel is then

TABLE 6. DATA FOR EMULSION TEST (MODIFIED ASTM D 1401)
FUEL AND FUEL MIXTURE

Time Period	AL-8012-F	AL-8012 + Dispersant	AL-7753-F	AL-7753 + Dispersant
5 min	Clean water - 30 ml (bottom); Bubbly emulsion - 90 ml; Oil layer - Creamy - 80 ml (top); interface - fuel/ emulsion - very ill defined; bubbly; emulsion/water - very bubbly and lacy.	Total emulsification with water droplets occurring in bottom 50 ml.	Top 78 ml fuel layer milky Fuel/Emulsion interface- sharp, well-defined; Emulsified layer; 80-122 ml dark creamy with bubbles; 0-80 ml light brown and creamy with bubbles.	Top 84 ml-fuel layer clear; Fuel/Emulsion interface-sharp, well defined; Emulsion layer- 0-70 ml light brown and creamy; 70-116 ml dark brown and bubbly.
10 min	No change from above.	Water droplets now occurring throughout entire sample.	Same as above except fuel layer becoming clearer.	No change from above.
15 min	Water layer now 35 ml (bottom); Bubbles within emulsion growing and emulsion clearing toward bottom; no other changes.	Same as above.	0-82 ml now classified as milky water layer with large water bubbles; Water/Emulsion interface- 111 defined bubbles; 92-124 ml - Emulsion dark brown and bubbly; Fuel/Emulsion interface- sharp, well defined; 124- 200 ml-fuel layer-clear.	Emulsion-0-70 ml light brown and creamy; 70-116 ml dark brown and bubbly (creamy); Fuel/Emulsion interface- sharp/well defined; Fuel 116-200 ml clear.
30 min	Water layer 0-38ml; Emulsion/ top-dark and creamy; bottom- clearing and breaking up; Emulsion/water interfaces- ill-defined, bubbly Oil/ Emulsion interface-oil layer 110-200ml milky towards top bubbly and creamy towards interface.	Very creamy emulsion with large bubbles near the top and small bubbles near the bottom.	No change.	No change except fuel now occupies 85 ml.
1 hr	Water layer-0-40ml; Emulsion/ Water interface very ill defined bubbly; Emulsion-40-120ml, top dark with bubbles, bottom light with bubbles; Fuel/Emulsion interface-becoming more defined but still bubbly; Fuel Layer 50 ml-top portion milky, bottom 5 ml bubble.	Total emulsification very small bubbles (bottom 5 ml) remainder medium to large bubbles.	Emulsion now occupies between 86 and 170 ml marks.	Same as above except fuel now occupies 86 ml.
2 hr	Bottom 94 ml now primarily water; 0-30 ml clear, 30-94 bubbly with fuel; Emulsion/ Water interface-ill-defined bubbly; Emulsion-14 ml dark and bubbly; Fuel/Emulsion layer-111-defined bubbly; Fuel-92 ml; top 88 ml milky and bottom 4 ml bubbly.	Still completely emulsi- fied with large bubbles throughout entire sample.	No change.	Emulsion: 0-70 ml-light brown honeycombed with water bubbles; 70-113 ml dark brown with bubbles; Fuel/Emulsion interface- sharp, well defined.

warmed to room temperature, and the wax crystals are rinsed off with warmed heptane. The heptane solution is placed in a preweighed round-bottom flask, the solvent is removed, and the weight difference is determined as the free-wax content.

Evaluation of four fuel oils was conducted by the above techniques, and the results are shown in Table 7. A range in values was found for asphaltenes and particulates, depending on the type and grade of filter media. This range could be attributable to differences in surface activity of the filter media, differences in effective pore size and differential clogging, and/or differences in the rate of particle agglomeration.

In general, the two higher-pour products have higher wax contents (at 25°C) as would be expected since the agglomeration of high molecular weight normal alkanes (i.e., waxes) is a primary cause of high pour points in petroleum.

This procedure, with further refinement, may be useful in evaluating the free-wax content of heavy fuel oils and could be included in purchase specifications to preclude fuels having an undesirable wax content from the standpoint of long-term storage stability.

D. Microbiological Growth in Stored Fuels at Hydrocarbon-Water Interface

The Food Sciences Laboratory at the U.S. Army Natick Research and Development Command, Natick, MA, was requested to conduct a study to determine if microbial growth will occur at the interface between eight different petroleum oils and either sodium chloride brine or Bushnell-Haas medium.*

These studies were conducted at 30°C using both aerobic and anaerobic strains of bacteria and fungi and have been outlined.

* The Bushnell-Haas medium has the following composition:

	<u>g/l distilled water</u>
Magnesium Sulfate	0.2
Calcium Chloride	0.02
Monopotassium Phosphate	1.0
Ammonium Nitrate	1.0
Ferric Chloride	0.05

TABLE 7. FUEL OIL FILTERING AND FREE WAX FILTERING PROCEDURE RESULTS

Quantitative Fuel Oil Filtering Treatment	Fuel Oil Sample Code Nos.			
	AL-7680-F	AL-7753-F	AL-7757-F	AL-7679-F
	No. 4 Fuel Oil	No. 4 Fuel Oil	Desulfurized Cas Oil	Hydrotreated Distillate
A. Asphaltene-Like Material*				
Whatman No. 41, g	5.06	0.13	0.02	0.03
Whatman No. 42, g	0.21	0.03	0.02	0.01
Millipore 0.45 μ m, g	0.17	0.02	0.02	0.02
B. Particulates*				
Whatman No. 41, g	0.104	0.007	0.001	0.008
Whatman No. 42, g	0.001	0.002	0.001	0.001
Millipore 0.45 μ m, g	0.002	0.001	0.001	0.001
C. Free-Wax Filtration Procedure** at 25°C				
Original sample weight, g	24.39	24.13	27.55	23.71
Fuel filtered, g	19.39	21.42	4.90	15.46
Recovered fuel from fuel dissolving rinse, g	5.00	2.71	22.65	8.25
Filtered free wax Weight, g	0.633	0.276	4.864	2.365
Wt%	2.6	1.1	17.7	10.0
* Method in Appendix B				
** Method in Appendix C				

The outline for the microbiological studies is shown below:

(a) Eight hydrocarbon test samples:

- (1) AL-7753-F, No. 4 fuel oil
- (2) AL-7966-F, No. 6 fuel oil
- (3) AL-7756-F, No. 6 fuel oil
- (4) Mexican Isthmus crude oil from BETC
- (5) UK FORTIES crude oil from BETC
- (6) AL-8087-T, Jet A from San Antonio International Airport
- (7) AL-8280-F, API No. 2 burner oil from Texas A&M University
- (8) AL-8282-C, API Louisiana sweet crude oil from Texas A&M University

(b) Two water solutions:

- (1) Bushnell/Haas
- (2) Concentrated NaCl brine from salt dome solution

(c) Two inoculants under two conditions

- (1) Aerobic
- (2) Anaerobic

Note: The inoculum consisted of NARADCOM culture collection of fungi (QM) and ASTM fungal spore mixture.

(d) One test temperature:

- (1) 30°C

(e) Test duration of 120 days minimum

(f) Report information desired:

- (1) Experimental details
- (2) Experimental observations of presence or absence of growth and a description of the growth

It was thought that this level of effort would provide a base line from which further studies can be defined or recommended.

A verbal report on this work indicated that no microbial growth in any of the eight samples (used as control samples without inoculation) had occurred after

120 days over Bushnell-Haas solution or over the brine solution from the salt dome. Thus, it is concluded that the fuel samples as received contained essentially no bacteria or fungal spores. Inoculation of the eight individual fuel samples over Bushness-Haas medium, with aerobic strains produced growth in all but one sample. The fuel samples, inoculated with anaerobic sulfate reducers also over Bushness-Haas medium, produced no growth. None of the inoculated samples showed growth over the brine solution. Testing has continued, and further observations will be made available at a later date.

Task 3: Update and Expand Data Base for Crude Oil Characteristic Program

The Army's original "Crude Oil Characterization Data Program"⁽¹²⁾ used crude oil analysis data from the Bureau of Mines [now Department of Energy (DOE)] Bartlesville Energy Technology Center. This crude oil characterization data program enabled its users to search the data base for crude oils with certain characteristics. However, the data for this program contained only 800 crude oil analyses. A project task was initiated in the third quarter of 1978 to establish the data base in the DOE Energy Information Administration's computer facility and to update and expand the data base.

One phase of this task involved comparing the format of the customary Bureau of Mines crude oil assay with the purchase specifications shown in Table 8 currently used by the Strategic Petroleum Reserve Office, and resolving format incompatibilities. This new data base was to include analyses from nearly 3500 samples covering the years 1950 forward.

The basic crude oil data for the program were obtained from the DOE Bartlesville Energy Technology Center's analyses of crude oils for the years 1950 to 1977, some of which have been previously published.^(13,14) These data were transmitted to SPRO and stored in the Energy Information Administration's computer. However, the data in this form were unsuitable for direct search using the SPRO specifications as shown in Table 8. A new file referred to as the SPRO Search File was generated from the BETC file data for use in SPRO crude oil searches.

TABLE 8. CURRENT SPRO CRUDE OIL SPECIFICATIONS

	SPRO Crude Oil Type					
	I	II	III	IV	V	VI
API Gravity (°API)	30-36	40-45	30-36	34-40	36-40	26-30
Total Sulfur (wt%) max	1.99	0.25	0.50	0.25	0.50	1.25
Pour Point (°F) max	50	50	50	50	50	50
Salt Content, (Lb/1000 Bbl) max	50	50	50	50	50	50
Viscosity (SUS @ 60°F) max	150	150	150	150	150	200
Reid Vapor Pressure (psig @ 100°F) max	11	11	11	11	11	11
Mercaptans (ppm in 375°F- 500°F fraction) max	No limit	12	12	12	No limit	12
Yields (vol%)						
Naphtha (< 375°F)	24-30	35-42	21-29	29-36	30-38	15-20
Distillate (375°-620°F)	17-31	21-35	23-37	31-45	19-33	24-27
Gas Oil (620°-1050°F)	26-38	20-34	28-42	20-34	23-37	38-42
Residuum (> 1050°F)	10-19	4-9	7-14	0-5	7-14	15-20
Water and Sediment (vol%) max	1.0	1.0	1.0	1.0	1.0	1.0

The SPRO Search File was organized for each crude oil according to key items listed in Table 9. In generating the SPRO Search File from the BETC crude oil data file, some items are used directly while others must be calculated. Details of the SPRO search file methods used to modify the data from the BETC file and the computer program for converting the BETC data to the SPRO search file data are provided in the "Final Report on Strategic Petroleum Reserve Crude Oil Data Search File Documentation."⁽¹⁵⁾

TABLE 9. SPRO SEARCH FILE ORGANIZATION

Item	Description
A	Sample ID
B	API Gravity at 60°F
C	Weight % Sulfur Content
D	Pour Point, °F
E	SUS Viscosity at 100°F
F	SUS Viscosity at 77°F
G	SUS Viscosity at 60°F
H	Weight % Estimated Asphalt
I	% Naphtha (< 375°F)
J	% Distillate (375°-620°F)
K	% Gas Oil (620°-1050°F)
L	% Residuum (> 1050°F)
M	Location Code
N	Field Name
O	Comment

To search the SPRO crude oil Search File, an individualized SPRO Search Program must be written for each particular crude oil search. The searching of the SPRO file is performed by reading in the data for each crude, rejecting any crude which does not conform to prespecified limits, and storing in a new file any crude which is not rejected.

Task 4: Overall Assessment

The purpose of this task was to integrate the results of the other tasks and report on the overall program. The report would include an overall assessment of crude oil and petroleum product long-term storage experience as well as recommendations on practices associated with proposed future storage of crude and products for the Northeast United States and for noncontiguous areas of the country. Tasks 1, 2, and 3 have been summarized in earlier sections of this report, but are here drawn upon in greater detail and supplemented by additional information to provide an overall assessment.

A. Summary of Crude and Product Storage: State-of-the-Art Review and Assessment

The results obtained in Task 1 were reported in "Final Report on Crude and Product Storage: State-of-the-Art Review and Assessment."⁽⁴⁾ An assessment of long-term storage stability considerations specific to certain petroleum products and crude oil is presented below.

1. Crude Oil Storage

The underground storage of crude oil for extended periods has been practiced in Europe and in South Africa since about 1967. Although no systematic study of the stability of stored crude was found in the literature, an investigation in West Germany has recently been reported.⁽⁶⁾ This study, as well as informal reports from South Africa, indicates that the storage time and conditions have not affected the refinability of the stored crude.

2. Gasoline Storage

Storage stability of gasoline has undergone considerable variation over the years. Initially, the product was a straight run material and very stable. Increased demand caused production of thermally cracked and later catalytically cracked blending stocks which, at first introduction to the market, were unstable in storage. This brought about the development of oxidation inhibitors which stabilized these products and rendered them more acceptable to the market.

More recently, the introduction of various hydrogen refining processes produced more stable gasoline blending stocks. Storing gasoline and light naphthas underground has been practiced in the U.S.; however, oxidation inhibitors are added to the products before storage. Study groups within ASTM and various military specifications cover stability considerations regarding motor gasoline. Storage periods up to 5 years are considered reasonable, provided suitable precautions in handling and storage are observed and the gasoline meets the purchase specifications.

3. Jet Fuels

The storage stability of aircraft turbine fuels or jet fuels has been for some time defined and controlled through existent and accelerated gum tests. Investigations into the effect of storage on various properties have been conducted for many years in the U.S., as well as in other countries. The storage stability of jet fuel is well controlled through the extensive refining needed to meet the stringent requirements placed on jet fuels by various military and civilian specifications, and through the use of antioxidant additives. The high-temperature stability of aircraft jet fuels has been the subject of many investigations because these fuels may be subjected to thermal stresses arising during sustained supersonic flights and in some high-altitude subsonic applications. The storage stability of these high-temperature fuels has been the subject of other investigations. Long-term storage of jet fuels apparently has not been practiced extensively. Several investigations reported in the Russian literature suggest that they may have stored jet fuels in solution-mined salt caverns for prolonged periods. Jet fuels have been stored for limited periods in mined rock caverns in Scandinavian countries with reportedly satisfactory results.

4. Distillate Fuels

Before the advent of cracking processes, and up to about 1946, distillate fuels consisted predominantly of straight run products. Although they were subject to oxidative attack, their stability on the whole was adequate for the demands placed upon them. With the increase in catalytic cracking and greater demand for diesel fuel, both thermal- and catalytic-cracked stocks have been used in distillate fuels, which has greatly increased their susceptibility to oxidation. The oxidative attack results in the formation of soluble and insoluble materials of higher molecular weight and boiling point than the original fuel. This insoluble gum (or sediment) can cause plugging of filters, screens, and nozzles in both diesel and burner installations. The deleterious effects of soluble gums have not yet been well defined, but are believed to be precursors of insoluble gum, and also may form adherent deposits on injector nozzles and piston/cylinder walls.

The storage stability of middle distillates has been the subject of numerous field storage programs in which the determination of the storage life of these fuels was the main object. Some fundamental studies led to the discovery that certain nitrogen compounds that may be present in the distillates contribute significantly to sedimentation. Many of the storage stability investigations led to the development of accelerated stability and predictive tests for the storage of distillate fuels.

Many methods have been proposed and are used by oil companies to ensure the quality of their product. One study conducted by the Navy and reported in 1958 indicated that 26 different procedures have been proposed and/or utilized for predicting storage stability. An active group in ASTM is currently addressing the overall questions of distillate fuel stability and cleanliness.

Special refinery treatment of thermal- and catalytic-cracked stocks has been found to improve distillate fuel stability. The use of antioxidant, metal deactivator, and dispersant additives also are used to improve stability. One company especially interested in long-term storage of fuel intended for use in emergency standby generating equipment recommends the use of a dispersant containing a metal deactivator (but not antioxidants) as the most effective stabilizing package for diesel fuels. Fuel shelf life of up to 20 years is claimed.

If a water-fuel interface exists when the fuel is in storage, bacterial and fungal activity may occur. This activity has been the subject of many investigations, and it is generally agreed that it can best be prevented by good housekeeping practices, such as ensuring a minimum water bottom in the storage container. Certain biocidal additives have been found to be effective in controlling microbiological activity. Storage of distillate fuels over brine may preclude microbial growth because the brine may tend to act as a sterilizing agent.

5. Heavy or Residual Fuel Oils

Instability in residual fuel oils may manifest itself either as waxy sludge deposited at the bottom and sides of an unheated storage tank or as fouling of preheaters while heating the fuel to elevated temperatures. There is much speculation regarding the mechanism of sludge deposition. It may be due to oxidation, polymerization, or the actual method of producing the fuel. Whichever process is involved, insoluble compounds are formed which eventually settle to the tank bottom and form sludge. Asphaltene deposition may result from the mixing of fuels of different origin and treatment. Straight run fuels from the same crude source are normally stable and mutually compatible. Heavy fuels produced from thermal cracking and visbreaking operations can be incompatible if blended with straight run fuels. Blending of No. 2 fuels with residual fuel from cracking or visbreaking processes may result in asphaltene precipitation.

Light residual oils may contain waxy components which will separate if the fuel is stored at cool temperatures for extensive periods. The presence of waxy materials can have deleterious effects on handling of the fuels, thus cloud and pour point limits are generally specified when purchasing these fuels. It has been found, however, that these tests are unsatisfactory for predicting the low-temperature pumpability of these types of fuels. The development of a reliable pumpability test has been a major concern of the British Admiralty since the early fifties. These investigations have culminated in the development of a pumpability method designated IP 230/69. ASTM has also developed a similar method, ASTM D 3245, designed to give the minimum cold storage and minimum handling temperatures which may be used for a given fuel oil.

In 1960, a Swedish company began constructing underground storage caverns in suitable rock formations for use by oil companies and also for use by the governments of Sweden, Finland, France, and other European countries. Various designs are used for these caverns, depending on the material to be stored and whether or not the facility is for refinery operation. If the storage is for crude oil or heavy fuel oil, and especially if it is for reserve storage, then a system for heating the oil, the water bed, or both is incor-

porated into the construction of the storage cavern. To facilitate withdrawal of the oil, the storage temperature in these types of caverns is maintained at 50° to 60°C.

B. Selection of Products for Storage

In the proposed Amendment to the Strategic Petroleum Reserve Plan, it was stated that storage for twenty million barrels of residual fuel oil or substitute refined petroleum products will be provided for the Northeast United States; three million barrels of petroleum (2.3 million barrels of crude and 700,000 barrels of kerosine jet fuel) will be stored in Hawaii; one million, three hundred thousand barrels of petroleum (0.8 million barrels of crude oil and 0.5 million barrels of unfinished naphtha) will be stored in Puerto Rico.

As indicated by the findings of the state-of-the-art assessment, crude oils have reportedly been stored in South Africa for periods of 9 or more years aboveground in metal tanks, and below ground for comparable periods in abandoned coal mines converted into storage caves. Care in selecting generic crudes has reportedly precluded problems, such as solidification due to high pour point or waxy crude, that could have occurred with storage. Underground storage of crudes in Europe is becoming more widespread, but for the most part, the storage periods are not longer than 1 year. In West Germany, crudes have been stored in salt domes since 1971. The results of the KBB study for the Department of Energy indicate that complete mixing of different crude types occurred in one solution-mined cavern in West Germany and no deterioration has occurred in this crude mixture or in a single type crude stored in another solution-mined cavern. In both caverns, a viscous layer containing appreciable quantities of water, sediment, salt, and enriched in trace metals and acid components of crude oils, such as mercaptans and asphaltenes, has developed at the oil/brine interface. This layer, which also contains paraffin wax in greater than normal amounts, comprised only about 0.5 percent of the volume of crude stored in each cavern.

These experiences indicate that strategic storage of crude oil can be successfully accomplished through suitable site technical and crude selection criteria.

Underground storage of selected and inhibited gasolines, kerosine jet fuels, and No. 1 and No. 2 burner/diesel fuels has been practiced in limited cases in this country and in Europe. The Bell Laboratories of Murray Hill, NJ claim long-term storage of kerosine, No. 1 gas turbine, and No. 2 diesel fuels for up to 20 years with proper fuel selection and use of additives.⁽¹⁷⁾ Accelerated tests have been developed to evaluate the fuel storage life effectiveness of inhibitors.⁽¹⁷⁾

It is anticipated that unfinished naphtha can be stored in Puerto Rico in suitable storage vessels, with the proper selection of the naphtha to be stored, and judicious use of inhibitors. A number of accelerated storage tests can be used to select the proper naphtha for storage and evaluate inhibitors for their effectiveness. Acid number, corrosion tendencies, gum, and oxidation stability are some of the properties that should be monitored.

The recommended fuel for storage to supply users of No. 6 fuel along the Northeast United States originally was a hydrotreated vacuum gas oil as stated earlier in this report. An industry recommendation favored a No. 6 fuel labeled as low-pour/high-sulfur residual fuel because of its reported wide availability and ease of handling. At the request of SPRO, Technical Division E on Burner, Diesel and Turbine Fuel Oils of ASTM Committee D2 on Petroleum Products, formed an "Ad Hoc Committee" under Section I on "Burner Fuels" to provide guidance with respect to an acceptable fuel for storage in the Northeast United States. The committee discussed proposed specifications for a No. 4 hydrotreated vacuum gas oil, a low-pour/high-sulfur No. 6 fuel, a low-pour/low-sulfur No. 6 fuel, and a No. 5 light fuel.

The recommendation of the "Ad Hoc Committee" was that a high-sulfur/low-pour No. 6 fuel be regarded as the most practical product for storage in terms of availability, usability, and long-term storage stability.⁽¹⁸⁾ The recommended specifications are shown in Table 10 and are very similar to the low-pour/high-sulfur fuel specification, proposed earlier by an industry group, shown in Table 2.

TABLE 10. PLANNING ASSUMPTION LIMITS FOR RESIDUAL FUEL OIL
FOR STORAGE IN A REGIONAL RESERVE

Properties	High-Sulfur/Low-Pour Fuel Oil
Grade (ASTM)	6
Specific Gravity, 60/60°F (°API)	0.910-0.993 (11-24)
Saybolt Viscosity	
Universal at 38°C (100°F)	---
Furol at 50°C (122°F)	(50-250)*
Kinematic Viscosity, cSt	
at 38°C (100°F)	---
at 50°C (122°F)	(103-530)
Flash Point, °C(°F), min	66(150)
Pour Point, °C(°F), max	16(60)
Ash, wt%, max	0.1
Water and Sediment, by Centrifuge, vol%, max	1.0
or:	
Water by Distillation, vol%, max	1.0
and:	
Sediment by Extraction, wt%, max	0.1
Sulfur, wt%, max	2.7
Compatibility Rating (D 2781), max	2
Ramsbottom Carbon Residue, wt%, max	15
Asphaltenes (IP 143), wt%, max	15
Additives	None

* For oils having a viscosity of 250 SFS, it will be necessary to heat them to between 92° and 128°F for easy pumping.

C. Assessment of Residual Fuel Storage Stability

In the early days of the petroleum industry, residual fuel oils consisted of the residue remaining after removal of the lighter components (gasoline, kerosine, and gas oil) during atmospheric fractionation of the crude oil. The increase in demand for gasoline and lighter fractions resulted in the development of various cracking and other refinery processes. The residues and viscous byproducts from these processes are combined to make up residual fuel oils. Thus, instead of residual fuel oils today being simply the residue remaining after removal of the lighter products, they are the result of selective blending of the various residues and distillate cutter stocks to produce fuels suitable for a wide range of industrial applications. The characteristics

of these fuels depend largely upon the crude oil sources, refinery crude cracking capability, and resulting composition of the blend stocks.

Instability in residual fuels is manifested by waxy sludge deposits at the bottom of unheated storage tanks, or by fouling of preheaters when heating the fuel to elevated temperatures. Speculation on the mechanisms of sludge formation range from oxidation/polymerization to the actual method of manufacturing the fuel. Nevertheless, the consequences are formation of insoluble materials which settle to the bottom of the container as sludge. Mixing of fuels from different origins such as straight run distillate and residuals from cracking or visbreaking may result in asphaltene precipitation or formation of other deleterious products.

As indicated above, a number of problems can be associated with storage and use of residual fuel oils, and a wide variety of additives are available to reduce these problems.⁽¹⁹⁾ To be completely effective, the additives should (1) inhibit, disperse, and prevent sludge agglomeration, (2) prevent corrosion in fuel-handling systems, (3) demulsify water, (4) improve combustion and reduce ash or slag formation, (5) present no safety hazard, and (6) be entirely compatible with the fuel oil. Dispersant-type additives appear to be effective in improving stability during storage at normal temperatures. Such additives tend to keep sludge and sediment dispersed so that they do not accumulate in storage tanks and necessitate frequent cleaning. Some surface-active dispersant additives also have the ability to inhibit corrosion. Some corrosion inhibitors are alkaline and will neutralize acids present in the fuel.

Experience in storing residual fuels for extended periods (six months or longer) has been reported in Europe. In the United Kingdom, the Royal Navy is required to maintain large stocks of fuel oil which are stored for long periods in unheated tanks. The fuel may have to be pumped cold and the long period of unheated storage may have induced the formation of gel structures which cause pumping problems. The Admiralty fuels are made up by blending heavy residue with a distillate fraction; when in storage for long periods, they tend to develop a structure of wax miscelles, asphaltenes, or resins, which can be broken down by shearing. Investigation into these problems led to the development of a pumpability test which has been designated IP 230/69.

Construction of storage caverns in rock formations by a Swedish company for crude oil or residual fuel oil in the 1960's included systems for heating the oil to about 50° or 60°C to facilitate withdrawal.

Thus, it appears that the major problem to be encountered by storing residual fuel in underground caverns will be separation of wax and/or sediment. This separation can be overcome by supplying heat to the fuel as it is withdrawn. The low-pour/high-sulfur fuel proposed as the product to be stored in the Northeast U.S. has a maximum pour point of 16°C (Table 10). This material probably will have to be heated at the point and time of withdrawal.

D. Procurement Specifications

The naphtha proposed to be stored in Puerto Rico is intended for use by its petrochemical industry in the event of a supply interruption. The procurement specifications for the naphtha, therefore, should be dictated by the requirements of the industry and the type of containerization/handling equipment to be used for storage.

Kerosine jet fuel for storage in Hawaii should meet the requirements of ANSI/ASTM D 1655 Standard Specification for Aviation Turbine Fuels, Jet A and should be maintained in "active" storage under the supervision of the user airport authorities. A fuel storage and handling system patterned after those in use at O'Hare and JFK International Airports should be considered.

The ASTM "Ad Hoc Committee" from Technical Division E has recommended the selection of a low-pour/high-sulfur No. 6 residual fuel oil for regional storage. This recommendation is based on the relative availability of this fuel and the fact that all users of No. 6 fuel can make use of this product without the necessity of changing pumping equipment. The few users of lighter fuels such as No. 4 could also use a No. 6 fuel oil provided it is blended with a No. 2 fuel to reduce the viscosity. The high-sulfur level of this industry-recommended fuel is of concern because of environmental considerations, but could possibly be tolerated in the event of a fuel shortage emergency.

E. Periodic Monitoring of Stored Fuels

If regional and noncontiguous storage in the strategic petroleum reserve plan is implemented, the products in storage should be monitored by selected quality assurance tests, including accelerated aging tests for naphtha and kerosine jet fuels, and sedimentation tendency tests for residual or heavy distillate fuels. These tests should be performed at least annually, and the purchase specifications should reflect the same tests.

Should quality testing data indicate that products in storage are deteriorating, provisions should be made for turnover of the product within a six-month period by using the fuel directly or by blending and replacement with fresh fuel.

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APPENDIX A
TENTATIVE METHOD FOR MEASURING THE SEDIMENTATION
TENDENCIES OF BURNER FUEL OILS

1. SCOPE

1.1 This method describes a procedure for measuring the sedimentation tendencies of burner fuels using a high speed centrifuge. The method also describes a means of estimating the real time expected for formation of the same percentage of sediment found by centrifugation.

2. SUMMARY OF METHOD

2.1 Measured amounts of sample are added to preweighed centrifuge tubes which are then spun at a speed ranging from 7500 to 15,000 rpm, for periods of time from 15 to 240 minutes. The supernatant fuel is then removed from the sediment by aspiration. The sediment is washed first with n-heptane, dried and weighed, then washed with toluene, and dried and weighed again. The n-heptane-insoluble and toluene-insoluble sediments are determined in this manner for test times of 15, 30, 60, 120, and 240 minutes. The centrifuge time to form a given amount of sediment can be mathematically converted to an estimated real time in terms of weeks.

3. APPARATUS

3.1 Ten glass centrifuge tubes (30 ml), ten rubber jackets for tubes, high-speed centrifuge (speeds up to 20,000 rpm), n-heptane--99% pure grade, toluene--reagent grade, desiccator, balance--sensitive to 0.1 mg, water aspiration apparatus (Figure 1), and a stirring rod made of tetrafluoro ethylene and fluoronated ethylpropylene resins

4. TEST PROCEDURE

4.1 Weigh ten clean, dry centrifuge tubes to 0.1 mg and add 10 g (to nearest 0.1 mg) of fuel oil sample to each tube. The samples are divided into five sets of two tubes each. Each two-tube set is then subjected to an initial

spin of either 15, 30, 60, 120, or 240 minutes at the predetermined centrifuge speed. Then aspirate the resulting supernatant liquid from the tubes using a water aspiration apparatus (Figure 1).

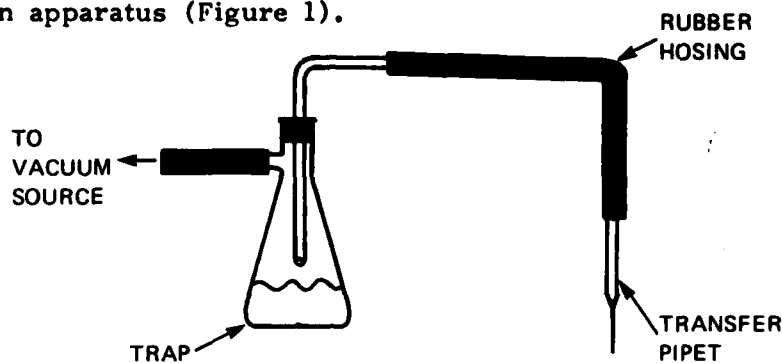


FIGURE 1. WATER ASPIRATION APPARATUS

Wash the remaining sediment with 15 ml of *n*-heptane, mixing thoroughly with the stirring rod. Then spin all tubes for 0.5 hour at the same predetermined speed. Again, aspirate the supernatant liquid and repeat the *n*-heptane wash. Remove excess heptane from the tubes by blowing with air. Place the tubes in an oven and dry for 1 hour at 90°C. Remove the tubes from the oven with forceps and place in a desiccator. Allow to cool for 1 hour and then weigh to the nearest 0.1 mg. Record the weight of the *n*-heptane insolubles. Table 1 gives a schedule for spinning the tubes and washing the

TABLE 1. TIME INTERVALS FOR CENTRIFUGING AND WASHING
FUEL OIL SAMPLES FOR A FIVE-TIME INTERVAL
STEPPED SEDIMENTATION DETERMINATION

Test Time Interval	Procedure*
0 min	Place tubes into centrifuge
15 min	Wash and replace tubes 1 and 2
30 min	Wash and replace tubes 3 and 4
45 min	Wash and replace 1 and 2
60 min	Wash and replace 3, 4, 5, and 6
75 min	Remove 1 and 2 for drying and weighing,
90 min	Remove 3 and 4 for drying and weighing, wash and replace 5 and 6
120 min	Remove 5 and 6 for drying and weighing, wash and replace 7 and 8
150 min	Wash and replace 7 and 8
180 min	Remove 7 and 8
240 min	Wash and replace 9 and 10
270 min	Wash and replace 9 and 10
300 min	Remove 9 and 10 for drying and weighing

* Wash with *n*-heptane

sediment with n-heptane. Perform the same washing procedure three times with toluene, each time drying and weighing the tubes, and recording the toluene insolubles. It must be emphasized that the tubes should not be touched after being in the oven because of the critical weight measurement. As a result, the use of forceps in handling the tubes is imperative.

5. PERCENT SEDIMENT CALCULATION

5.1 Sediment weight = (weight of tube + sediment) - initial weight of tube.

5.2 Percent sediment = (sediment weight/sample weight) x 100.

6. CONVERSION TO REAL TIME

6.1 The following formula is used to estimate the amount of sediment that will settle out of a given burner fuel oil during storage at room temperature for a given period of time. With use of the high-speed centrifuge, any desired period of real time may be simulated. As a result, the amount of sedimentation over that period of time may be estimated.

6.2 Real time in months = (RCF)(centrifugation time in hours)

6.3 Relative centrifugal force (RCF) can be calculated as follows:

$$RCF = W^2 r / 980$$

where:

W = rev/min x 2 π /60 = rev/min x 0.10472

r = radius of rotor, cm

980 = constant force of gravity

7. GENERAL REMARKS

7.1 Because of the low amount of sediment in many fuels (especially the No. 4 fuel oils), small weighing or handling errors may lead to relatively large discrepancies in calculated weight percent sediment values.

7.2 Also, this procedure does not measure any molecular stratification of the fuel that may occur. This stratification may lead to a different sedimentation tendency.

7.3 Preliminary investigations have shown that three washings with the given solvent (either the n-heptane or the toluene) are generally sufficient to dissolve all material that is soluble in that solvent. However, the more viscous No. 6 fuels may require as many as five washings (especially with the toluene) to remove all soluble material. The color of the solvent will indicate when the soluble material is removed.

7.4 These more viscous fuels generally have to be heated to 45°-60°C to ensure a homogeneous sample. If it is necessary to heat the samples to obtain a homogeneous mixture, do so. Then pour approximately 10g of solution into the centrifuge tube and weigh the tube after the sample has cooled to ambient temperature.

7.5 In the initial aspiration procedure, it is difficult not only to remove the supernatant liquid of these high-viscosity samples, but also to be certain that only supernatant, and not sediment, is being removed.

APPENDIX B
METHOD FOR QUANTITATIVELY DETERMINING PARTICULATE AND
ASPHALTENE-LIKE CONTAMINATION OF FUEL OIL

1. SCOPE

1.1 This method* describes a quantitative procedure to determine particulate and asphaltene-like contamination of fuel oil by laboratory filtration. This procedure is also used to pretreat fuel oil samples for removal of particulates and asphaltene-like contamination when such material would interfere with subsequent analysis.

2. SUMMARY OF METHOD

2.1 A known amount of solvent-diluted fuel oil is filtered through pre-weighed test and control filters. The weight of the asphaltene-like material is determined by rinsing the filter papers with an aromatic solvent into a pre-weighed flask and removing the solvent. The flask is then weighed, and the difference between the initial and final weights is the weight of the asphaltene-like material. The particulate contamination is determined by the increase in weight of the test filter in relation to the control filter. In this method, three filter sets of different porosity are used. Unless some of the coarser and gelatinous material is removed with a previous, less porous filter, the material found in fuel oil will usually clog a fine-porosity filter.

3. APPARATUS

3.1 Apparatus for Determining Particulate Contamination

Analytical balance, single or double pan, with a precision standard deviation of 0.07 mg or better; laboratory balance, single or double pan, with a capacity of 1000 g and weights readable to ± 0.01 g; oven, of the static type

* Portions of this method are from ASTM D 2276, Particulate Contaminant in Aviation Turbine Fuels.

(without fan-assisted air circulation), controllable to $90^{\circ} \pm 5^{\circ}\text{C}$; petri dishes, approximately 125 mm in diameter; forceps, flat bladed with unserrated, nonpoint tips; separatory funnel, 125 ml, tetrafluoro ethylene stopcock; vacuum system; test filters, a plain 7-cm diameter Whatman No. 41, a plain 7-cm diameter Whatman No. 42, a plain 47-mm diameter membrane filter with a nominal pore size of 0.45 micrometer (Millipore-type MF cellulose-acetate, cellulose-nitrate); control filters, same as test filters; funnel, Buchner, porcelain, with minimum interior diameter of 72 mm with rubber stopper to fit a 1000-ml filtering flask; analytical filter holder, with stainless steel screen filter support (Millipore catalog No. XX10-047-30); flask, filtering, 1000-ml capacity; and graduated mixing cylinder, stoppered, 100-ml capacity.

3.2 Additional Apparatus Required for Determining Asphaltene-Like Contaminant

Flasks, round-bottom type with 24/40 ground joint, various sizes; and evaporator, rotating vacuum, flask.

4. REAGENTS

4.1 n-heptane, 99 percent pure, filtered through a filter of 0.45-micrometer nominal pore size.

4.2 Toluene, reagent grade, filtered through a filter of 0.45-micrometer nominal pore size.

5. PREPARATION OF APPARATUS

5.1 Preparation of Petri Dishes

Wash the petri dishes and supports with warm detergent water. Rinse first with clean warm water and then with deionized water. Then rinse thoroughly with filtered isopropyl alcohol followed by a thorough rinse with filtered (4.2) n-heptane. Drain for a few seconds, then air or oven dry.

5.2 Preparation of Other Laboratory Glassware

Wash the glassware with warm detergent water. Rinse first with warm clean water and then with deionized water. Alternatively, if the funnels or glass-

ware appear clean, soak them overnight in a water solution of critical laboratory cleaner. Afterwards, rinse with warm water and then with deionized water. Oven dry the funnels and glassware and rinse them thoroughly with filtered n-heptane. Then air dry funnels and glassware in a location where airborne particulate matter cannot contaminate them.

5.3 Preparation of Filters

Using forceps, place the test and control membrane filters side by side in a clean petri dish. To facilitate handling, the membrane filters should rest on clean glass support rods in the petri dish. Place the petri dish, with its lid slightly ajar, in an oven at $90^{\circ} \pm 5^{\circ}\text{C}$ for 30 minutes. Remove the petri dish from the oven and place it near the balance. The petri dish cover should be ajar, but still protecting the membrane filters from airborne particulate contamination. Allow 30 minutes for the membrane filters to equilibrate with the ambient air temperature and humidity. Then remove the control membrane filter, handling by the edge only, from the petri dish with forceps, and center it on the weighing pan. Weigh the filter and return it to the petri dish. Record the weight of the filter. Repeat this step for the test membrane filter.

5.4 Preparation of Flasks

Dry a clean round-bottom flask in an oven at $90^{\circ} \pm 5^{\circ}\text{C}$ for 30 minutes. Allow the flask to cool to ambient temperature and humidity near the balance for 30 minutes. Then, using clean forceps to move the flask, weigh the flask and record the weight. Repeat drying procedure until two succeeding weighings give the same weight.

6. PREPARATION OF SAMPLE

Note 1: The fuel sample should be taken from its original container at a temperature high enough to have melted or dissolved all the wax-like material in the fuel oil. The sample must also have been sufficiently agitated and/or heated to ensure that the asphaltene-like material is suspended or dissolved and the sample is homogeneous.

6.1 The clean, stoppered, graduated cylinder is weighed to the nearest 0.01 g. Approximately 25 g of homogeneous sample (hot if necessary) are

introduced into the cylinder. The cylinder is allowed to cool to ambient temperature (if sample was heated), and the weight of the cylinder plus fuel oil is recorded to the nearest 0.01 g.

7. PREPARATION OF FILTRATION SOLUTION

7.1 Dissolve the 25 g of fuel in enough filtered n-heptane to prepare 100 ml of solution. Shake the solution vigorously with stopper in place.

8. PROCEDURE

8.1 Determination of Particulate Contamination and Collection of Asphaltene-Like Material

Removal of large crystalline and gelatinous precipitates--Place the preweighed, control and test, 7-cm Whatman No. 1 filter papers in the clean Buchner filtering apparatus (control filter in first). Apply vacuum to the apparatus. Using a clean separatory funnel, allow the n-heptane/fuel oil solution to drip slowly onto the filter papers. Maintain the solution addition at a rate slow enough to prevent the fuel from flowing to the edge of the filter paper, but fast enough to perform the analysis in a reasonable time. After all the solution has been filtered, remove and retain the filtrate. Rinse with filtered n-heptane the sample storage container (graduated mixing cylinder and stopper), the separatory funnel, Buchner funnel, and the filters. Store the added n-heptane rinse separate from the fuel/solvent filtrate. Rinse the filter with filtered toluene to remove the asphaltene-like precipitation. Continue to rinse until the toluene coming through the filter is clear. Temporarily hold the toluene filtrate in a preweighed round-bottom flask or other suitable clean container. After removing the filters from the funnel, dry and weigh them.

Removal of fine crystalline precipitates--Place the preweighed, control and test, 7-cm Whatman No. 42 filter papers in the clean Buchner filtering apparatus (control filter in first). Apply vacuum to the apparatus. With a clean separatory funnel, slowly add the n-heptane/fuel oil solution filtered previously to the filter papers. Add the solution at a rate slow enough to

prevent fuel from flowing to the edge of the filter paper, but fast enough to perform the analysis in a reasonable time. Continue adding the solution until it has all been filtered. Remove and save the filtrate. Filter the n-heptane rinse solution from above. Rinse the container. Rinse with filtered n-heptane the sample storage container, the separatory funnel, Buchner funnel, and filters. Retain the combined added n-heptane rinse and previous n-heptane rinse solution separate from the fuel/solvent filtrate. Rinse the filter with filtered toluene to remove the asphaltene-like precipitation. Continue to rinse until the toluene coming through the filter is clear. Combine this toluene filtrate and the previous toluene filtrate in the preweighed round-bottom flask or other suitable clean temporary container. Remove the filters from the funnel, and dry and weigh them.

Removal of very fine crystalline precipitates--Place the preweighed, control and test, 0.45-micrometer membrane filter papers in the analytical filter holder (control filter in first). Add the n-heptane/fuel oil solution from the above step to the filter funnel. Apply vacuum to the apparatus and filter the solution. Remove and retain the filtrate. Filter the n-heptane rinse solution from the above step. Rinse the container. Rinse with filtered n-heptane the sample storage container, Buchner funnel, and filters. While applying vacuum, remove the filter funnel. Rinse the surface of the funnel that touched the filter with filtered n-heptane, allowing the solvent to flow through the filters. Rinse the edge of the filters sufficiently to remove any fuel that may have soaked into that part of the filters. Once dried (by vacuum), replace the funnel with the vacuum on. Save the combined added n-heptane rinse and previous n-heptane rinse solution separate from the fuel/solvent filtrate. This solution may be used in another procedure at a later time. Save both solutions. Rinse the filter with filtered toluene to remove the asphaltene-like precipitation. Continue to rinse until the toluene coming through the filter is clear. While applying vacuum, remove the filter funnel. Rinse the surface of the funnel that touched the filters with filtered toluene, allowing the solvent to flow through the filters. Rinse the edge of the filters sufficiently to remove any material that may have soaked into that part of the filters. Dry these filters by vacuum. Remove the filters from the filter support, dry and weigh them. Combine this toluene filtrate and the previous toluene filtrate in the preweighed round-bottom flask or other temporary clean suitable container used in the previous step.

8.2 Determination of Asphaltene-Like Contamination

Evaporate the solvent from the toluene filtrate in the preweighed round-bottom flask on an evaporator. If there is more filtrate than the flask can safely accommodate, flash off some of the solvent, add more of the filtrate solution, and flash off more solvent. Repeat as necessary. After all the solvent is evaporated, reweigh the flask as described in 5.4. Save the dried precipitate in the flask in a suitable container.

9. CALCULATION AND REPORT

9.1 Calculation of Particulate Contamination on Each Filter Type

For each filter set, determine the particulates as follows:

$$P = (T_f - T_i) - (C_f - C_i)$$

where

P = particulate weight, mg

T_f = final test filter weight, mg

T_i = initial test filter weight, mg

C_f = final control filter weight, mg

C_i = initial control filter weight, mg

Express the particulate weight as mg particulate per 25 g of sample as follows:

$$M = PG/W$$

where

M = mg particulates/25 g

P = particulate weight in mg (from above)

G = 25 g

W = actual weight of fuel oil analyzed in g

9.2 Calculation of Total Particulate Contamination

For all filter sets, determine the total mg particulate as follows:

$$T = M_1 + M_2 + M_3$$

where

T = total mg particulates per 25-g sample obtained on all filters

M_1 = mg particulates per 25-g sample obtained on the Whatman No. 41 filter

M_2 = mg particulates per 25-g sample obtained on the Whatman No. 42 filter

M_3 = mg particulates per 25-g sample obtained on the 0.45-micrometer membrane filter.

9.3 Calculation of Total Asphaltene-Like Material

For the round-bottom flask, determine the total asphaltene-like contaminant as follows:

$$D = G(F-I)$$

where

D = total asphaltene-like contaminant, mg

F = final weight of round-bottom flask plus contaminant, g

I = initial weight of clean round-bottom flask, g

G = 1000 mg/g

D = Total asphaltene-like contaminant in milligrams

Reduce the total asphaltene-like contaminant to mg per 25-g sample as follows:

$$M = DG/W$$

where

M = mg asphaltene-like contaminant or 25-g sample

D = total asphaltene-like contaminant in mg (from above)

G = 25 g

W = actual weight of fuel oil analyzed in grams

APPENDIX C
METHOD FOR QUANTITATIVELY DETERMINING FREE WAX
IN RESIDUAL FUEL OILS BY FILTRATION

1. SCOPE

1.1 This method describes a procedure for quantitatively determining filterable free-wax content in residual fuel oils by laboratory filtration at a specified temperature. This method approximates the amount of wax-like material that may precipitate from fuel oil. Generally, this wax-like material is predominantly n-saturate paraffins, but other fuel components may also be deposited with the filterable free wax. The temperature at which the filtration occurs allows determination of filterable free wax at that specified temperature. This procedure will determine a temperature at which the fuel oil could be pumped with minimal problems from wax clogging.

2. SUMMARY OF METHOD

2.1 A known amount of prefiltered fuel oil* is filtered through a jacketed filter funnel with a coarse porosity fritted glass filter at a specified temperature. The filter funnel is then cooled to 0°C. The funnel is rinsed with a fuel solvent, also maintained at 0°C, to remove any fuel remnants. The filter funnel is then warmed to room temperature, and the wax crystals are rinsed off with warmed heptane.

2.2 The heptane solution is placed in a preweighed round-bottom flask, the solvent is removed, and the weight difference is the free wax content.

3. DEFINITIONS

Filterable Free Wax--The filterable wax-like material containing n-paraffins and other fuel components that precipitate from fuel oil.

* Refer to the procedure entitled "Method for Quantitatively Determining Particulate and Asphaltene-Like Contamination of Fuel Oil".

Fuel-Dissolving Solvent--A solvent which dissolves excess fuel trapped on the filter as the fuel recedes from the filter, but dissolves very little of the filtered free wax.

Specified Temperature--The temperature at which the fuel oil is filtered.

4. APPARATUS

4.1 Analytical balance, single or double pan, with a precision standard deviation of 0.07 mg or better; laboratory balance, single or double pan, with a minimum capacity of 100 g and weights readable to ± 0.01 g; oven, of the static type (without fan-assisted air circulation), controllable to $90^{\circ} \pm 5^{\circ}\text{C}$; vacuum system, water aspirator and mechanical; flask, filtering, 250-, 500-, or 1000-ml capacity; flasks, round-bottom type with 24/40 ground joint, various sizes; evaporator, rotating vacuum, flash; filter funnel, Buchner, glass, jacketed (with inlet and outlet for water cooling or heating) with a fused-in coarse-porosity fritted glass disc, 60-ml capacity with rubber stopper to fit filtering flask; separatory funnel, cylindrical, jacketed (with inlet and outlet for water cooling or heating) with tetrafluoro ethylene stopcock, 125, 250, or 500 ml; circulating water bath and associated tubing, must provide water with temperatures ranging from 0° to 65°C ; cold-finger condenser; and dewar flask.

5. REAGENTS

5.1 n-heptane, 99 percent pure, filtered through a filter of 0.45-micrometer nominal pore size.

5.2 Fuel-dissolving solvent, composed of 10 vol% reagent grade toluene and 90 vol% reagent grade acetone.

6. PREPARATION OF APPARATUS

6.1 Preparation of Funnels and Laboratory Glassware for the Unfiltered Fuel
The jacketed separatory funnel, jacketed fritted glass filter funnel, and associated glassware should be clean and free of adherent particulate matter.

Wash the glassware with warm detergent water. Then rinse with warm water and finally deionized water. If the funnels or glassware appear clean, soak in a water solution of critical laboratory cleaner overnight. Then rinse with warm water and finally deionized water. Oven dry funnels and glassware.

6.2 Preparation of Flasks

Dry a clean round-bottom flask in an oven maintained at $90^{\circ} \pm 5^{\circ}\text{C}$ for 30 minutes. Place the flask near the balance, handling with clean forceps, and allow to cool for 30 minutes. After cooling, again using clean forceps, weigh the flask and record the weight. Repeat the drying procedure as necessary until two succeeding flask weights are the same.

7. PREPARATION OF THE SAMPLE

7.1 If the original fuel oil sample is filterable and asphaltene-like/particulate contamination is not a factor, omit step 7.2.

7.2 Treat the fuel oil by the procedure given in "Method for Quantitatively Determining Particulate and Asphaltene-Like Contamination of Fuel Oil". Reduce heptane rinse solution in a round-bottom flask on a rotary evaporator. Reduce the fuel oil/solvent solution in the same round-bottom flask on a rotary evaporator. To remove the last traces of solvent, switch the rotary evaporator to mechanical vacuum pump with a cold-finger condenser cooled by liquid nitrogen or dry ice-alcohol in a dewar flask.

Note 1: The sample should be taken from the fuel oil at a temperature such that all the wax-like material is dissolved. The sample must also be sufficiently agitated and/or heated so that the asphaltene-like material (if present) is suspended or dissolved.

7.3 The clean, jacketed, separatory funnel is weighed to ± 0.01 g. Approximately 25 g of homogeneous sample is introduced to the separatory funnel. The funnel is allowed to cool to ambient temperature (if sample was heated), and the weight of the separatory funnel plus fuel oil is recorded to ± 0.01 g.

8. PROCEDURE

8.1 Set up the circulating bath so that the coolant will pass through both the jacketed filter funnel and the jacketed separatory funnel. Raise the temperature of the circulating bath to the fuel oil homogeneity temperature and allow the sample to flow within the separatory funnel and reach equilibrium temperature. This step may be omitted if the homogeneity temperature of the sample is room temperature or lower. Adjust the temperature of the circulating bath to the specified temperature for the analysis. After the bath and fuel oil sample reach equilibrium with the specified temperature, turn on the vacuum source on the filter funnel to begin transferring fuel oil from the separatory funnel into the filter funnel. After all fuel oil has passed through the filter funnel, discontinue the vacuum and lower the temperature of the circulating bath to 0°C.

Note 2: Ensure that condensation does not collect in the filter funnel. It may suffice to place a large watch glass over the filter funnel opening.

8.2 After the bath has reached equilibrium, rinse the separatory funnel and the filter funnel with fuel-dissolving solvent that has been precooled to 0°C. Use sufficient solvent to dissolve any adhering fuel from both the separatory funnel and the filter funnel. Remove the fuel oil and solvent from the filtering flask and clean the flask with solvent. Raise the circulating water bath temperature to 65°C. After the bath reaches equilibrium, rinse the separatory funnel and the filter funnel with filtered n-heptane, preheated to 65°C, to dissolve the filtered free wax crystals. Collect the n-heptane/wax solution and transfer it to a round-bottom flask. Remove the solvent with an evaporator from the n-heptane/wax filtrate in the preweighed round-bottom flask. If the flask cannot safely accommodate all the filtrate, flash off some of the solvent, add more of the filtrate solution, then flash off more solvent. Repeat as necessary. After all the solvent has been removed, reweigh the flask as described in 8.1.

9. CALCULATION AND REPORT

9.1 Calculate percent filtered free wax as follows:

$$D = [(F_f - F_i) / (S_f - S_i)] \times 100$$

where

D = percent filtered free wax

F_f = final weight of round-bottom flask with filtered free wax, g

F_i = initial weight of clean round-bottom flask, g

S_f = final weight of separatory funnel with sample, g

S_i = initial weight of clean separatory funnel, g

Report percent filtered free wax.

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SUPPLEMENTAR

INFORMATION

20 October 1980

ERRATA SHEET

AD-A082365

Report Title: Final Report on Assessment of Crude Oil and Refined Petroleum Product Quality During Long-Term Storage

Report No.: Ad No. A082365; AFLRL Report No. 121

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Please make the following corrections on the above mentioned report.

<u>Page No.</u>	<u>Correction</u>
19	Change ash values for Fuels 8281, 8508, and 8513 from 9.3 to 0.032; 4.1 to 0.025; and 7.5 to 0.026, respectively.
20	In first paragraph at top of page, delete last sentence beginning, "Samples AL-8281-F...".
30	In sixth line of page, change spelling of Bushness-Hass to medium to Bushnell-Hass medium.