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Recycled Oil Program: Phase I - Test Procedures for Recycled Oil Used as Burner Fuel

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Office of Recycled Materials
National Measurement Laboratory
National Bureau of Standards
Washington, DC 20234

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Report to the
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U.S. DEPARTMENT OF COMMERCE, Juanita M. Kreps, ***Secretary***
Jordan J. Baruch, ***Assistant Secretary for Science and Technology***
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, ***Director***

Abstract

The Energy Policy and Conservation Act requires the National Bureau of Standards (NBS) to develop test procedures which can be used to establish the "substantial equivalence" of recycled oils with new oils. This report covers the first phase of the NBS program, and contains test procedures which may be used for establishing the substantial equivalency of recycled petroleum oils (including blends of recycled oils with new oils) to new oils for use as a burner fuel. Test procedures were selected and evaluated for their ability to reliably measure the property under test.

Key words: Fuel oil; petroleum standards; petroleum test methods; recycled burner fuel oil; substantial equivalency; used oil; waste oil.

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Executive Summary

This report was prepared in response to the Energy Policy and Conservation Act (EPCA, Public Law 94-163; 42 U.S.C. 6201 et seq.). Section 383(c) of this law requires the National Bureau of Standards (NBS) to "...develop test procedures for the determination of substantial equivalency of re-refined or otherwise processed used oil or blend of oil... with new oil for a particular end use." It also requires that after development of these test procedures they be reported to the Federal Trade Commission.

This report covers the first phase of the NBS program, and the purpose of this report is to provide a set of evaluated test procedures which may be applied to a recycled oil to establish its substantial equivalency to a new oil for the specific end use as a burner fuel. For the purposes of this report, the term "substantially equivalent" (as used in the EPCA) has been taken to mean equal performance of the oil with respect to the important operational parameters concerned with this particular end use.

The NBS program plan has been (a) to review existing burner fuel oil specifications and test procedures and, utilizing available information and data on used and recycled oils, identify the properties of recycled oils which are related to the important operational parameters; (b) to evaluate the existing test procedures for these properties; and (c) to develop new or modified test procedures where required. To the maximum extent possible, existing test methods are utilized and the simplest method employed, consistent with obtaining the required results.

Fuel oils found in commerce exhibit a range of values for each specified property, as do the recycled oils which may be used separately or blended with them. Used petroleum oils recycled for use as burner fuel oils are obtained from a variety of sources. Examples of such sources include automobile garages and service stations, truck and taxi fleets, military installations, industrial plants and manufacturing facilities of all types, and waste water treatment plants. Indications are that at the present time much of the used oil recycled as fuel receives minimal processing to remove contaminants. These contaminants may be of concern for either operational or environmental considerations.

The important properties of a burner fuel oil are controlled through the use of specifications of which two, the American

Society for Testing and Materials (ASTM) Specifications D 396-76 and the Federal Specification VV-F-815C, are the primary specifications in current use. These specifications are discussed further in the body of this report, and include test procedures which are designed to evaluate the significant and important properties of the fuel as these properties are related to operational performance. The primary objective of these tests is to assure that the consumer receives a product of consistent and satisfactory quality for the purpose intended.

The test procedures called for in specifications for new burner fuel oils have been developed over a considerable period of time, in response to the specific problems and needs of various industries and users. Because the test procedures which are contained in the ASTM D 396 Specification were those believed by ASTM to be of greatest significance in determining the performance characteristics of the oils for the types of burners in which they are most commonly used, this group of test procedures served as a starting point for the NBS investigation. The NBS evaluation of specific test procedures was made using the following evaluation process:

1. Determination of those properties for which recycled oils used for fuel should be tested.
    a. Based on virgin fuel oil specifications (ASTM and Federal).
    b. Based on information and data from external publications and sources.
2. Preliminary review of the test procedures on the basis of established physical and chemical principles by a scientist knowledgeable in the technical area which the test encompassed.
3. Preliminary selection of most appropriate test procedure from those tests available.
4. Experimental evaluation of the test to establish whether it was capable of reliably measuring the property under test. This evaluation included one or more of the following:
    a. Verification of the performability of the test by evaluating the repeatability with a variety of recycled and used oils and, where appropriate, blends of used oils with virgin fuel oils.
    b. Examination of the effects of known recycled oil impurities on the performability of the test where these effects were significant.

   c. Establishing the ability of the test procedure to provide the correct or "true" concentrations for those tests which measure impurity levels.

5. Development of new test procedures or modification of existing tests where necessary to provide an acceptable test procedure to measure the desired property.

6. Final selection of the evaluated test procedure.

The test procedures contained in this report have been separated into four general groups: sampling, bulk properties, impurities, and impurities of potential environmental concern. The section on sampling contains a procedure for providing a representative sample needed for each of the ensuing test procedures, and a recommendation for the evaluation of homogeneity of the bulk lot. The second section contains test procedures for the bulk properties of flash point, pour point, distillation temperature, viscosity, density, copper corrosion, aniline point, and heating values. The third section contains test procedures for determining various impurities in a recycled oil: water and sediment, carbon residue, ash, total sulfur, and acidity. The final section contains test procedures for impurities having potential environmental concern. It includes lead, polynuclear aromatic hydrocarbons, and two of the halogens (chlorine and bromine).

The test procedures listed above are described in the report, with citation of the most recent publication of the complete procedure, and include a detailed description of any necessary modifications. They have been evaluated for recycled oil which is to be used as burner fuel oil. These tests are capable of establishing the "substantial equivalence" of such recycled oils to virgin burner fuel oils for purposes of operational performance.

TEST PROCEDURES FOR RECYCLED OIL USED AS BURNER FUEL

1. Introduction

This report was prepared in response to the Energy Policy and Conservation Act (EPCA, Public Law 94-163; 42 U.S.C. 6201 et seq.). Section 383(c) of this law requires the National Bureau of Standards (NBS) to "...develop test procedures for the determination of substantial equivalency of re-refined or otherwise processed used oil or blend of oil...with new oil for a particular end use." It also requires that after development of these test procedures they be reported to the Federal Trade Commission (FTC). A copy of this section of the EPCA is included as Appendix A. This report covers the first phase of the NBS program and contains test procedures which may be used for establishing the substantial equivalency of recycled petroleum oils (including blends of recycled oils with new oils) to new oils for use as a burner fuel.

The following definitions are taken from the EPCA and are adopted for this report:

> "(1) the term 'used oil' means any oil which has been refined from crude oil, has been used, and as a result of such use has been contaminated by physical or chemical impurities.
>
> (2) The term 'recycled oil' means
>
> (A) used oil from which physical and chemical contaminants acquired through use have been removed by re-refining or other processing, or
>
> (B) any blend of oil, consisting of such re-refined or otherwise processed used oil and new oil or additives,
>
> with respect to which the manufacturer has determined, pursuant to the rule prescribed under subsection (d)(1)(A)(i), is substantially equivalent to new oil for a particular end use.

> (3) The term 'new oil' means any oil which has been refined from crude oil and has not been used, and which may or may not contain additives. Such term does not include used oil or recycled oil.[1]
>
> (4) The term 'manufacturer' means any person who re-refines or otherwise processes used oil to remove physical or chemical impurities acquired through use or who blends such re-refined or otherwise processed used oil with new oil or additives.
>
> (5) The term 'Commission' means the Federal Trade Commission."

In the EPCA, the purposes of the section on recycled oil were stated as (a) to encourage recycling of used oil, (b) to promote the use of recycled oil, (c) to reduce the consumption of new oil, and (d) to reduce the environmental hazards from disposal of used oil. It is well known that there are serious environmental problems associated with improper disposal practices for used oil, including widespread contamination by the high heavy-metal concentrations in used oil and by the basic hydrocarbons themselves.

The purpose of this report is to provide a set of evaluated test procedures which may be applied to a recycled oil to establish its substantial equivalency to a new oil for the specific end use as a burner fuel. For the purposes of this report, the term "substantially equivalent" as used in the EPCA has been taken to mean equal performance of the oil with respect to the important operational parameters concerned with this particular end use.

The NBS program plan has been (a) to review existing burner fuel oil specifications and test procedures and, utilizing available information

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[1] In this report, the term "new oil" is used interchangeably with the term "virgin oil."

and data on used and recycled oils, identify the properties of recycled oils which are related to the important operational parameters; (b) to evaluate the existing test procedures for these properties; and (c) to develop new or modified test procedures where required. To the maximum extent possible, existing test methods are utilized and the simplest method employed, consistent with obtaining the required results.

2. Burner Fuel Oil Specifications

Fuel oils found in commerce exhibit a range of values for each specified property, as do the recycled oils which may be used separately or blended with them. The first general set of fuel oil classifications in the U.S. was issued by the National Bureau of Standards in 1929 [1].[2] They were the first industrywide attempt to classify fuels according to significant properties. These standards, based on a joint conference of consumers, burner manufacturers, and general interest groups held on January 9, 1929, were issued as Commercial Standard (CS) 12-29. This standard was revised in 1933, 1934, 1938, and 1940, with the final revision issued in 1948 as CS 12-48 [1], and remained in effect until 1966, at which time it was withdrawn. These first standards established the presently used fuel oil grades.

At the present time, the following sets of specifications are, or in the recent past have been, used for burner fuel oils:

ASTM[3] D 396-76, Standard Specification for Fuel Oils

VV-F-815C, Federal Specification, Fuel Oil, Burner

MIL-F-859E, Military Specification, Fuel Oil, Burner

MIL-F-16884G, Military Specification, Fuel Oil, Diesel, Marine

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[2] Numbers in brackets indicate the literature references at the end of this report.

[3] American Society for Testing and Materials.

These specifications are included in this report as Appendix B. The first two, ASTM D 396 and VV-F-815C, are the primary specifications in current use and are summarized in table 1. These two widely used specifications are virtually identical, except as noted in table 1. Also, the VV-F-815C specification contains the statement "...suppliers are prohibited from adulterating either Grade No. 5 or Grade No. 6 fuel oil with waste crankcase lubricants or similar products" (section 3.1).

The general requirements of these specifications are that the fuel oil consist of petroleum-derived products, with two broad general classifications employed--distillates and residuals. The approximate atmospheric boiling point ranges for distillate fuel oils are, for No. 1 (kerosine), 149° C (300° F) to 302° C (576° F) and, for No. 2, 160° C (320° F) to 343° C (649° F). Distillate fuel oils consist of overhead or distilled fractions and are classified on the basis of distillation temperature (10-percent point and 90-percent point) and viscosity. Residual fuel oils are bottoms remaining after distillation or blends of these bottoms with distillates and are classified on the basis of viscosity.

The fuel oil grades in general use are described in the ASTM fuel oil specification (D 396) as follows [2]:

> "X1.3 Grades
>
> "X1.3.1 *Grade No. 1* is a light distillate intended for use in burners of the vaporizing type in which the oil is converted to a vapor by contact with a heated surface or by radiation. High volatility is necessary to ensure that evaporation proceeds with a minimum of residue.

Table 1. Summary of Specifications Contained in D 396 and VV-F-815C

Test procedures	Fuel oil grades					
	No. 1	No. 2	No. 4	No. 5 (Light)	No. 5 (Heavy)	No. 6 (Bunker C)
Flash point, °F (°C)	100 (38) or legal[a]	100 (38) or legal	130 (55) or legal	130 (55) or legal	130 (55) or legal	140 (60) or legal
Pour point, °F (°C)	0 (-18)	20 (-7)	20 (-7)	--	--	--
Water and sediment, volume %	0.05	0.05	0.50	1.00	1.00	2.00
Carbon residue on 10% bottoms, weight %	0.15	0.35	--	--	--	--
Ash, weight %	--	--	0.10	0.10	0.10	--
Distillation temp. °F (°C)						
10% point (Max)	420 (215)	--	--	--	--	--
90% point (Min)	--	540 (282)	--	--	--	--
(Max)	550 (288)	640 (338)	--	--	--	--

[a] "Legal" refers to applicable laws or regulations setting maximum sulfur levels and minumum flash point levels.

Table 1. Summary of Specifications Contained in D 396 and VV-F-815C (Continued)

Test procedures	Fuel oil grades					
	No. 1	No. 2	No. 4	No. 5 (Light)	No. 5 (Heavy)	No. 6 (Bunker C)
Kinematic viscosity, cSt						
At 100° F (38° C)						
Minimum	1.4	2.0	5.8	>26.4	>65	--
Maximum	2.2	3.6	26.4	65	194	--
At 122° F (50° C)						
Minimum	--	--	--	--	(42)[a]	>92
Maximum	--	--	--	--	(81)	638
API gravity, degrees (Min)	35	30	--	--	--	--
Copper strip corrosion (Max) [ASTM spec. at 50° C; Fed. spec. at 100° C]	No. 3	No. 3	--	--	--	--
Sulfur, weight % (Max)	0.5 or legal[b]	0.5 or legal	Legal	Legal	Legal	Legal
Aniline point, °F (°C) [Fed. spec. only]	Report	Report				

[a] Viscosity values in parentheses are for information only and not necessarily limiting.

[b] "Legal" refers to applicable laws or regulations setting maximum sulfur levels and minimum flash point levels.

> X1.3.2 *Grade No. 2* is a heavier distillate than grade No. 1. It is intended for use in atomizing type burners which spray the oil into a combustion chamber where the tiny droplets burn while in suspension. This grade of oil is used in most domestic burners and in many medium capacity commercial-industrial burners where its ease of handling and ready availability sometimes justify its higher cost over the residual fuels.
>
> X1.3.3 *Grade No. 4* is usually a light residual, but it sometimes is a heavy distillate. It is intended for use in burners equipped with devices that atomize oils of higher viscosity than domestic burners can handle. Its permissible viscosity range allows it to be pumped and atomized at relatively low storage temperatures. Thus, in all but extremely cold weather it requires no preheating for handling.
>
> X1.3.4 *Grade No. 5 (Light)* is residual fuel of intermediate viscosity for burners capable of handling fuel more viscous than grade No. 4 without preheating. Preheating may be necessary in some types of equipment for burning and in colder climates for handling.
>
> X1.3.5 *Grade No. 5 (Heavy)* is a residual fuel more viscous than Grade No. 5 (light) and is intended for use in similar service. Preheating may be necessary in some types of equipment for burning and in colder climates for handling.
>
> X1.3.6 *Grade No. 6*, sometimes referred to as 'Bunker C,' is a high-viscosity oil used mostly in commercial and industrial heating. It requires preheating in the storage tank to permit pumping, and additional preheating at the burner to permit atomizing. The extra equipment and maintenance required to handle this fuel usually preclude its use in small installations.
>
> X1.3.7 Residual fuel oil supplied to meet regulations requiring low sulfur content may differ from the grade previously supplied. It may be lower in viscosity (and fall into a different grade number). If it must be fluid at a given temperature, Method D 97 may not accurately reflect the pour point which can be expected after a period of storage. It is suggested that the purchaser and supplier discuss the proper handling and operating techniques for a given low-sulfur residual fuel oil in the installation where it is to be used."

Fuel oil specifications include "...control tests which aim at evaluating significant and important properties of the fuel....The tests may be physical or chemical in character and in very many cases, are empirical procedures, and as such, are designed to provide an indication of certain characteristics of the fuel" [3]. The primary objective of

such tests is to assure that the "...consumer receives a product of consistent and satisfactory quality for the purpose intended" [3].

3. Characteristics of Recycled Oils Used as Burner Fuel

Used petroleum oils recycled for use as burner fuel oils are obtained from a variety of sources. These sources include automotive garages and service stations, truck and taxi fleets, military installations, industrial plants and manufacturing facilities of all types, and waste-water treatment plants. The major types of used petroleum oils which are recycled into burner fuel oils are listed in table 2. Also listed are some of the additives and contaminants which are typical of these oils. These impurities can cause both performance-related and environment-related problems [4,5]. A recent Environmental Protection Agency (EPA) estimate (1976) indicates that as much as 90 percent of the easily recoverable used oil was being used as fuel with little or no processing to remove contaminants [6].

In addition to the additives and contaminants listed in table 2, there have been many analyses of used oils and waste oils, primarily for inorganic constituents. These analyses are found in references 4 through 15 and are summarized in table 3. Very little information is available in the literature on the direct effect of these contaminants on recycled oil used as burner fuel. A 1974 report by the EPA discussed some environmental impacts of the combustion of untreated waste oil and was particularly concerned with the lead emissions from burning used automobile crankcase oil [5]. A current EPA research effort is focused on the experimental evaluation of the environmental effects of combusting

Table 2. Lubricating Oil Additives and Contaminants Likely to be Found in Used Oils [4, 5, 7]

Used oil type	Typical kinds of additives	Primary Source and Type of typical contaminants
Motor oils	Antiwear: zinc organo-dithiophosphates; organic phosphorus compounds.	Gasoline: lead and lead compounds; halogens.
	Corrosion inhibitors: sulfonates; amine phosphates; organic phosphites.	Additives: zinc and zinc compounds; phosphorus compounds, etc.
	Detergents and dispersants: calcium, magnesium, barium, and zinc sulfonates, phosphonates, and phenates; alkenyl succinimides; acrylic polymers.	Combustion products: polynuclear aromatics; water; oxygenated compounds; sludge; varnish.
	Viscosity index improvers: isobutylene polymers; acrylate polymers.	Fuel: volatile liquid.
	Pour-point depressants: polymethacrylates; polyacrylamides.	Contamination: dirt; wear metals.
	Antifoam agents: silicones; synthetic polymers.	Coolant leaks: water, ethylene glycol
	Antioxidants: zinc organo-dithiophosphates; hindered phenols; aromatic amines; sulfurized phenols.	
Hydraulic and industrial oils	Many of the above plus:	Many of the above plus:
	Extreme pressure additives: organo-sulfur compounds; organo-chlorine compounds; lead compounds; amines.	Additives: sulfur and sulfur compounds; chlorine and chlorinated compounds; fatty oils.
	Emulsifiers: surfactants; sulfonates; naphthenates; fatty acid soaps.	Contamination: metal particles.
	Antiseptics: alcohols; phenols; chlorine compounds.	Solvents: volatile liquid.

Table 3. Summary of Reported Used Oil Analyses [4-15][a]

Property or test	Motor oils	Industrial oils[b]
Viscosity (SUS at 40° C)[c]	87 - 837	143 - 330
API gravity (60° F)	19.1 - 31.3	25.7 - 26.2
Water (% by volume)	0.2 - 33.8[d]	0.1 - 4.6
BS&W (% by volume)[h]	0.1 - 42	N.A.[e]
Benzene insolubles (% by weight)	0.56 - 3.33	N.A.
Gasoline dilution (% by volume)	2.0 - 9.7	N.A.
Flash point (°F)	175 - 427	315 - 355
Heating value, Btu/lb	13,571 - 19,300	17,250 - 17,990
Ash, sulfated (% by weight)	0.03 - 6.43	3.2 - 5.9[f]
Carbon residue (% by weight)	1.82 - 4.43	N.A.
Fatty oils (% by weight)	N.A.	0 - 60
Chlorine (% by weight)	0.17 - 0.47	<0.1 - 0.83
Sulfur (% by weight)	0.17 - 1.09	0.54 - 1.03
Zinc (ppm)[g]	260 - 1,787	N.A.
Calcium (ppm)	211 - 2,291	N.A.
Barium (ppm)	9 - 3,906	N.A.
Phosphorus (ppm)	319 - 1,550	N.A.
Lead (ppm)	85 - 21,676	N.A.
Aluminum (ppm)	<0.5 - 758	N.A.
Iron (ppm)	97 - 2,401	N.A.

[a] Most references did not provide data on all tests listed; therefore, data may be inconsistent between different tests.

[b] Very limited data were available for used industrial oils, on only 5 oils [4].

[c] SUS = Saybolt Universal Seconds (see sec. 5.2.4, Viscosity, this report).

[d] One sample had a water content of 46.5 percent, but is considered an outlier.

[e] N.A. = data not available.

[f] Values for the industrial oils were stated to be for the regular ash, not sulfated.

[g] ppm (as the element) = 0.0001 weight percent or 10^4 ppm = 1 weight percent.

[h] BS&W = Bottom Settlings and Water (see sec. 5.3.1, Water and Sediment, this report).

recycled used oil as a burner fuel and, when completed, should provide additional information and data on these questions [16].

4. Evaluation of Test Procedures

The test procedures called for in specifications for new burner fuel oils have been developed over a considerable period of time in response to specific problems and needs of the various industries and users. These test procedures have essentially all been developed by ASTM Committee D-2 (Petroleum Products and Lubricants), with continuous review and revision, as necessary. New or modified tests are developed by this same organization as required when new concerns or problems are identified.

The properties selected for inclusion in the ASTM D 396 specification are "...those that are believed to be of the greatest significance in determining the performance characteristics of the oils in the types of burners in which they are most commonly used" [2]. Because the purpose of this study is to enable the ultimate determination of substantially equivalent performance between new fuel oils and recycled fuel oils, this group of test procedures served as a starting point for the NBS investigation.

As described in section 3 of this report, a recycled oil may be derived from a variety of used oils including automotive oils, industrial oils, hydraulic oils, or any combination of these. For these recycled used petroleum oils, the base hydrocarbons do not significantly change as a result of use [13]. Rather, the impurities and contaminants may make the oils unfit for further use in certain applications. Any

determination of "substantial equivalence" requires that for each test procedure, the necessary properties of a recycled fuel oil be evaluated with respect to the impurities and contaminants which could reasonably be expected to affect that test. Where it has been found that a property or impurity is important to the performance of a recycled oil and an acceptable virgin fuel oil test procedure is not available, a new or modified test procedure has been developed.

The evaluation of specific test procedures in the following section is separated into four parts. The first part (section 5.1) covers a procedure to provide a representative sample needed for each of the test procedures, and a recommendation for the evaluation of homogeneity of the bulk lot. A procedure for sampling is especially important because of the differing densities of oils obtained from a variety of sources, which may result in an inhomogeneous recycled oil [8]. Section 5.2 covers the tests recommended for the bulk properties of a recycled fuel oil. Section 5.3 contains the test procedures recommended for measuring the impurities and contaminants which may be found in a recycled fuel oil and which may affect the performance of that recycled fuel oil. Section 6 contains additional test procedures which may be needed as a result of environmental concerns about recycled oil used as a burner fuel.

The bulk properties of a fuel oil, as discussed in section 5. 2, include characteristics such as flash point, pour point, and density. The evaluation of test procedures for these kinds of properties with recycled oils involves a determination of whether or not impurities or

contaminants in recycled oils interfere with the measurement of that property. It further requires that acceptable precision be obtained with the test procedure when using recycled oils.

Section 5.3 contains test procedures for measuring impurities in a recycled fuel oil. The impurities which are normally found in such a recycled oil include water, sediment, ash, sulfur, and carbon residue. These same impurities are also found in new fuel oils, although usually at much lower levels. Test procedures for these impurities must be evaluated for their ability to reliably measure the component under test when used with recycled oils and to provide an accurate and precise result. Since recycled oils often contain different types and/or amounts of impurities, care must be taken during the evaluation to consider the potential effects of these on the test procedure.

Section 6 of this report includes test procedures for three impurities in recycled oil which may be significant because of environmental considerations. These impurities are lead, polynuclear aromatic hydrocarbons, and the halogens (chlorine and bromine). While it is recognized that environmental regulation is the responsibility of the EPA and that these effluents are not now regulated in fuel oils (new or recycled), test procedures for measuring the impurity levels have been developed for them and are included in this report.

The test procedure evaluation process is described in detail in table 4 and schematically in figure 1. In these evaluations, used

Table 4. NBS Test Procedure Evaluation Process

1. Determination of those properties for which recycled oils used for fuel should be tested.

    a. Based on virgin fuel oil specifications (ASTM and Federal).

    b. Based on information and data from external publications and sources.

2. Preliminary review of the test procedures on the basis of established physical and chemical principles by a scientist knowledgeable in the technical area which the test encompases.

3. Preliminary selection of most appropriate test procedure from those tests available.

4. Experimental evaluation of the test to establish whether it is capable of reliably measuring the property under test. This evaluation may include one or more of the following:

    a. Verify the performability of the test procedure by evaluating the repeatability with a variety of recycled and used oils and, where appropriate, blends of used oils with virgin fuel oils.

    b. Examine the effects of known recycled oil impurities on the performability of the test where these effects are significant.

    c. Establish the ability of the test procedure to provide the correct or "true" concentrations for those tests which measure impurity levels.

5. Development of new test procedures or modification of existing tests where necessary to provide an acceptable test procedure to measure the desired property.

6. Final selection of the evaluated test procedure.

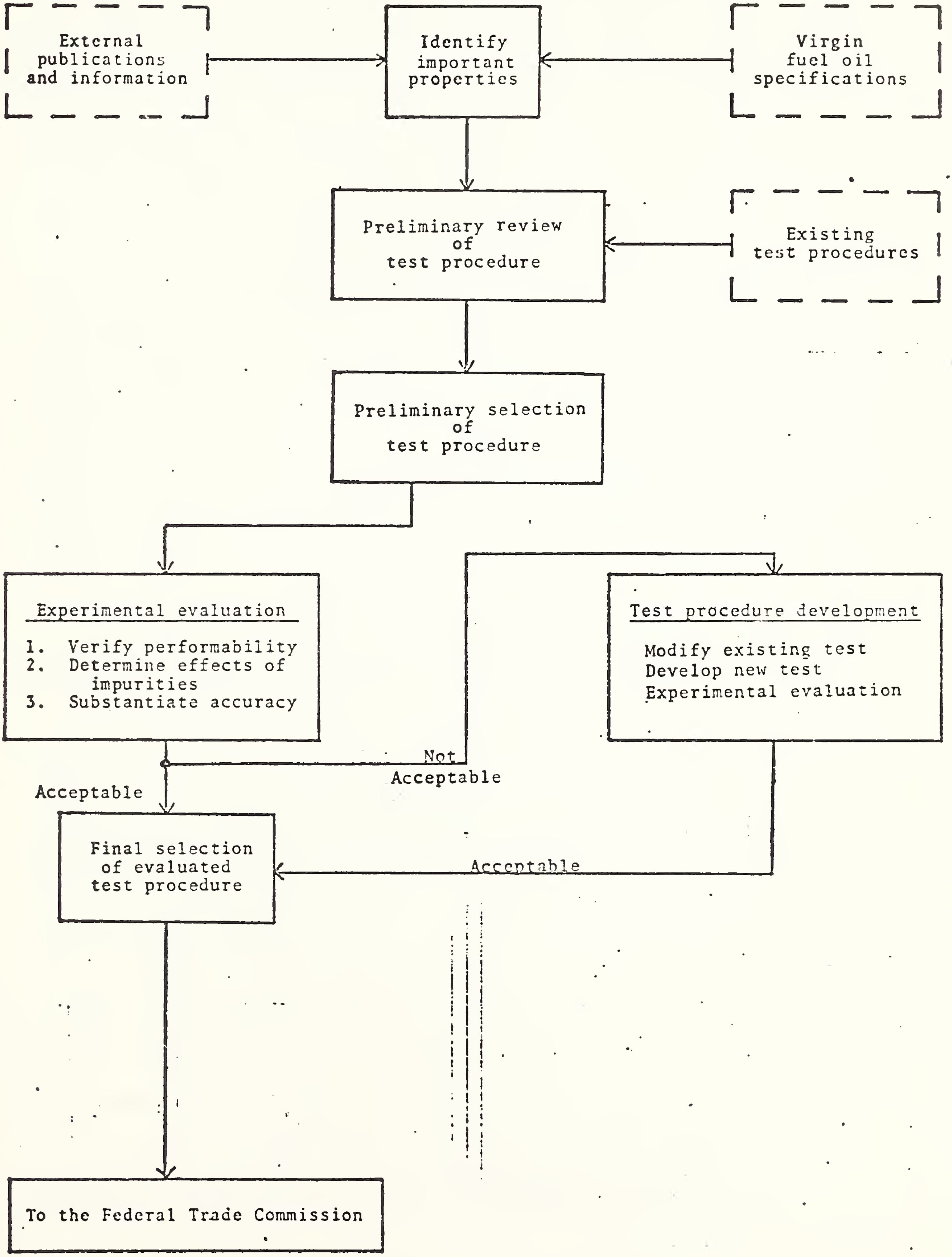

Figure 1. NBS test procedure evaluation process.

automotive oils were often taken as samples because of their generally high levels of contaminants. The contaminants contained in these composite oils include water, volatiles (e.g., gasoline), polymeric additives, ethylene glycol, lead, halogens, and both wear metals and dirt. As described in table 4, the effects of such impurities and contaminants on a test procedure were evaluated in part by examining the analytical precision (i.e., repeatability and/or reproducibility) of the test with oils containing such contaminants. Other types of samples, e.g., recycled oils and virgin fuel oils, were also used in the evaluation process. Where possible, independent determinations were made using other methods to verify the accuracy of the procedure and the effects of other impurities on the test under examination.

With regard to establishing the precision of a petroleum oil test procedure, a detailed discussion of concepts and terms is found in ASTM E 177-71, "Standard Recommended Practice for Use of the Terms Precision and Accuracy as Applied to Measurement of a Property of a Material." In E 177, note 7 states that, "Some ASTM standards contain the terms 'repeatability' and 'reproducibility'.... Usually 'repeatability' has meant single-laboratory-operator precision and 'reproducibility' multi-laboratory-operator precision...." ASTM D 3244-74T, "Tentative Recommended Practice for Defining a Basis for Petroleum Product Quality Disputes," defines "repeatability" and "reproducibility" as the terms are used by ASTM Committee D-2 on Petroleum Products and Lubricants: Repeatability "...is defined as that difference between two such [single-operator-laboratory] single results as would be exceeded in the long run

in only one case in twenty in the normal and correct operation of the test method" [17]. Reproducibility is defined in exactly the same way referring to the difference between two results obtained by "...operators working in different laboratories, each obtaining single results on identical test material when applying the same method" [17]. D 3244, in turn, cites ASTM Research Report D-2-1007, "Manual on Determining Precision Data for ASTM Methods on Petroleum Products and Lubricants," published in 1972, which provides detailed guidance for experimental evaluation of precision.

Wherever appropriate, special impurities or problems found in other likely types of recycled oils besides used automotive oils have also been considered in the individual tests (e.g., copper corrosion for used industrial oils). Occasionally, the presence of an unusual contaminant in a used oil may make the oil unsuitable for use as a fuel. Examples of such unusual contaminants may include chlorinated solvents, certain transformer fluids such as polychlorinated biphenyls (PCB's), nitrosamines, and other toxic chemicals. (Listings of hazardous and toxic chemicals may be obtained from the Occupational Safety and Health Administration (OSHA) and/or the EPA.) Although the presence of such unusual contaminants has occasionally been noted in the literature or in various reports, they were considered to be beyond the scope of this report and their effect on these test procedures was not evaluated.

5. Test Procedures

This section contains test procedures which have been evaluated for use with recycled oil for use as a burner fuel. These tests aim at evaluating important performance-related properties of the fuel oil. In addition to specific requirements for the various test procedures and limiting values, fuel oil specifications also contain general requirements. Since these general requirements are also required for adequate performance of a recycled oil, they are included here as stated in ASTM D 396-76.

> "2. General Requirements
>
> "2.1 The grades of fuel oil specified herein shall be homogeneous hydrocarbon oils, free from inorganic acid,[4] and free from excessive amounts of solid or fibrous foreign matter likely to make frequent cleaning of suitable strainers necessary.
>
> "2.2 All grades containing residual components shall remain uniform in normal storage and not separate by gravity into light and heavy oil components outside the viscosity limits for the grade."

Specific test procedures are discussed below.

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[4] A qualitative determination of the acidity of a hydrocarbon liquid may be made using ASTM D 1093-65, "Acidity of Distillation Residues or Hydrocarbon Liquids" [2] (see sec. 5.3.5, Acidity, this report).

5.1 Sampling

5.1.1 Sampling

Proper sampling of fuel oils is important because the commercial value of a petroleum product is judged by the characteristics of the sample as determined by laboratory tests [18]. The sample obtained for evaluation in the laboratory must be representative of the lot or a wrong evaluation will be made, regardless of the accuracy of subsequent tests.

Physical sampling methods used to obtain representative samples from bulk lots of fuel oil are described in the ASTM method D 270-65[5] (reapproved in 1975), "Sampling Petroleum and Petroleum Products" [19]. Method D 270 describes and specifies many different procedures, depending on the type of container (ship, barge tank, tank car, etc.) and the vapor pressure of the product.

Another sampling procedure applicable to fuel oils is given by ASTM E 300-73, "Sampling Industrial Chemicals." In addition to a procedure for physical sampling of simple liquids (based on D 270), it includes several sections on statistical considerations. In the discussion of simple liquids, E 300 notes that, "Although single-phase liquids are homogeneous by definition, it may be desirable to check for this condition by sampling from various sections of the container" [20]. The statistical sections of E 300 are currently undergoing revision [21].

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[5] The first number, i.e., D 270, is the ASTM test method, while the second number, i.e., -65, is the year of last revision (1965).

Fuel oil specifications and standards vary considerably in their requirements for sampling, ranging from none to fairly detailed requirements. The sampling requirements of existing fuel oil specifications are summarized in table 5, followed by a more detailed discussion of the requirements of each specification.

Table 5. Summary of Sampling Requirements

Specification	Requirement
D 396-76	No requirement.
VV-F-815C	Take one sample in accordance with D 270 (physical methods).
MIL-F-859E	Take upper, middle, and lower samples according to D 270; composite the samples if their API[5] gravities do not vary from the average by more than 0.3° (0.0012 density units).
MIL-F-16884G	Same as VV-F-815C

1. ASTM D 396-76, Standard Specification for Fuel Oils

The D 396-76 specification provides minimum criteria for fuel oils and is widely used in the marketplace for procurement purposes. This specification contains no requirement or suggestion for sampling. Under section 2.1, the grades of fuel oil are required to be "homogeneous

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[6] American Petroleum Institute; see also Section 5.2.5, Density of this report.

hydrocarbon oils," but criteria for the determination of homogeneity are not included.

2. <u>VV-F-815C, Federal Specification, Fuel Oil, Burner</u>

This specification is identical to ASTM D 396-76 in most respects. One major difference exists, however, in the sampling requirements.

In VV-F-815C, a bulk lot is defined in section 4.2 as follows:

> "4.2 <u>Lot</u>
>
> "4.2.1 <u>Bulk lot</u>. An indefinite quantity of a homogeneous mixture of one grade of fuel oil offered for acceptance in a single, isolated container; or manufactured in a single plant run (not exceeding 24 hours), through the same processing equipment, with no change in the ingredient materials."

For the details of sample collection, ASTM method D 270 is cited. Several methods are specified in D 270 for bulk sampling, depending on the type of container. For example, storage tanks, ships, and barges require bottle sampling; storage tanks with taps, tap sampling; open discharge streams, dipper sampling; and tank cars and storage tanks, thief sampling. Thief samplers may be used for bottom sampling, while bottle sampling may be used to obtain an all-levels sample, upper-, middle-, and lower-tank samples, multiple composite tank samples, etc. The sampling details must be recorded for each specific sample.

3. MIL-F-859E, Military Specification, Fuel Oil, Burner (Navy Special)

This military specification provides very specific directives for sampling. Section 4.2.1 specifies the sampling method and criteria for determining homogeneity of the sampled lot.

> "4.2 Sampling
>
> "4.2.1 *Bulk lot.* An indefinite quantity of material from one storage tank offered for acceptance. To establish homogeneity, upper, middle, and lower samples as prescribed in ASTM D-270 shall be taken from each lot and subjected to API gravity determinations in accordance with method 401 of FED-STD-791. To be considered homogeneous, those gravities shall not vary from the average more than 0.3°. If the lot is homogeneous, samples shall be composited for acceptance testing. If the lot is not homogeneous, acceptance tests shall be performed separately upon the upper, middle, and lower samples."

Federal Test Method Standard No. 791B-Method 401, referred to above, is actually the ASTM method D 287-67, "API Gravity of Crude Petroleum and Petroleum Products (Hydrometer Method)." An identical and preferred method is the international version, ASTM D 1298-67, "Density, Specific Gravity or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method" [2] (see Section 5.2.5, Density).

MIL-F-859E is presently not used by the U.S. Navy, which now uses MIL-F-16884G [22].

4. MIL-F-16884G, Military Specification, Fuel Oil, Diesel, Marine

This specification contains essentially the same sampling requirements as VV-F-815C, which calls for samples to be taken in accordance with ASTM D 270.

For recycled oils, an adequate sampling procedure is especially important in order to provide acceptable evaluation of the product by testing. This is so because of the high levels of impurities often found in used oils collected for recycling (see section 3 of this report). These impurities include water, sediment (including fine particulates), volatile solvents, lead, and the like. Processing of used oil for use as a fuel by low-level techniques such as settling and/or centrifugation is not likely to remove all or even most of these impurities. Stratification resulting from differing densities may occur due to settling of particulates or water, lack of adequate homogenization of used oils from different sources, improper blending with virgin fuel oil in a large tank, or for other reasons [5].

Stratification of several recycled used oils was noted in the literature for used oil/virgin distillate oil blends [5,14]. This stratification apparently occurred largely due to the difficulty of adequately mixing dissimilar oil types in large tanks. The problems with reprocessed used oils and virgin residual oils are less well documented; however, an API Task Force recognized the homogeneity problems

of used oil and used the following method to assure homogeneity [9]. First, a special pump was installed to allow the used oil in storage tanks to be recirculated. Second, the tank supplying the used oil/virgin residual fuel oil to the combustion system was equipped with a large stirrer. Finally, the density of the waste oil in the supply tank was measured every half-hour during operation of the test system to monitor homogeneity (note: used oil/virgin residual oil blends ranged from 0 percent up to 15 percent by volume, v/v).

The recommended sampling requirements for recycled used oils used for fuel are the physical sampling procedures as given in ASTM D 270, which are applicable to recycled oils, with a modification to check homogeneity. This modification utilizes variations in density, or API gravity, to indicate an inhomogeneity of the material in the sampled lot. To check for this a sampling procedure based on MIL-F-859E is suggested for evaluating bulk lots. An evaluation of the test procedure is given in this report.[7] Possible language for specifying the examination of a bulk lot for homogeneity is as follows:

> For bulk lots where a bulk lot is defined as an indefinite quantity of hydrocarbon oil of one grade in a single isolated container, upper, middle, and lower samples will be taken using thief or bottle samples as described in ASTM D 270, section 14.

---

[7] See Section 5.2.5, Density of this report.

Samples may be composited to a single sample if the lot is homogeneous. If the lot is not homogeneous, specification tests will be performed separately on the upper, middle, and lower samples.

Homogeneity will be determined on the basis of density ASTM D 1298 or ASTM D 287. Lots will be considered homogeneous if the gravity determinations for the upper, middle, and lower samples do not vary from the average by more than 0.0012 density units or 0.3° API gravity.

CONCLUSION

The ASTM D 270-65 sampling procedures are applicable to recycled oil for use as burner fuel with the modification described above to check homogeneity. These procedures are recommended to obtain samples for the various tests used to characterize bulk lots of recycled oil to be used as fuel.

5.2 Test Procedures for Bulk Properties

This section contains test procedures for the bulk properties of a recycled used oil to be used as a burner fuel. The bulk properties which are tested and specified for virgin burner fuel oils are flash point, pour point, distillation temperature, viscosity, density, and copper corrosion. Test procedures for these properties are also recommended for recycled oils, some with modifications as described in the individual test procedures. Two additional tests, aniline point and heating value, are recommended for use with recycled oils. A test for the heating value is particularly important since the combustion energy is the primary commodity of trade for a fuel oil.

These test procedures were evaluated for use with recycled oils using the evaluation process described in section 4 of this report. In general, for this category of test procedures, the test itself attempts to simulate actual performance (e.g., flash point is the lowest temperature at which the petroleum product "flashes"). Therefore, the test procedure itself defines the correct or "true" value for the measurement. The evaluation of this type of test procedure is thus concerned primarily with whether or not contaminants and impurities interfere with the performance of the test.

The individual test procedures are discussed below.

5.2.1 Flash Point

Flash point is the temperature to which a fuel must be heated to produce a vapor/air mixture capable of being ignited with an open flame. It is also an indication of maximum safe handling temperature of a burner fuel oil - both important aspects of performance. The flash point of recycled oils may be lowered by contamination of the specified fuel oil grade by a more volatile component. Therefore, a major concern for the flash point test is its ability to detect contamination of a recycled oil with a more volatile material such as a solvent or gasoline dilution from a used crankcase oil.

The usual test procedure for determining flash point of virgin fuel oils is the ASTM method D 93-77, "Flash Point by Pensky-Martens Closed Tester." This test procedure is identical to the British Institute of Petroleum Test Method 34/71 and the Federal Test Method 1102 - Federal Standard Number 791B. This test is stated to be applicable to virgin petroleum products such as all burner fuel oils, lubricating oils, and other petroleum liquids. D 93 is the ASTM referee method for flash point in cases of dispute for both the ASTM fuel oil specification and the Federal specification for burner fuel oils.

Two additional flash point test procedures are available but were not evaluated in this program. In the Cleveland Open Cup test method (ASTM D 92-72) the procedure states it is inappropriate for use with

fuel oils or for the detection of the presence of small concentrations of a lower flash point material [2]. The other method is ASTM D 56-77, "Test for Flash Point by Tag Closed Tester." Since D 56 can only be used with the distillate fuel oils (grade numbers 1 and 2), it is therefore of limited applicability to recycled fuel oils.

In the Pensky-Martens test method (D 93-77), the sample is contained in a cup that has a cover containing a shutter, which is normally closed during heating and opened only briefly at intervals for the test. "The sample is heated at a slow, constant rate with continual stirring. A small flame is directed into the cup at regular intervals with simultaneous interruption of stirring. The flash point is the lowest temperature at which application of the test flame causes the vapor above the sample to ignite" [2]. D 93-77 includes a basic procedure, method A, and also a method B, "Determination of Flash Point of Suspensions of Solids and Highly Viscous Materials" [2]. Method B is the same as method A except for requiring a higher stirring speed and a slower heating rate. The precision, as developed with virgin fuel oils and as stated in D 93-77, is shown in table 6 for both methods.[8]

The Pensky-Martens test procedure was evaluated for recycled oil used as burner fuel. As part of this evaluation the D 93-77 test

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[8] In D 93-77, the repeatability and reproducibility table for method B is for viscous materials "...which tend to form a surface film" [2]. The samples tested which required method B do not form such films; therefore, we compared against the method A table.

procedure was applied to a number of used oils, recycled oils, virgin distillate fuel oils, virgin distillate fuel oil/used oil blends, and used oil mixed with gasoline. These data are shown in table 7 and indicate that the repeatability of the flash point test for these samples is consistent with that of virgin fuel oils, as shown in table 6. The D 93 test method states in note 2 that this method may be employed for the detection of contamination of lubricating oils by minor amounts of volatile materials, which indicates that this test procedure should be effective in measuring this type of contamination.

Table 6. Precision of Flash Point Test Procedures for Virgin Fuel Oils[a]

Flash point range	Repeatability[b]	Reproducibility[c]
104° C and under	2° C (4° F)	3.5° C (6° F)
Above 104° C	5.5° C (10° F)	8.5° C (15° F)

[a] Table and footnotes are from ASTM method D 93-77. The method should be consulted for additional details.

[b] Duplicate results by the same operator should be considered suspect if they differ by more than these amounts.

[c] Results submitted by each of two different laboratories should be considered suspect if they differ by more than these amounts.

Table 7. Repeatability of the Flash Point Test Procedure (D 93-77)

Sample	Experimental flash point, °C (°F)
No. 2 fuel oil (F131)	68.3 (155); 69.2 (157)
No. 2 fuel oil + 5% W022[a]	68.3 (155); 67.8 (154)
No. 2 fuel oil + 15% W022	68.3 (155); 68.9 (156)
No. 1 fuel oil (F132)	51.1 (124); 51.7 (125)
No. 5 recycled fuel oil (F134)	121.7 (251); 121.7 (251)
No. 5 recycled fuel oil (F133)	138.3 (281); 137.8 (280)
Used oil (W024)[a]	58.1 (138); 56.7 (134)
Used oil (W022)[a]	91.7 (197); 89.4 (193)
Used oil (W022) with 5% gasoline added (v/v)	22.8 (73); 23.9 (75)[b]

[a] W022 and W024 are used automotive crankcase oils.

[b] Apparent flash point; sample flashed at room temperature without heating.

CONCLUSION

The flash point test is used to indicate both the safety and the adequate performance of the burner fuel [19]. The Pensky-Martens test procedure, ASTM D 93-77, has been evaluated with recycled fuel oils, blends of virgin fuel oil with recycled oil, and oils containing volatile contaminants. This test may be used to establish that a product meets the specified minimum value of flash point.

5.2.2 Pour Point

Fuel oils are often stored in outside tankage, and a knowledge of the lowest temperature at which the fuel can be transferred from tank to burner is necessary. The pour point describes the flow characteristics of an oil and the lowest temperature at which the oil will flow under standard test conditions [2,19]. An indication of this temperature is given by the pour point, which is the temperature at which wax crystals crystallize out of the hydrocarbon fuel and the wax structures build up sufficiently to prevent the flow of the oil under low forces [3]. This temperature can also be used as an indication of the low temperature pumpability of the oil. Additives are sometimes used to lower the pour point.

The test procedure used for virgin fuel oils is ASTM D 97-66 (reapproved in 1971), "Pour Point of Petroleum Oils." This test is identical to IP 15/67, to Method 201 - Federal Test Method Standard No. 791B, and to British Standard 4452, and is intended for use on any petroleum oil [2].

To determine the pour point using D 97, the sample is heated and then cooled at a specified rate and examined at intervals of 5° F (3° C) for flow characteristics. The lowest temperature at which movement of the oil is observed is the experimentally determined pour point. This test is generally applied to grade Nos. 1, 2, and 4 fuel oil [2]. It is usually not specified for Nos. 5 and 6 since preheating may be

required for handling, transfer, and use of these oils, depending on climate and equipment; however, a "low pour" fuel oil may be specified for grade No. 6 [2].

The precision of method D 97 for virgin fuel oils is stated to be as follows [2].

> "7. Precision
>
> "7.1 *Repeatability*--Duplicate results by the same operator should be considered suspect if they differ by more than 5 F (or 3 C).
>
> 7.2 *Reproducibility*--The results submitted by each of two laboratories should be considered suspect only if the two results differ by more than 10 F (or 6 C).
>
> 7.3 For oils tested by the procedure described in 5.9, reproducibility of this order cannot be expected, as these oils show anomalous pour points depending on their thermal history.[5]" [These special-case oils include black oil, cylinder stock, and nondistillate fuel oil.]

"[5] It is a recognized property of these oils that the temperature to which they have been subjected before testing influences their pour points. Although the lower pour points as determined by the special procedure will show approximately the reproducibility given, the upper pour points will show greater variations depending on the previous thermal history of the oils. Further information on this subject is contained in *Proceedings*, ASTEA, Am. Soc. Testing Mats., Vol 31, Part I, 1931, pp. 468-470, and Vol 32, Part I, 1932, pp. 402-405."

The D 97 test procedure was evaluated for use with recycled oils. As part of this evaluation the test was applied to a number of virgin and recycled distillate fuel oils, distillate fuel oil/used oil blends, and heavier recycled fuel oils. These data are shown in table 8, and

Table 8. Precision of the Pour Point Test on Fuel Oils and Fuel Oil Blends (D 97)

Fuel oil grade	Sample	Sample number	% Recycled oil[a]	Pour point, °C (°F) Operator 1	Pour point, °C (°F) Operator 2
1	Distillate fuel oil (virgin)	F132	----	-46 (-51)	-46 (-51)
2	Distillate fuel oil (virgin)	F131	---	-23 (-10) -23 (-10)	
2	Distillate fuel oil blend	(F131)[b]	(1)[a]	-32 (-25)	-32 (-25)
2	Distillate fuel oil blend	(F131)	(5)[a]	-37 (-35) -37 (-35)	
2	Distillate fuel oil blend	(F131)	(10)[a]	-54 (-65) -54 (-65)	-48 (-55)
---[c]	Recycled distillate fuel oil	7L24	100	-14 (+ 7) -14 (+ 7)	
5	Recycled fuel oil	F133	100	-45 (-49) -44 (-47)	
5	Recycled fuel oil	F134	100	-41 (42) -44 (-47)	

[a] W022 composite used automotive oil; not processed beyond collection and storage.

[b] Sample number in parentheses for blends indicates the sample number for the virgin distillate fraction.

[c] Viscosity measurements on this oil placed it between grade Nos. 2 and 4.

the repeatability and reproducibility of the pour point test for these samples are consistent with those for virgin fuel oils as discussed above. Most used automotive crankcase oils will lower the pour point of virgin fuel oils, both distillate and residual. This effect is shown in table 8 for the distillate fuel oil/used oil blends, and is most likely due to the presence of pour point depressants in these high additive oils. The results of our evaluation indicate that the pour point test procedure, D 97, can be effectively used with a recycled fuel oil.

CONCLUSION

The pour point of a fuel oil is a useful indicator of the low-temperature flow characteristics of fuel oil. ASTM method D 97-66, "Pour Point of Petroleum Oils," has been evaluated with recycled fuel oils and with blends of virgin fuel oils and used oils, and may be used to measure the pour point of recycled petroleum oils to be used as fuel.

5.2.3 Distillation Temperature

Distillation (volatility) characteristics of distillate fuel oils are important indicators of performance. Heating installations which use vaporizing or atomizing burners operated with distillate fuel oils require fuels that contain sufficient volatile components to ensure ready ignition and a stable flame [19]. In addition, the volatility of the fuel must be uniform from batch to batch to avoid frequent resetting of burner controls and to maintain maximum performance and efficiency of the heating system [19]. The distillation temperature test is generally not applied to residual fuel oils [19].

There are five different ASTM distillation test procedures, but only one of them is normally used for fuel oils [19]. This test is D 86-77, "Distillation of Petroleum Products," and is identical to Method 1001 - Federal Test Method Standard No. 791B, Institute of Petroleum designation 123/68, British Standard 4349, and Deutsche Norm DIN 51751. The D 86 test procedure provides that "A 100-ml sample is distilled under prescribed conditions which are appropriate to its nature.... Systematic observations of thermometer readings and volumes of condensate are made, and from these data, the results of the test are calculated and reported" [2]. For the distillate fuel oils the temperatures at which 10 percent and 90 percent of the total volume have distilled are the values usually used in specifications. In addition, the initial boiling point and the 50-percent volume point are also often recorded.

The precision of this test procedure is dependent upon the rate of change of the thermometer reading at each stage at which a result is obtained. There are two nomographs given with the test procedure which provide estimates of repeatability and reproducibility based on information taken during the test [2]. For example, in our evaluation of this test procedure using virgin distillate fuel oils, the repeatability according to the ASTM nomographs ranged from 1° to 3° C. The ASTM reproducibility was higher by a variable factor.

The distillation temperature test procedure (D 86) was evaluated for use with recycled oils. As a part of this evaluation, D 86 was applied to a series of distillate fuel oil samples including virgin oils, recycled oil, and blends of virgin distillate fuel oils with 10-percent used automotive crankcase oil. The results of these tests are found in table 9. Two of the test samples examined, a 10-percent blend of used automotive oil with a grade No. 1 virgin fuel oil and the distillate fuel oil product from a recycler, failed to distill to the 90-percent point within the temperature range limitations of the test apparatus. [This temperature limitation is also due to the fact that if oils are heated above 370° C (700° F) they tend to decompose ("crack") and provide unreliable results [19].]

This evaluation indicates that the D 86 test procedure for distillation temperature is a useful test for the volatility characteristics

Table 9. Repeatability of Distillation Temperatures for Distillate Fuel Oils (D 86)

Fuel oil grade	Sample	Sample number	% Recycled oil	% Sample recovered	Distillation temperatures, °C	ASTM repeatability of method, °C[a]
1	Virgin fuel oil	F132	---	BP	181.1, 179.6, 179.6	1.6
				10	184.6, 195.7, 194.7	1.3
				50	219.7, 220.7, 220.2	1.3
				90	257.8, 258.8, 256.8	1.8
2	Virgin fuel oil	F131	---	BP	191.3, 194.3, 186.6, 190.7	2.5
				10	214.3, 213.3, 216.7, 217.7	1.7
				50	258.3, 257.3, 258.8, 259.8	1.5
				90	318.4, 312.4, 318.9, 316.9	2.2
(1)[b]	Virgin oil/used oil blend	F132	10[c]	BP	178.3, 178.3	1.9
				10	194.3, 196.3	1.6
				50	223.3, 223.3	1.4
				90[d]	--- ---	
(2)[b]	Virgin oil/used oil blend	F131	10[c]	BP	188.4, 196.5	2.2
				10	215.0, 217.5	1.7
				50	264.5, 266.5	1.6
				90[e]	352.6, 357.6	2.6
---[f]	Recycled fuel oil	7L24	100	BP	138.7, 128.6	Off scale
				10	207.7, 211.2	2.9
				50[g]	349.0, 354.0	1.5

[a] The D 86-77 test procedure states in a footnote that "Precision for this method is under review. Indications are that precision for initial boiling point...may be indeterminate" [2].

[b] Indicated grade is for the distillate virgin oil fraction; the blended fuel oil sample is not considered a distillate fuel for some uses.

[c] Used oil sample blended with the distillate fuel is W022, a composite used automotive crankcase oil which was not processed beyond collection and storage.

[d] Unable to distill 90 percent of sample within temperature range of test apparatus; 80 percent distilled at 338.4° C, leaving a black, gummy residue.

[e] Sample near end of distillate fraction and had rapid temperature rise.

[f] The viscosity characteristics of this recycled distillate fuel oil placed it between fuel oil grade Nos. 2 and 4.

[g] Due to excessive temperature rise, unable to go above the 50-percent point.

for recycled fuel oils. While the test results for both the recycled oils and the virgin oils often fell somewhat outside the indicated ASTM repeatability, this is not considered to be a serious problem. In fact, footnote 8 in the test procedure indicates that the precision of this test is under review, especially for the initial boiling point measurement [2]. However, this test procedure will provide appropriate information on the volatility characteristics of distillate recycled fuel oil samples.

CONCLUSION

The distillation (volatility) characteristics are important indicators of performance for distillate fuel oils. The D 86-77 test procedure, "Distillation of Petroleum Products," has been evaluated with recycled distillate fuel oil and blends of virgin distillate fuel oils with used automotive oil. This test procedure may be used to obtain the appropriate volatility chatacteristics of distillate recycled oils to be used for fuel.

5.2.4 Viscosity

Viscosity, or the internal resistance exhibited as one portion or layer of a liquid is moved in relation to another portion, is an important characteristic of fuel oil. It is indicative of the rate at which the oil will flow in fuel systems and the ease with which it can be atomized in a given type of burner. Overly viscous oils can produce problems throughout the heating oil system, including pumping difficulties, burner ignition problems, and flashback or erratic operation of the burner [19]. An unsuitable viscosity also affects the output or delivery of a spray nozzle and the angle of spray, with subsequent poor atomization and possible carbonization of the burner tip, carbon deposition on the walls of the firebox, or other problems caused by poor combustion [19].

The test procedure generally used for determining the viscosity of virgin fuel oils is ASTM method D 445-74, "Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity)" [2]. This test procedure is identical to Method 305.6 - Federal Test Method Standard No. 791B, the Institute of Petroleum Designation IP 71/66, the British Standard 4708, and the Deutsche Norm DIN 51550. This test procedure is applicable to liquid petroleum products, both transparent and opaque, and covers all grades of fuel oil.

Another test procedure for the viscosity of fuel oils is ASTM D 88, "Saybolt Viscosity," but this method has now been withdrawn by ASTM Committee D-2, and the D 445 test for kinematic viscosity is the method

now preferred by this ASTM committee [19]. If desired, the Saybolt viscosities can be calculated from the kinematic viscosity using ASTM method D 2161-74, "Conversion of Kinematic Viscosity to Saybolt Universal Viscosity or to Saybolt Furol Viscosity" [2].

In the kinematic viscosity method, D 445, "The time is measured in seconds for a fixed volume of liquid to flow under gravity through the capillary of a calibrated viscometer under a reproducible driving head and at a closely controlled temperature. The kinematic viscosity is the product of the measured flow time and the calibration constant of the viscometer" [2]. The cgs unit of kinematic viscosity is one centimeter squared per second and is called one stokes (St). The SI unit of kinematic viscosity is one meter squared per second and is equivalent to 10^4 St. Frequently, the centistokes (cSt) is used (1 cSt = 10^{-2} St).

The precision of the D 445 test procedure for "...clean, transparent oils tested between 15 and 100 C (60 and 212 F)" is stated as follows [2]:

> "*Repeatability*--Duplicate results by the same operator, using the same viscometer, should be considered suspect if their difference is greater than 0.35 percent of their mean."
>
> "*Reproducibility*--The results submitted by each of two laboratories should not be considered suspect unless their difference is greater than 0.7 percent of their mean."

No statement of precision is given for oils which are not clean and transparent.

The D 445 kinematic viscosity test procedure was evaluated for use with recycled oils to be used as fuel. As part of this evaluation, the D 445 test procedure was applied to recycled oils, used oils, virgin fuel oils, and used oil/virgin fuel oil blends. The results of these tests are found in table 10. With the exception discussed below, the results are consistent with the ASTM repeatabilities for transparent oils even though many of the recycled oils and oil blends are opaque.

During this evaluation, two potential problems were examined. One potential problem is the presence of volatile components in the recycled, used or waste oils. A second potential problem is the effect of particulates which are suspended in many used lubricating oils, and which pass through the 75 μm sieve recommended in D445 for solids removal.

Since viscosities are measured at 40° C or 50° C, evaporation of volatile contaminants may occur during the measurement process. This, in fact, does occur with some used oils and is evidenced by increased viscosity with time leading to a lack of repeatability (e.g., table 10, sample W011). However, the less viscous (presumably higher volatility) Nos. 1 and 2 virgin fuel oils did not show such changes with time, leading to the tentative conclusion that used oil sample W011 (and perhaps W022) contains quite volatile components -- likely to be due to gasoline contamination.

It is possible to strip volatile components by using ASTM method D3607-77, "Removing Volatile Contaminants from Used Engine Oils by Stripping". The procedure involves passing a stream of nitrogen for 4.5 hours through a weighed 25-mL sample maintained at 90 °C (194°F) and determining the weight loss. Viscosity measurements made before and after this procedure on samples of used oil and a sample of recycled oil are listed in table 11. The percentage of volatiles stripped from the various samples is also given, as well as the percentage of water in the samples, since the water contributes to the total volatiles removed at this temperature. (Water was determined by distillation, D95; see Section 5.3.1, Water and Sediment.) It can be seen that repeatable values are obtained by this procedure, yet the change in viscosity after stripping is large and strongly correlated with the volatiles concentration in these particular samples. It is concluded that this stripping procedure, in removing volatile contaminants of the oil, also removes components which contribute to its viscosity (and undoubtedly higher heating value, an attribute of great importance for use as a fuel). A lower stripping temperature would appear not to be a satisfactory solution to this problem. Consequently, for those oils where the presence of highly volatile contaminants is suspected, as evidenced by changes in viscosity measurements with time leading to values outside the ASTM repeatability limit, and as evidenced by low flash point values (see Section 5.2.1, Flash Point), it is recommended that the test report indicate lack of repeatability for ASTM D445. This will allow purchasers to learn the value of the viscosity of the "as-is" material, while at the same time, alerting them to possible contamination by highly volatile compounds.

Table [illegible]. Repeatability of the Kinematic Viscosity (ASTM D 445) of Recycled Oils, Used Oils, and Used Oil/Virgin Fuel Oil Blends

Description	Sample number	Virgin fuel oil grade	Percent recycled oil[a]	Kinematic viscosity (cSt)[b]
Virgin fuel oil	F132	1	0	1.561, 1.562
Used oil (W022)/fuel oil (F132) blends	----		(1)	1.647, 1.649
	----		(5)	1.805, 1.801
	----		(10)	2.086, 2.093
	----		(20)	2.782, 2.782
Virgin fuel oil	F131	2	0	2.125, 2.120
Used oil (W022)/fuel oil (F131) blends	----		(1)	2.389, 2.389
	----		(5)	2.652, 2.639
	----		(10)	2.956, 2.956
	----		(20)	3.892, 3.898
Recycled distillate fuel oil	7L24	---[c]	100	5.405, 5.402
Recycled fuel oil (source A)	F133	5	100	74.55 , 74.41
Recycled fuel oil (source B)	F134	5	100	56.98 , 57.02
Composite used crank-case oil	W022	---	(100)	60.73 , 60.84
Composite used crank-case oil	W011[d]	---	(100)	65.97, 66.24, 67.27
Virgin fuel oil	F130	6	0	67.02[e] , 66.90[e]

[a] Numbers in parenthesis indicate percentages of a used automobile crankcase oil, which was not processed beyond collection and storage.

[b] Obtained at 40° C unless otherwise noted. (Temperature as listed in ASTM 396-77).

[c] Viscosity characteristics place this fuel oil between grades 2 and 4.

[d] Not within ASTM repeatability due to loss of volatiles (See text).

[e] Obtained at 50 °C. (Temperature as listed in ASTM 396-77 for this grade).

Table 11. Effect of Volatiles Removal on the Kinematic Viscosity Test Procedure (D 445)

Sample number	Description	Volatiles[a] (% by vol.)	Water (% by vol.)[b]	Kinematic viscosity (cSt)	
				Initial	Stripped
W022	Composite used motor oil	3.42	0.19	60.73	78.60
		3.70		60.84	78.59
W011	Used automotive crankcase oil	4.68	0.10	65.97[c]	103.65
		4.56		66.24	103.65
				67.27	
F134	Recycled fuel oil	2.26	0.64	56.98	63.47
		2.36		57.02	63.44

[a] Obtained using ASTM D 3607-77.

[b] Obtained using ASTM D 95; note that water is also removed from the sample by the stripping procedure.

[c] This series of results is not within the ASTM repeatability (see text).

To evaluate the effect of small particulates, samples of used oils were centrifuged at high speed (15.5K revolutions per minute) for 20 minutes. Preliminary experiments had shown that centriguation caused significant temperature increases in the samples, undoubtedly leading to viscosity increases due to volatiles loss. Consequently, the stripping method described above (ASTM D 3607-77 was used to remove volatile components before the samples were measured. Viscosities of the samples before and after centrifugation are given in Table 12. The results are consistent with the presence of colloidal particles suspended in a liquid (viscosity of the suspension greater than the fluid). The magnitude of the effect is very small: within the repeatability of the test procedure itself. For the used oils examined then, the presence of these small particles will not affect viscosity measurements to any great extent.

Table 12. Effect of Particulates on the Kinematic Viscosity of Used Oils (D 445)

Sample number	Description	Viscosity (cSt at 40° C)	
		Initial[a]	After centrifugation
W022	Composite used motor oil	78.60, 78.59	78.42, 78.44
W004	Used automotive crankcase oil	66.61, 66.40	65.60, 65.55
W011	Used automotive crankcase oil	103.65, 103.65	103.35, 103.37

[a] Initial viscosity measurement made after stripping with D 3607-77 (see text).

CONCLUSION

The viscosity characteristics of a fuel oil are important for assuring acceptable flow and pumpability performance in service. ASTM test method D 445-74, "Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity)," is an appropriate test procedure for the measurement of this characteristic for recycled fuel oils, with one modification for oils which give evidence (increased viscosity with time outside repeatability limits, low flash point) of contamination by volatiles: a notation in the test report that repeatability was not obtained, and the viscosity values listed in sequence.

5.2.5 Density

The density, or mass per unit volume, of a fuel oil enters into most pricing structures and is used by refiners in the control of refinery operations [19]. The determination of the density serves at least three purposes: (1) it provides a check on uniformity for bulk quantities of fuel oils (see also Section 5.1.1, Sampling); (2) it permits the calculation of weight per gallon; and (3) it provides information for estimation of the heating value of a fuel oil (see also Section 5.2.8, Heating Value).

Values for the mass unit volume may be reported in three ways for petroleum products: as density, as specific gravity, or as API gravity. The density of a fuel oil is the mass of a unit volume at a specified temperature (15° C and 60° F are the usual temperatures for petroleum product measurements [2]). The specific gravity (or relative density) of a fuel oil is the ratio of the mass of a given volume of the product at some temperature to the mass of an equal volume of distilled water at the same temperature, both masses being corrected for buoyancy in air. The API gravity of petroleum products is based on an arbitrary hydrometer scale which is related to the specific gravity in accordance with the formula

$$\text{API gravity, in degrees} = \frac{141.5}{\text{specific gravity at } 60^\circ\ \text{F}/60^\circ\ \text{F}} - 131.5.$$

The API gravity is generally used for most commercial transactions in the United States as well as in refinery practice, while the specific gravity is in general use in some foreign countries. The value for API gravity is required in existing fuel oil specifications only for grade Nos. 1 and 2.

Two procedures are available for measuring this characteristic. The first one is ASTM D 1298-67 (reapproved in 1977), "Density, Specific Gravity or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method" [2]. D 1298 is identical to API Standard 2547, to the Institute of Petroleum Designation IP 160/68, to the British Standard 4714, and to the Deutsche Norm DIN 51757. The second procedure is ASTM D 287-67 (reapproved in 1977), "API Gravity of Crude Petroleum and Petroleum Products (Hydrometer Method)," which is identical to API Standard 2544 and to Method 401 - Federal Test Method Standard No. 791B [2]. D1298, used internationally, is the preferred one since it provides means for converting values determined in any one of the three systems of measurement to equivalent values in either of the other two. For the measurement of API gravity, the two test procedures are essentially equivalent, so an evaluation of D1298 will serve to evaluate D287 at the same time.

Both of the above procedures are based on the principle that the depth of immersion of body floating in a liquid is inversely proportional to the density of the liquid. The floating body, with appropriate graduations, is called a hydrometer. The sample is brought to the prescribed temperature,

transferred to a cylinder, and the appropriate hydrometer is lowered into the sample and allowed to float. After temperature equilibrium is reached, the hydrometer scale is read and the temperature noted [2].

The ASTM repeatabilities and reproducibilities of D 1298 and D 287 are shown in table 13. For very viscous products, the D 1298 test procedure states that "...no specific variations can be given" [2].

The hydrometer test procedure for determining the density of fuel oils (D 1298) was evaluated for use with recycled oils. As part of this evaluation the test procedure was applied to a number of used oils, recycled oils, virgin oils, and virgin fuel oil/used oil blends. These data are shown in table 14 and indicate that the repeatability of the API gravity for these samples is consistent with the ASTM repeatability as shown in table 13.

One problem encountered during the NBS evaluation was the entrapment and slow release of small bubbles in some samples of recycled oil after very vigorous agitation (e.g., use of a mechanical shaker). These air bubbles could result in an apparent increase of one degree or more for the API gravity. This problem is eliminated by the use of gentle agitation for the sample container, or any method which does not introduce air bubbles. The D1298 procedure indicates in Sections 7.2 and 7.5 of the procedure that the formation of air bubbles in the sample is to be avoided, and if formed, sufficient time must be allowed for all such

Table 13. ASTM Precision for D 1298 and D 287 [2]

Test procedure	Type of petroleum product	Temperature range	Units	Repeat-ability	Reproduc-ibility
D 1298	Transparent, nonviscous	-2 to 24.5°C	Density (kg/L at 15°C)	0.0005	0.0012
		29 to 76°F	Specific gravity (at 60°F/60°F)	0.0005	0.0012
		42 to 78°F	API gravity (degrees at 60°F)	0.1	0.3
D 1298	Opaque, nonviscous	-2 to 24.5°C	Density (kg/L at 15°C)	0.0006	0.0015
		29 to 76°F	Specific gravity (at 60°F/60°F)	0.0006	0.0015
		42 to 78° F	API gravity (degrees at 60°F)	0.2	0.5
D 287	All	42 to 78°F	API gravity (degrees at 60°F)	0.2	0.5

Table 14. Measurement of the API Gravity for Recycled Oils, Used Oils, and Fuel Oil/Used Oil Blends (D 1298)[a]

Fuel oil grade	Description	Sample number	Percent recycled oil	API gravity, degrees [at 60° F (15.6° C)]	
				Operator 1	Operator 2
1	Virgin distillate fuel oil	F132	0	42.3	42.9, 43.0
	Blend	(F132)	(5)[b,c]	41.9	41.7, 41.7
	Blend	(F132)	(10)[b,c]	----	41.2, 41.3
2	Virgin distillate fuel oil	F131	0	35.0	35.0
	Blend	(F131)	(5)[b,c]	34.7	34.6
	Blend	(F131)	(10)[b,c]	34.1	34.0
---[d]	Recycled distillate fuel oil	7L24	100	----	34.1, 34.1 (trial 1) 34.3, 34.3 (trial 2)
5	Recycled fuel oil	F133	100	26.4	25.8, 25.8
.5	Recycled fuel oil	F134	100	26.8, 26.8	26.6, 26.6, 26.4, 26.5(trial 1) 25.8, 25.7 (trial 2) 25.6 (trial 3)[e]
---	Composite used oil	W023	(100)[c]	26.8	26.6 (trial 1) 26.4, 26.4 (trial 2)[e]
---	Composite used oil	W022	(100)[c]	26.6	26.8, 26.8 (trial 1) 26.4, 26.4 (trial 2)[e]
---	Composite used oil	W033	(100)[c]	----	28.6, 28.6, 28.7, 28.7 (trial 1) 28.8, 28.8 (trial 2)[e]
5	Virgin residual fuel oil	F125	---	23.2	23.8, 23.9 (trial 1) 23.7, 23.7 (trial 2)[e] 23.5 (trial 3)
6	Virgin residual fuel oil	F130	---	17.9	17.9
6	Virgin residual fuel oil	F022	---	11.0	11.2

[a] For purposes of the ASTM repeatability and reproducibility (Table 13), these samples are assumed to be "non-viscous".

[b] W022 composite used oil.

[c] Not processed beyond collection and storage.

[d] Viscosity characteristics of this oil place it between grade Nos. 2 and 4.

[e] For these trials, efforts were made to minimize bubble formation (see text).

bubbles to come to the surface and be removed from the cylinder. The data in table 14 demonstrate this problem, and the API gravity values for several heavier residual oils were generally lower in later trials after more gentle agitation was employed.

CONCLUSION

The density, specific gravity, or API gravity is a useful characteristic for the evaluation and monitoring of fuel oils. The ASTM test procedures D 1298-67, "Density, Specific Gravity or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method," and D 287-67, "API Gravity of Crude Petroleum and Petroleum Products (Hydrometer Method)," have been evaluated for use with recycled fuel oils, used oils, and blends of virgin fuel oils with used oils. These tests may be used to establish that a fuel oil product meets the appropriate requirements for density, specific gravity, or API gravity.

5.2.6 Copper Corrosion

Tests for corrosion are of a qualitative type and are made to ascertain whether fuel oils are free of a tendency to corrode copper fuel lines and brass or bronze parts used in the burner assemblies [19]. The copper corrosion test is considered to be a test for "active" or "corrosive" sulfur in petroleum products and, as such, complements the test for total sulfur, which is discussed in Section 5.3.4, Total Sulfur, of this report.

Organic sulfur compounds (e.g., mercaptans, sulfides, polysulfides, thiophenes, etc.) are present in most petroleum products in variable amounts, depending on the crude oil origin and the refining processes [3]. Tests of the tendencies of the fuel oil to corrode copper and copper alloys are made using specially prepared copper strips. The effects due to corrosive species in the oil are indicated by discoloration and blackening of the strip [3]. Fuel oil specifications usually place limits on the degree of staining permitted by distillate fuel oils.

The test procedure commonly used to measure copper corrosion is ASTM D 130-75, "Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test" [2]. This method is identical to Method 5325 - Federal Test Method Standard No. 791B, Institute of Petroleum designation IP 154/69, British Standard 4351, and Deutsche Norm DIN 51756.

The D 130 procedure is conducted as follows: "A polished copper strip is immersed in a given quantity of sample and heated at a temperature and for a time characteristic of the material being tested. At the end of this period the copper strip is removed, washed, and compared with the ASTM Copper Strip Corrosion Standards" [2]. It is assigned a numerical rating from 1a (slight tarnish) to 4c (corrosion). Thus, the corrosiveness of the sample is interpreted "...accordingly as the appearance of the test strip agrees with one of the strips of the ASTM Copper Strip Corrosion Standards" [2]. Consequently, the ASTM D 130 test procedure is a qualitative one, and no statements are included in the test regarding repeatability and reproducibility [2].

The D 130 copper corrosion test was evaluated for use with recycled oils. As a part of this evaluation, the test was applied to virgin fuel oils, used oils, and recycled oils. The results are summarized in tables 15 and 16. Table 15 contains the results of the D 130 test with the conditions called for in the ASTM D 396 fuel oil specification, 3 hours at 50° C. Increasing the test temperature to 100° C, as called for in the Federal specification VV-F-815C, resulted in a moderate increase in the severity of the test (i.e., increased corrosion of the copper strip) as indicated by the test results shown in table 16. Note that one of the recycled oils, the distillate oil (7L24), caused copper corrosion as defined by the ASTM standard strips (i.e., number 4 rating) at the 100° C temperature but did not at 50° C.

Table 15. Copper Corrosion Test on Fuel Oils at 50° C for 3 Hours (D 130)

Fuel oil grade	Sample number	Description	Tarnish classification	Designation	Color
2	F131	Virgin fuel oil	1a	Slight tarnish	Light orange
			1a	Slight tarnish	Light orange
---	7L24	Recycled distillate fuel oil	2b	Moderate tarnish	Violet pink
			2b	Moderate tarnish	Violet pink
Blend		90% No. 2; 10% used oil[b]	1a	Slight tarnish	Yellow/brassy
			1a	Slight tarnish	Yellow/brassy
Blend		50% No. 2; 50% used oil[b]	1a	Slight tarnish	Yellow/brassy
			1a	Slight tarnish	Yellow/brassy
---	W022	Composite used automotive oil	1a	Slight tarnish	Light orange
			1a	Slight tarnish	Light orange
---	W037	Industrial waste oil (Source B)	4a	Dark tarnish/ corrosion	Multicolored/ black
			4a	Dark tarnish/ corrosion	Multicolored/ black
---	W033	Composite used oil from service station	1a	Slight tarnish	Light yellow
			1a	Slight tarnish	Light yellow

---

[a] Viscosity measurements on this oil place it between garde Nos. 2 and 4.

[b] Used oil was W022; virgin distillate fuel oil was F131.

Table 16. Copper Corrosion Test on Fuel Oils and Used Oils at 100° C for 3 Hours (D 130)

Fuel oil grade	Sample number	Description	Tarnish classification	Designation	Color
2	F131	Virgin fuel oil	1a 1a	Slight tarnish Slight tarnish	Light orange Light orange
Blend		90% No. 2; 10% used oil[a]	1b 1b	Slight tarnish Slight tarnish	Yellow/orange Yellow/orange
Blend		50% No. 2; 50% used oil	1b 1b	Slight tarnish Slight tarnish	Yellow/orange Yellow/orange
4	F126	Virgin fuel oil	1b 1b	Slight tarnish Slight tarnish	Dark orange Dark orange
4	F129	Virgin fuel oil	1c 1b	Slight tarnish Slight tarnish	Dark orange Dark orange
5	F125	Virgin fuel oil	1a 1a	Slight tarnish Slight tarnish	Light orange Light orange
6	F130	Virgin fuel oil	1a 1a	Slight tarnish Slight tarnish	Light orange Light orange
6	F022	Virgin fuel oil (high sulfur)	1a 1a	Slight tarnish Slight tarnish	Light orange Light orange
---	W022	Composite Used Automotive oil	2c 2c	Moderate tarnish Moderate tarnish	Multicolored Multicolored
---	W033	Composite used automotive oil from service station A	3b 3b	Dark tarnish Dark tarnish	Magenta/ multicolored Magenta/ multicolored

Table 16. Copper Corrosion Test on Fuel Oils and Used Oils at 100° C for 3 Hours (D 130) (continued)

Fuel oil grade	Sample number	Description	Tarnish classification	Designation	Color
---	W040	Composite used automotive oil from service station B	2a	Moderate tarnish	Red
---[b]	7L24	Recycled distillate fuel oil	4a 4b	Corrosion Corrosion	Black Black
5	F133	Recycled fuel oil (source A)	2c 3a	Moderate tarnish Dark tarnish	Multicolored Multicolored
5	F134	Recycled fuel oil (source B)	2b 2b	Moderate tarnish Moderate tarnish	Magenta Magenta
---	W036	Industrial waste oil (source A)	1a	Slight tarnish	Light orange
---	W037	Industrial waste oil (source B)	4c	Corrosion	Black

[a] Used oil was W022; virgin distillate fuel oil was F131.

[b] Viscosity measurements on this oil placed it between grade Nos. 2 and 4.

CONCLUSION

The corrosive properties of a recycled fuel oil are measured in order to assure long burner life and adequate performance in the field. ASTM test procedure D 130-75 has been evaluated for recycled oils and can be used to indicate the relative corrosiveness of the fuel oil for copper and copper-alloy components.

5.2.7 Aniline Point

The aniline point is defined as the minimum equilibrium solution temperature for equal volumes of aniline and sample [2]. The aniline point is useful as an aid in the characterization of pure hydrocarbons and in the analysis of hydrocarbon mixtures. Aromatic hydrocarbons exhibit the lowest and paraffins the highest aniline point values [2]. Because of these differences, the aniline point is often used to provide an estimate of the aromatic hydrocarbon content of petroleum mixtures. Oils with high aromatic content have swelling and deteriorating effects on natural and synthetic rubbers [18]. The aniline point may therefore be of interest for distillate fuel oil products that come in contact with rubber gaskets or seals.

The test procedure for aniline point is ASTM D 611-77, "Aniline Point and Mixed Aniline Point of Petroleum Products and Hydrocarbon Solvents." In this method, "Specified volumes of aniline and sample, or aniline and sample plus *n*-heptane, are placed in a tube and mixed mechanically. The mixture is heated at a controlled rate until the two phases become miscible. The mixture is then cooled at a controlled rate and the temperature at which two phases separate is recorded as the aniline point or mixed aniline point" [2].

Test procedure ASTM D 611-77 is called for in the Federal and military specifications for distillate fuel oils, although limits are

not specified. It is not included in the ASTM fuel oil specifications. The repeatability for the D 611 test for virgin fuel oils is given as 0.16° C (0.3° F) for clear or light-colored samples, and 0.3° C (0.6° F) for moderately dark to very dark samples [2]. Alternative variations of this method (methods A through E) are given in the ASTM test procedure. Method A was used in this study and is used with transparent distillate fuel oils. Method B was not specifically evaluated in this study but is a thin-film version of method A (based on the same chemical principle) for use with highly colored samples. Methods C and D are not appropriate for burner fuel oils, and method E is used only with a specific automatic aniline point apparatus. The aniline points of several virgin distillate fuel oils were determined, and the repeatability of the results, as shown in table 17, is consistent with the stated ASTM repeatabilities.

The D 611 test procedure (method A) was evaluated for use with recycled oils. As part of this evaluation the aniline point was determined for several virgin distillate fuel oil/used oil blends and a recycled distillate fuel oil. These data are also shown in table 17 and indicate that the repeatability of the aniline point test for these samples is consistent with the stated ASTM repeatability.

The aniline point could be determined for several blends of virgin distillate fuel oil with up to 10-percent used automotive crankcase oil using supplementary lighting behind the sample. If even darker samples are to be measured, the thin-film variation of D 611, method B, may need to be used.

Table 17. Repeatability of the Aniline Point Test Procedure for Distillate Fuel Oils (D 611, Method A)

Fuel oil grade	Sample number	Description	Color	Aniline point [°C (°F)]
1	F132	Virgin fuel oil	Light yellow	64.0, 64.0 (147.0)
2	F131	Virgin fuel oil	Medium yellow	59.0, 59.0 (138.0)
---[a]	7L24	Recycled distillate fuel oil	Yellow-brown	80.0, 80.0 (176.0)
(2)[b]	F131[c]	Blend (1% W022)	Medium brown	59.2, 59.2 (138.5)
(2)[b]	F131[c]	Blend (5% W022)	Dark brown[d]	62.0, 62.2 (143.6, 144.0)
(2)[b]	F131[c]	Blend (10% W022)	Very dark[d]	80.0, 80.0 (176.0)

[a] Viscosity characteristics of the recycled distillate fuel oil place it between Grades Nos. 2 and 4.

[b] Such blends are not considered distillate fuels for some purposes.

[c] Sample number indicated is for the virgin distillate fraction.

[d] These samples required special illumination (light behind aniline point apparatus) to observe the aniline point.

CONCLUSION

The aniline point may be of interest to obtain a relative indication of the aromatic content of a distillate fuel oil. Method A of ASTM method D 611 "Aniline Point and Mixed Aniline Point of Petroleum Products and Hydrocarbon Solvents," has been evaluated and may be used to obtain the aniline point of recycled distillate oils to be used for fuel.

5.2.8 Heating Value

Since the primary function of a fuel oil is to produce heat, the combustion energy, often referred to as heating value or calorific value, is an important fuel property. A knowledge of the heating value (i.e., heat of combustion) is necessary to determine the combustion efficiency and performance of all types of oil-burning equipment, as well as to assure equity in commerce [3].

The heating value of a fuel is the amount of heat given off as a result of its complete combustion. The results are usually expressed as "megajoules per kilogram" (MJ/kg) or, more conventionally, "British thermal units per pound" (Btu/lb) [19]. (Note: One Btu/lb is equivalent to 2.326 kJ/kg; 1000 kJ/kg = 1 MJ/kg. The Btu used throughout this section is the International Table Btu.)

The variation in heating value within a particular virgin fuel oil grade is small, and it is often stated that the value can normally be calculated with sufficient accuracy from other known data [19]. The heating value is often not quoted in virgin fuel oil specifications as it is not directly controllable in the manufacture of the fuel [3, 19]. The specific gravity or the related quantity API gravity, normally included in fuel oil specifications, is often used to estimate the heating value of virgin fuel oils [19], and this will be discussed later in this section.

The direct determination of the heating value is made in an oxygen bomb calorimeter under specified conditions involving careful standardization of equipment and rigid adherence to prescribed details of operation. When properly run, the bomb calorimeter test can yield highly accurate results, but is time consuming and costly to perform on a routine basis [19].

The test procedure used to experimentally determine the heating value of virgin fuel oils is ASTM D 240-76, "Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter" [2]. This test is identical to Method 2502 - Federal Test Method Standard No. 791B, and is similar to the Institute of Petroleum test IP 12/73 and British Standard BS 4379:1969. The D 240 test procedure states that the "Heat of combustion is determined in this method by burning a weighed sample in an oxygen bomb calorimeter under controlled conditions. The heat of combustion is computed from temperature observations before, during and after combustion, with proper allowance for thermochemical and heat transfer corrections" [2].

A second test procedure, ASTM D 2382-76, "Heat of Combustion of Hydrocarbon Fuels by Bomb Calorimeter (High-Precision Method)," is similar to D 240, but modified to provide increased measurement precision for special applications such as weight-limited vehicles. D 2382 is based on procedures developed at NBS [23]. This high-precision test procedure is not required for routine measurements on burner fuel oils.

The results of D 240 can be expressed in two ways, as the "Gross Heat of Combustion" [H_g or Q_v(gross)], or as the "Net Heat of Combustion" [H_n or Q_p (net)]. The gross heat of combustion is defined as "...the heat released by the combustion of a unit mass of fuel in a constant volume bomb with substantially all of the water condensed to the liquid state" [2]. The net heat of combustion is "...the heat released by the combustion of a unit mass of fuel at a constant pressure of 1 atm [atmosphere] (0.1 MPa) with the water remaining in the vapor state..." [2]. The gross heat of combustion is the value measured directly when using conventional bomb calorimetry, and is the quantity preferred by the ASTM for reporting the heating value of fuel oils [2]. The net heat of combustion, H_n, is stated to be the most significant value for estimation of heat system efficiencies. However, the accurate determination of H_n requires knowledge of the hydrogen content of the fuel [2,24]. Since the emphasis of this report is on more routine test methods, only the gross heat of combustion was considered.

The precision of the D 240 test procedure is stated to provide a repeatability of 0.13 MJ/kg (55 Btu/lb) and a reproducibility of 0.40 MJ/kg (175 Btu/lb) [2].

The D 240 test procedure was evaluated for use in determining the heating value of recycled oils to be used for fuel. As a part of this evaluation, the D 240 test procedure was applied to a number of virgin fuel oils, recycled used oils, and composite used automotive oils. The data are shown in table 18. The NBS Reference Method given in the table

Table 18. Experimental Heat of Combustion Data

Fuel oil grade	Sample number	Description	Experimental gross heat of combustion [MJ/kg (Btu/lb)]		
			NBS Reference Method[a]	Commercial laboratory A[b]	Commercial laboratory B[b]
5	F125	Virgin fuel oil	44.05 (18,939) 44.07 (18,948)	43.88 (18,867)	44.12 (18,969)
5	F133	Recycled fuel oil[c]	42.95 (18,466) 42.97 (18,472)	44.50 (19,133)	44.17 (18,989)
5	F134	Recycled fuel oil	44.04 (18,935) 44.05 (18,940)	44.18 (18,993)	44.28 (19,037)
6	F022	Virgin fuel oil	42.15 (18,120) 42.13 (18,112)	41.98 (18,050)	42.38 (18,218)
6	F130	Virgin fuel oil	43.49 (18,696) 43.50 (18,701)	43.42 (18,668)	43.53 (18,713)
---	W022	Composite used automotive oil	43.65 (18,768) 43.66 (18,769)	44.02 (18,924)	43.23 (18,586)
---	W023	Composite re-refiners feedstock (dried)	44.29 (19,042) 44.29 (19,042)	44.31 (19,050)	44.36 (19,073)
---	W033	Composite used automotive oil from service station (dried)	44.98 (19,338) 44.98 (19,337)	45.01 (19,350)	44.82 (19,270)

[a] Reference method was similar to ASTM D 2386, which is a more precise method than D 240 [23].

[b] Test procedure used was ASTM D 240.

[c] Note discussion of this sample in text.

is described in reference 23, from which test procedure D 2382 is derived, and is more accurate than D 240. The use of this reference method on used and recycled oils provided a precise baseline against which a comparison of the heating value of recycled oils, as measured by two commercial testing laboratories using D 240, could be made.

With one exception, the results from both commercial laboratories were in good agreement with the NBS values. Sample F133 results were considerably higher than the NBS results (3.6 percent and 2.8 percent), even though they agreed with each other well within the stated D 240 reproducibility. This sample contains an unusually high ash content (4.7 percent sulfated ash, D 874) and was identified during analyses of other impurities as having a high rate of particulate settling. These characteristics of F133 are consistent with the possibility that the commercial laboratories did not obtain a representative portion of the ash-forming constituents, which would result in a high heating value. The NBS analyst was aware of the high particle content of most used and recycled oils, and employed very vigorous agitation immediately prior to removing the analytical sample. It therefore is reasonable to suggest that the higher results of the commercial laboratories compared to the NBS results for sample F133 may well represent the difficulties in representative sampling of an inhomogeneous material. (See also discussion on this sample later in this section.)

The results from the two commercial testing laboratories also agreed well with each other. Laboratory A obtained heating values which

fell within 1 percent of the heating values obtained by laboratory B for 7 of the 8 oil samples. Our conclusion is that the D 240 test procedure is effective in measuring the heating value of recycled oils used for fuel when a representative sample is taken for analysis.

In addition to the direct determination of fuel oil heating value for fuel oils, indirect methods for estimating the heating value are often used in practice [19]. These indirect methods have gained wide popularity due to their simplicity and low cost. These indirect methods are based on the correlation of the heat of combustion with the specific gravity or API gravity, and empirical tables have been prepared for virgin oils [24, 25]. Values in these tables can be corrected for the amounts of water, sulfur and ash found in fuel oils to obtain a more accurate heating value [24]. Reference 24 states that this procedure gives estimates of the heating value of virgin fuel oils good to within 1 percent of the measured heating value.

The equation upon which these tables are based is given in reference 24:

Q_v (gross) = 12,400 - 2100 d^2 in calories/g where

d = specific gravity at 60°/60° F

To convert this equation to International Table Btu/lb, it must be multipled by the following factors:

$$Q_v \text{ (gross)} = 1.8[(12{,}400 - 2100\ d^2) \times \frac{4.183}{4.1868}] \qquad (1)$$

Equation (1) can also be written in terms of API gravity, using the relationship between specific gravity and API gravity given in Section 5.2.5 of this report:

$$Q_v \text{ (gross)} = 22{,}300 - \frac{75{,}615{,}000}{(131.5 + °\text{API})^2} \quad (\text{Btu/lb})_{\text{IT}} \qquad (2)$$

$$Q_v \text{ (gross)} = 51.869 - \frac{175{,}880}{(131.5 + °\text{API})^2} \quad (\text{MJ/kg}) \qquad (3)$$

Table 19 gives the gross heat of combustion for mixed hydrocarbon fuels having no water, sulfur, or ash, calculated from the API gravities. The Btu/lb values in the table are calculated from equation (2) and rounded to the nearest 10. The MJ/kg values are calculated from equation (3), and rounded to the nearest 0.01.

Reference 24 gives an equation to correct the gross heating value for the amounts of water, sulfur, and ash found in fuels:

$$\bar{Q}_v = Q_v - 0.01\ Q_v \cdot (\%\ H_2O + \%\ \text{ash} + \%\ S) + X \cdot (\%\ S) \qquad (4)$$

where $\bar{Q}_v$ = corrected heat of combustion.[7]

Q_v = uncorrected heat of combustion (from eq. (2) or (3) in the text).[8]

---

[7] The symbols $\bar{Q}_v$ and Q_v are those used in reference 24; $\bar{Q}_v$ corresponds to H_g as H_g is defined in D 240.

[8] With slightly less accuracy, table 19 may be used.

Table 19. Uncorrected Gross Heat of Combustion for Fuel Oils as Estimated from Their Gravity [24]

Gravity		Density	Uncorrected gross heat of combustion at constant volume (Q_v)	
Degrees API at 60° F	Specific at 60°/60° F	Pounds per gallon	MJ/kg[a]	Btu/lb[b]
10	1.0000	8.337	43.08	18,520
11	.9930	8.279	43.21	18,580
12	.9861	8.221	43.33	18,630
13	.9792	8.164	43.45	18,680
14	.9725	8.108	43.56	18,730
15	.9659	8.053	43.67	18,780
16	.9593	7.998	43.78	18,820
17	.9529	7.944	43.89	18,870
18	.9465	7.891	44.00	18,920
19	.9402	7.839	44.10	18,960
20	.9340	7.787	44.21	19,000
21	.9279	7.736	44.31	19,050
22	.9218	7.686	44.40	19,090
23	.9159	7.636	44.50	19,130
24	.9100	7.587	44.60	19,170
25	.9042	7.538	44.69	19,210
26	.8984	7.490	44.78	19,250
27	.8927	7.443	44.87	19,290
28	.8871	7.396	44.96	19,330
29	.8816	7.350	45.04	19,360
30	.8762	7.305	45.13	19,400
31	.8708	7.260	45.21	19,440
32	.8654	7.215	45.29	19,470
33	.8602	7.171	45.37	19,510
34	.8550	7.128	45.45	19,540
35	.8498	7.085	45.52	19,570
36	.8448	7.043	45.60	19,600
37	.8398	7.001	45.67	19,640
38	.8348	6.960	45.75	19,670
39	.8299	6.920	45.82	19,700
40	.8251	6.879	45.89	19,730
41	.8203	6.839	45.96	19,760
42	.8155	6.799	46.03	19,790
43	.8109	6.760	46.09	19,820
44	.8063	6.722	46.16	19,840
45	.8017	6.684	46.22	19,870
46	.7972	6.646	46.29	19,900
47	.7927	6.609	46.35	19,930
48	.7883	6.572	46.41	19,950
49	.7839	6.536	46.47	19,980

[a] The column in MJ/kg does not appear in the original reference but was added for the purposes of this report (calculated from the basic equation).

[b] The values were calculated from the basic equation in terms of International Table Btu/lb (see text).

$$X = 0.0941 = 22.5 \times 4.183 \times 10^{-3} \text{ for units of MJ/kg;}$$

$$= 40.5 = 22.5 \times \frac{4.183}{4.1868} \times 1.8 \text{ for units of Btu/lb.}$$

% H_2O = water content of fuel oil in percent by weight.

% ash = noncombustible content of fuel oil in percent by weight.

% S = sulfur content of fuel oil in percent by weight.

In order to examine the indirect method for estimating the heating value of recycled fuel oils, a number of recycled fuel oils and composite used automotive oils were investigated. The density (API gravity) of these oil samples was measured using ASTM test procedure D 1298 (see also this report, Section 5.2.5, Density, for a discussion of density measurements on recycled oils). Using equations (2) and (3), the uncorrected gross heats of combustion were then obtained (Q_v). These values were corrected for the water, ash, and sulfur contents of the samples using equation (4), and the corrected gross heats of combustion calculated ($\overline{Q}_v$). It should be noted that these corrections can be substantial--up to 5.5 percent of the heat of combustion--for even this relatively small sample group. Final values were rounded to the nearest 0.01 MJ/kg (10 Btu/lb) and are given in table 30.

The test procedures used to obtain the various corrections in table 20 were ASTM D 95-70, "Water in Petroleum Products and Bituminous

Table 20. Comparison of Estimated and Experimental Gross Heats of Combustion [MJ/kg (Btu/lb)]

Fuel oil grade	Sample number	Description	Specific gravity, °API	$\overline{Q}_v$ (corrected)[a] Using D 482 ash	Using D 874 ash	Experimental heat of combustion[b]
5	F133	Recycled fuel oil	25.8	42.46 (18,260)	42.41 (18,230)	42.96 (18,469)
5	F134	Recycled fuel oil	25.7	43.87 (18,860)	43.74 (18,800)	44.05 (18,938)
---	W022	Composite used automotive oil	26.4	43.78 (18,820)	43.39 (18,650)	43.66 (18,768)
---	W023	Composite re-refiner's feed-stock (dried)	26.4	44.11 (18,960)	44.03 (18,930)	44.29 (19,042)
---	W033	Composite used automotive oil from service station (dried)	28.7	44.62 (19,180)	44.61 (19,180)	44.98 (19,338)

[a] $\overline{Q}_v$ (corrected) = estimated gross heat of combustion corrected for water, ash, and sulfur contents (see text).

[b] Average experimental gross heat of combustion value using high-precision oxygen bomb calorimetry (NBS Reference Method) [23].

Materials by Distillation," for the water content (see also Section 5.3.1, this report), and ASTM D 1552-64, "Sulfur in Petroleum Products (High-Temperature Method)," for the sulfur content (see also Section 5.3.4, this report). The appropriate test method for ash required additional evaluation since equation (4), an empirical equation developed through analyses of many samples of virgin fuels, was apparently based on results obtained using the ASTM D 482 (regular) ash method, or equivalent. However, as discussed in detail in Section 5.3.3 of this report, the sulfated ash (ASTM D 874) is required to retain all the ash-forming constituents in a recycled or used oil. Since the sulfated ash value was always greater than the regular ash value for the used and recycled oils examined, the substitution of the sulfated ash value in the heating value calculation may produce a systematic shift. Therefore, corrected estimated heating values were calculated for both ash methods (see table 20), and the results are discussed below.

These estimated heating values can be compared with the experimental results from the NBS Reference Method of high-precision oxygen bomb calorimetry, also given in table 20. It can be seen that the estimates agree well with the experimental values for the oils; with one exception--recycled fuel oil (F133)--all of the estimated heating values fall within 1 percent of the NBS values, regardless of the ash test procedure used. The F133 value was overcorrected by somewhat more than 1 percent for both cases.

There is a small systematic difference in the results: the estimated heating values based on the regular (D 482) ash correction more closely approximate the NBS experimentally determined values than the estimates based on the sulfated (D 874) ash correction by about 0.3 percent, a negligible amount. Thus, for this group of oils the sulfated ash (D 874) correction is adequate.

These results suggest that the gross heat of combustion may be obtained for recycled oils through use of density measurements and corrections (the indirect method). Given the limited specific gravity range examined (25.7 - 28.7° API), further investigation would appear necessary before the indirect method could be recommended.

CONCLUSION

The heating value or combustion energy is an important characteristic of fuel oils. ASTM test D 240-76, "Heat of Combustion of Hydrocarbon Fuels by Bomb Calorimeter," has been evaluated for use with recycled fuel oils, and used oils. This test procedure may be used to establish the heating value of a recycled oil to be used as fuel, with the modification that the recycled oil sample be vigorously agitated immediately prior to taking the test sample so that all particulate material be in complete suspension.

In addition, our limited results indicate that the indirect method for estimating heating value, as described above and with the appropriate corrections, may be able to be used to obtain the heating value of recycled oils. It is suggested, however, that at the present time primary reliance be placed on the D 240 method as standard.

5.3 Test Procedures for Impurities

This section contains evaluated test procedures for the determination of impurities which are deleterious to the performance of a recycled oil to be used as a burner fuel. The impurities which are currently included in virgin fuel oil specifications are water and sediment, carbon residue, ash, total sulfur, and acid. Test procedures for measuring these impurities are also recommended for use with recycled oils, with the modifications as described in the individual test procedures.

These test procedures were evaluated for use with recycled oils using the evaluation process described in section 4 of this report. In general, test procedures for these impurities must be evaluated for their ability to reliably measure the constituent under test.

The individual test procedures are discussed below.

5.3.1 Water and Sediment

Water and insoluble impurities (sediment) are present in most crude oils and in some semi-refined products such as fuel oils [18]. Appreciable amounts of water and sediment in a fuel oil tend to cause fouling of handling facilities and to give trouble in burner mechanisms. Sediment may accumulate in storage tanks and on filter screens or burner parts, resulting in obstruction to free passage of oil from the tank to the burner. Significant amounts of water can lead to the production of emulsions which are removable only with difficulty [3]. Water is considered an important cause of corrosion in tanks and equipment (excluding copper and copper-containing alloys), and the corrosive deterioration of storage tanks is often associated with the water bottoms which accumulate from atmospheric condensation and contamination [3].

The amounts of water and sediment in petroleum products are determined by three general techniques: centrifugation, distillation, and extraction. In centrifugation, water and sediment are separated from the petroleum product and measured volumetrically; in distillation, water is separated from the petroleum product and measured volumetrically; and in extraction, the solid insoluble components above a certain size are separated from the petroleum product and measured by weight.

The specific test procedures which are commonly used for the determination of water and sediment in petroleum products are the following:

ASTM D 1796-68 (reapproved in 1973), "Water and Sediment in Crude Oils and Fuel Oils by Centrifuge" [27]; ASTM D 96-73 (reapproved in 1977), "Water and Sediment in Crude Oils" [2]; ASTM D 95-70 (reapproved in 1975), "Water in Petroleum Products and Bituminous Materials by Distillation" [2]; and ASTM D 473-69 (reapproved in 1974), "Sediment in Crude and Fuel Oils by Extraction" [2]. The D 1796 and D 96 Methods are actually multiple test procedures and reference the D 95 test for water and the D 473 test for sediment, calling them "Base Methods" (D 96) or for "difficult types of oils" (D 1796).

ASTM method D 1796 is the test procedure generally used for virgin fuel oils and is the method cited in the ASTM specification (D 396-76) and the Federal specification (VV-F-815C) for burner fuel oil grades 1 through 5. (Note: For grade 6 fuel oil, these specifications cite methods D 95 for water and D 473 for sediment.) D 1796 is identical to Method 3000 - Federal Test Method Standard No. 791B, to the API Standard 2548, to the Institute of Petroleum Designation 75/69, to the British Standard 2882, and to the Deutsche Norm DIN 51793. This method (D 1796) covers the determination of water and sediment in crude oils and fuel oils by diluting with an equal volume of toluene saturated with water, thorough, mixing, heating to a prescribed temperature, and then spinning at a specified centrifugal force and time period. Centrifuging is repeated until two consecutive readings of the combined water and sediment agree. For domestic usage in the United States, the D 1796 method refers the user to ASTM method D 96 and notes that (1) some oils may require other

solvents or solvent-demulsifier combinations for adequate separation of the water and sediment, and (2) "...with some types of oils it is difficult to obtain water and sediment contents with this method. When this situation is encountered, ASTM Method D 95-API 2560, Test for Water in Petroleum and Other Bituminous Materials or IP 74 and ASTM Method D 473-API 2561-IP 53, Test for Sediment in Crude and Fuel Oils by Extraction may be used" [27].

A second test procedure is ASTM D 96-73, "Water and Sediment in Crude Oils" [2]. This procedure is identical to Method 3003 - Federal Test Method Standard No. 791B, to the API Standard 2542, and to the Deutsche Norm DIN 51793. The D 96 test procedure defines a primary centrifuge method and two alternative centrifuge methods for determining the volume of combined water and sediment in crude oil. It further specifies Base Methods for water (by distillation, using ASTM D 95) and sediment (by extraction, using D 473), determined separately. [Note: Although the D 96 procedures are described as being for crude oil, the D 1796 centrifuge test for water and sediment in fuel oils refers the user to the D 96 method for unusual or difficult samples.] The D 96 Primary Method (and Alternative Method A) describes various possible solvents, demulsifiers, and temperatures to consider for difficult to analyze oil samples. Alternative Method B describes a simplified test procedure. In cases of dispute as to which water and sediment test value is the "true" value, the D 96 Base Method states that "The sum of the results

obtained in accordance with the latest edition of Method D 95 - API 2560 [note: water by distillation] and Method D 473 - API 2561 [note: sediment by extraction], shall be the correct value for water and sediment. These methods shall be considered as the Base Method and shall be used when agreement cannot be reached between the purchaser and seller when using any of the other methods described" [2].

The distillation test procedure for water is ASTM D 95-70 (reapproved in 1975), "Water in Petroleum Products and Bituminous Materials by Distillation" [2]. This procedure is identical to the API Standard 2650, the Institute of Petroleum Designation 74/70, and the British Standard 4385. This method is stated to be applicable to crude petroleum, fuel oil, road oil, lubricating oil, and petroleum sulfonates (e.g., dispersants, detergents) [2]. In this method, the sample is refluxed with a water immiscible solvent which co-distills with the water in the sample; condensed solvent and water are continuously separated in a trap, the water settling in the graduated section of the trap and the solvent returning to the still [2].

The sediment by extraction test procedure is ASTM D 473-69 (reapproved in 1974), "Sediment in Crude and Fuel Oils by Extraction" [2]. This procedure is identical to Method 3002 - Federal Test Method Standard No. 791B, to the API Standard 2561, the Institute of Petroleum Designation 53/66, the British Standard 4382, and the Deutsche Norm DIN 51789. In this method, the sample is placed in a refractory thimble and extracted with hot toluene until the residue reaches constant weight.

Test procedures based on centrifugation are more rapid and less costly than the others available for water and sediment determinations. In addition, the specifications for virgin fuel oils place limits on the combined contaminants for all grades except grade 6. Thus, initial evaluation studies were directed towards this particular measurement technique. A number of recycled fuel oils and used automotive crankcase oils were analyzed for water and sediment using both D 1796 and D 96 (with 1 percent by volume of a demulsifier, n-butyl diethanolamine). The results from these two test procedures were then compared to results obtained by the D 96 Base Method (D 95 plus D 473). [Note: As recommended in D 96 for converting the D 473 results to a volume basis before combining with the D 95 results, the sediment value (obtained on a weight basis) was arbitrarily assigned a specific gravity of 2.0 for conversion to a volume basis.] These results are shown in table 21, and indicate that both these centrifuge methods, D 1796 and D 96 with demulsifier, give results very different from those obtained by the Base Method. These results can be explained by the high concentrations of contaminants such as dispersants, detergents, and finely divided particulates found in many recycled and used oils. These types of contaminants are known to cause difficulties with centrifugation methods [2]. Consequently, the D 96 and D 1796 test procedures utilizing centrifugation were not considered further, and the evaluation directed towards the test procedures constituting the D 96 Base Method (i.e., D 95 for water and D 473 for sediment).

The precision of D 95 (water by distillation) is stated to be as as

Table 21. Results from Centrifugation Methods for Water and Sediment

Fuel oil grade	Description	Sample number	Water and sediment concentrations, percent by volume		
			Centrifuge only (D 1796)	Centrifuge with demulsifier (D 96)[a]	Base Method (D 95 & D 473)[b,c]
5	Recycled fuel oil (source A)	F133	4.8, 4.7	4.8, 4.6	0.53
5	Recycled fuel oil (source B)	F134	6.4[d], 4.0[d] 0.6[e], 0.5[e]	6.0[d], 5.8[d] 6.6[e], 6.0[e]	1.29
---	Composite used automotive oil	W022	0.2, 0.1	6.0	0.22
---	Used oil feedstock to re-refiner (sampling period A)	W023	3.0	14.0, 13.4	5.73

[a] Demulsifier used was n-butyl diethanolamine at 1 percent by volume.

[b] The sediment concentrations used to calculate these values were those obtained with new extraction thimbles (see text).

[c] Percent by volume; sediment as determined by method D 473 assigned a specific gravity of 2.0 as recommended in D 96 (see text).

[d] Operator 1.

[e] Operator 2.

as follows (on samples of equal volume, using 10 mL or 25 mL traps) [2]:
"Repeatability" - Duplicate determinations of water by the same operator should be considered suspect if they differ by more than the following amounts:

Water Collected mL	
0 to 1.0	0.1 mL
1.1 to 25	0.1 mL or 2 percent of the mean, whichever is greater."

"Reproducibility - The results submitted by each of two laboratories should be considered suspect if they differ by more than the following amounts:

Water Collected mL	
0 to 1.0	0.2 mL
1.1 to 25	0.2 mL or 10 percent of the mean, whichever is greater."

It should be noted that D 95 does not require reporting of the sample volume taken nor the water volume actually collected, leading to possible problems in comparing the precision of results. It is therefore recommended that the test procedure for water by distillation (ASTM method D 95) be modified to include reporting the sample volume taken for analysis.

The ASTM D 95 test procedure for water by distillation was evaluated for use with recycled oils. As a part of this evaluation, the repeatability of the D 95 test procedure was determined for recycled fuel oils and used oils. The results of these tests are found in table 22, and indicate acceptable repeatabilities for these samples. These results tend to

confirm that the determination of water by distillation (D 95) is an acceptable test procedure for use with recycled oils to be used for fuel.

The ASTM D 473 test procedure for sediment by extraction was investigated next. The precision of the D 473 method is stated by ASTM as follows (for 0.0 to 0.4 percent sediment) [2]:

"Repeatability - Duplicate results by the same operator should be considered suspect if they differ by more than 0.017 + 0.255 S, where S is the average result in weight percent.

"Reproducibility - The results submitted by each of two laboratories should be considered suspect if the two results differ by more than 0.33 + 0.255 S, where S is the average result in weight percent."
The ASTM procedure does not provide precision criteria for sediment levels above 0.4 percent by weight.

The ASTM D 473 test procedure for sediment by extraction was then evaluated for use with recycled oils. As a part of this evaluation, the repeatability of the D 473 test procedure was determined for recycled oils, used oils and virgin fuel oils. The results of these tests are found in table 23.

As can readily be seen from table 23, test results for sediment

which include tests made with both new and reused thimbles vary widely. During this test evaluation, two details were detected which required further investigation. First, from visual observation of the extract it was apparent that fine particulates were passing through the refractory thimbles for the recycled oils and used oils. Second, it was noticed that the sediment values for recycled or used oils were lower for new thimbles, in spite of using the appropriate methods as specified in the D 473 procedure for reuse of the thimble. In some cases, as noted in table 23, reuse resulted in plugging of the thimbles, and therefore caused solvent and sample retention in the thimble throughout the remainder of the test procedure.

To investigate whether particulates were in fact passing through the refractory thimble during the extraction procedure, an extraction was performed on sample W022, and the toluene solvent containing the dissolved used oil plus any particles passing through the thimble was collected for examination with an electron microscope. To prepare the sample for this examination, a thin carbon-film grid was dipped into the thoroughly mixed solvent and oil, air dried, and coated with a thin layer of carbon. The samples were examined by scanning electron transmission microscopy, and a random collection of images taken. Three of these images are shown in figures 2, 3 and 4, with different magnifications as noted in the scale. It is apparent that large numbers of very small particles are present in this sample extract, and these particles have apparently readily passed through the refractory thimble. The particles

Table 22. Repeatability of the Water by Distillation Test Procedure (D 95)

Fuel oil grade	Description	Sample number	Test sample volume (mL)[a]	Water by distillation, D 95 (% by volume)
5	Recycled fuel oil (source A)	F133	100	0.13, 0.20
5	Recycled fuel oil (source B)	F134	100	0.60, 0.70, 0.63
---	Composite used automotive oil	W022	100	0.20, 0.19, 0.20, 0.18
---	Used oil feedstock to re-refiner (sampling period A)	W023	50	5.78, 5.60
---	Used oil feedstock to re-refiner (sampling period B)	W024	50	3.60, 3.50
6	Virgin residual fuel oil	F022	50	0.04, 0.04

[a] Sample volume not required to be reported by ASTM D 95 method, but necessary in order to establish repeatability and reproducibility.

Table 23. Repeatability of Test for Sediment by Extraction (D 473)

Fuel oil grade	Description	Sample number	Sediment concentrations (% by weight)	
			New thimbles	Reused thimbles
2	Virgin fuel oil	F131	0.018, 0.011	----
6	Virgin fuel oil, (source A)	F130	0.039, 0.016, 0.043	0.033, 0.030, 0.038 0.101, 0.019
6	Virgin fuel oil, (source B)	F022	0.016, 0.019	0.004, 0.002
5	Recycled fuel oil, (source A)	F133	1.05, 0.61, 0.57	4.28[a], 4.45, 4.11, 3.90, 3.78
5	Recycled fuel oil, (source B)	F134	1.01, 1.43, 1.37, 1.39, 1.34	6.15[a], 6.56[a], 0.96
---	Composite used automotive oil	W022	0.067, 0.070, 0.017	0.44, 1.71, 0.32, 0.24
---	Used oil feedstock to re-refiner (source A)	W023	0.085, 0.062	2.54, 1.42

[a] Thimble plugged during extraction (see text).

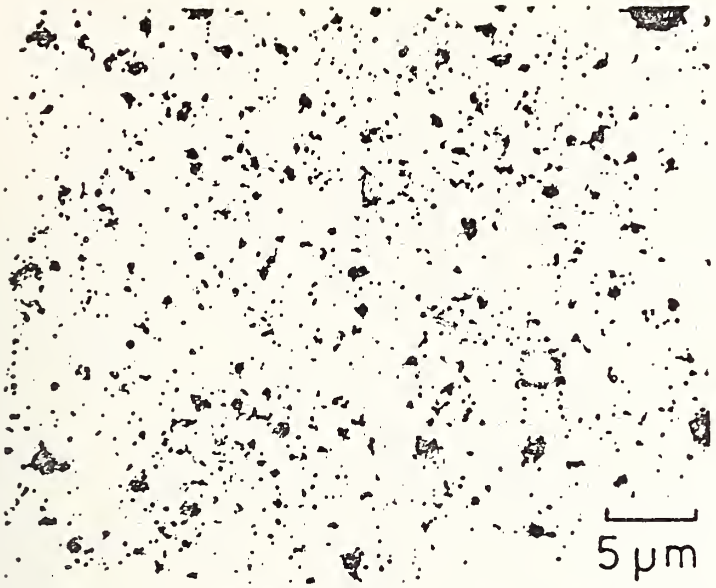

Figure 2.

Electron Photomicrograph of Particles in Used Automotive Oil Extract at 2500 X Magnification.

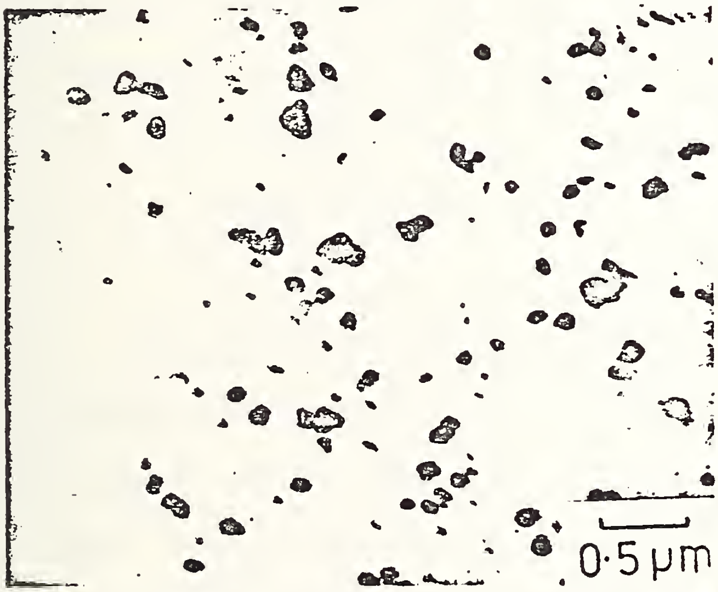

Figure 3.

Electron Photomicrograph of Particles in Used Automotive Oil Extract at 25,000 X Magnification.

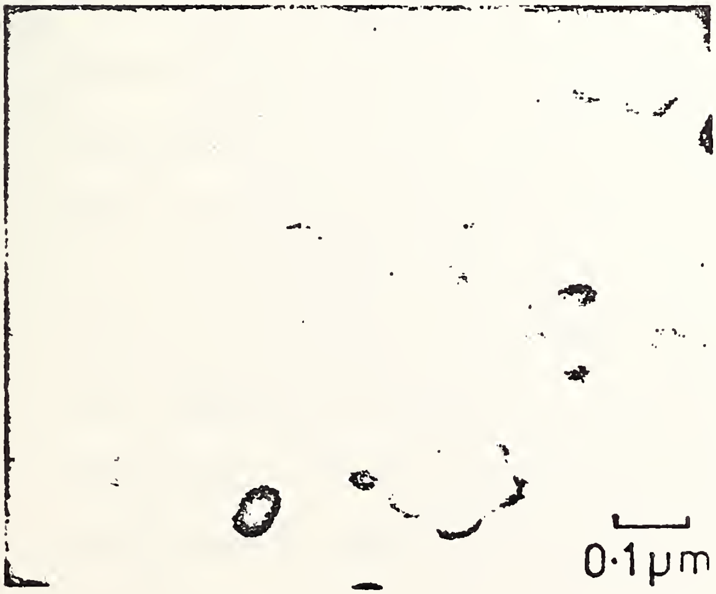

Figure 4.

Electron Photomicrograph of Particles in Used Automotive Oil Extract at 100,000 X Magnification. (Note apparent agglomeration of particles)

observed have a size range of 20 nanometers (nm) to 0.3 micrometer (µm), with the majority of particles having dimensions of about 100 nm. Particle aggregation is observed, and many of the larger particles may be aggregates. Most of the particles have smooth, nearly spherical shapes.

The second detail noticed, the lower values obtained using only new thimbles, was investigated further. A series of experiments was made on six oils (two virgin fuel oils, two recycled fuel oils, and two used oils) using a single thimble for three consecutive runs on each oil. The results of this series of experiments, shown in table 24, clearly show cases of increasing sediment values.

The data shown in table 23 indicate that the D 473 test procedure for sediment by extraction can capture and measure the larger particles in a recycled fuel oil, when a new extraction thimble is used for each run. Note, however, that for the recycled or used oils, in two cases out of four (F133, W022) some of the differences between duplicate measurements exceed the ASTM repeatability (assuming the ASTM repeatability can be extrapolated above the 0.4 percent sediment level as stated in the procedure). While it is known that there are large numbers of very small particles present in a used automotive crankcase oil, some of which readily pass through the refractory thimbles specified for use with the test procedure, there is no information available to indicate that these fine particles cause problems in the operational performance of the fuel oil. Therefore, for the purposes of this test procedure, sediment can be defined as those

Table 24. Sequential Sediment Determinations Using Single Thimble (D 473)

Fuel oil grade	Description	Sample number	Sediment by extraction (% by weight) New thimble	Second use	Third use
6	Virgin fuel oil	F130	0.039	0.033	0.030
		F130	0.043	0.101	0.019
6	Virgin fuel oil	F022	0.019	0.004	0.002
5	Recycled fuel oil (source A)	F133	1.05	4.28[a]	----
5	Recycled fuel oil (source B)	F134	1.01	6.15[a]	6.56[a]
---	Composite used automotive oil	W022	0.017	0.438	1.71
---	Industrial waste oil (source B)	W037	0.795	0.699	0.796

[a] Thimble plugged during extraction.

particles retained in the extraction thimbles at the completion of the tests.

While the test procedure for sediment by extraction (D 473) determines the quantity of larger particles in a recycled fuel oil (those particles which could reasonably be expected to cause operational performance problems in service), there may also be a need at some later date to measure the total solids content of a recycled fuel oil. Therefore, an additional test procedure which was available for determining the substances insoluble in pentane and/or toluene was investigated.

The solids content of an oil may be determined using ASTM D 893-69 (amended in 1978), "Insolubles in Used Lubricating Oils."[10] This method is identical to Method 3121 - Federal Test Method Standard 791B. It covers the determination of substances which are insoluble in pentane and/or toluene (Procedure A--Pentane Insolubles and/or Toluene Insolubles), and substances which are insoluble in pentane and/or toluene with the use of a coagulant (Procedure B--Coagulated Pentane Insolubles, and/or Coagulated Toluene Insolubles). The test procedure is stated to be

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[10] The original D 893-69 test procedure included <u>benzene</u> as the second solvent; however, this was amended in 1978 to conform to health and safety regulations, and toluene was substituted for benzene. The amended test procedure is essentially the same as the older method, with substitution of the toluene solvent for benzene, plus a revision of the precision portion of the procedure [26].

useful for the determination of "insolubles in used lubricating oils," and for the coagulated insolubles," ...additional finely divided materials that may have been held in suspension because of the detergent character of the oil" [2]. Since these finely divided materials were of particular interest for this study, only the test for coagulated insolubles (Procedure B) was investigated.

The D 893 test method (Procedure B) is summarized as follows [26]: "A sample of used lubricating oil is mixed with pentane-coagulant solution and centrifuged. The precipitate is washed twice with pentane, dried, and weighed to give coagulated pentane insolubles. For coagulated toluene insolubles a separate sample of the oil is mixed with pentane-coagulant solution and centrifuged. The precipitate is washed twice with pentane, once with toluene-alcohol solution, and once with toluene. The insoluble material is then dried and weighed to give coagulated toluene insolubles." The revised section on precision for reference [26] gives the repeatabilities and reproducibilities for Procedure B as shown in table 25.

The D 893 test method (Procedure B) was evaluated for use with recycled oils used for fuel and with used automotive crankcase oils. As part of this evaluation, the coagulated pentane and coagulated toluene insolubles were determined for a number of virgin fuel oils, recycled fuel oils, and used lubricating oils. The results of these tests are

found in table 26, and the experimental repeatability is consistent with the stated ASTM repeatabilities. In two cases, samples W023 and W038, the coagulated pentane insolubles would not dry properly and resulted in a semisolid material, (even after drying as described in the test procedure), apparently due to a resinous component of the used oil. The difference between the coagulated pentane insolubles and the coagulated toluene insolubles is defined as the "insoluble resins" contained in the product [26]. The latter value, coagulated toluene insolubles, always resulted in a dry product and was always equal to, or less than, the coagulated pentane insolubles.

In addition, one of the samples (F 134) had a coagulated toluene insolubles result which was less than the sediment by extraction. In an attempt to resolve this inconsistency, a second set of tests was run using D 893 (Procedure B) with a higher level of coagulant. The results were approximately 30 percent higher than those using the coagulant concentration prescribed in the D 893 method.

The above results indicate that the test procedure for coagulated toluene insolubles, D 893, appears to provide a useful indication of the insoluble solids content of a recycled fuel oil. However, this test should be used with caution since for some recycled fuel oils the recommended coagulant level may not allow separation of all of the fine particulates in the oil sample.

Table 25. Precision Criteria for Procedure B of D 893 [26]

Type	Solvent used	Average insolubles content (percent)	Precision criteria (percent insolubles)
Repeatability	Pentane	0.0 - 1.0	0.07
		Over 1.0	10% of mean
Repeatability	Toluene	0.1	0.068[a]
		0.4	0.14
		0.8	0.19
Reproducibility	Pentane	0.0 - 1.0	0.10
		Over 1.0	15% of mean
Reproducibility	Toluene	0.1	0.30[b]
		0.4	0.60
		0.8	0.86
		1.1	1.00

[a] These precision data were derived from the equation:

$$\text{Repeatability} = 0.216 \sqrt{I_B}$$

where I_B = coagulated toluene insolubles.

[b] These precision data were derived from the equation:

$$\text{Reproducibility} = 0.957 \sqrt{I_B}$$

where I_B = coagulated toluene insolubles. In addition, at the June 1978 ASTM it was decided to add the following note: "The poor interlaboratory precision (reproducibility) of this portion of the test is such that Procedure B, coagulated toluene insolubles, is unsuitable for the purpose of comparison of interlaboratory results" (Minutes of ASTM Committee D-2, RDD VI Section B, July 20, 1978). It is unclear at present whether this poor reproducibility is due to the test procedure or to the substantial problems of reliable sampling of used oils for their insolubles content.

Table 26. Repeatability of the Coagulated Insolubles Test Procedure (D 893)

Fuel oil grade	Description	Sample number	Coagulated insolubles (% by weight) Pentane insolubles	Toluene insolubles
1	Virgin fuel oil	F132	0.00, 0.00	0.00
2	Virgin fuel oil	F131	0.021, 0.013	0.012, 0.017
6	Virgin fuel oil (source A)	F130	3.27, 3.30	0.59, 0.67
6	Virgin fuel oil (source B)	F022	7.75, 7.73	0.12, 0.27
5	Recycled fuel oil (source A)	F133	5.29, 5.27	4.56, 4.88
5	Recycled fuel oil[a] (Source B)	F134 F134	0.94, 0.93 1.33,^{b} 1.34^{b}	0.70, 0.67 0.93,^{b} 0.89^{b}
---	Composite used automotive oil	W022	3.21, 3.43	2.30, 2.26
---	Used oil feedstock to re-refiner (source A, sampling period A)	W023	15.98^{c}, 15.89^{c}	0.96, 0.93
---	Used oil feedstock to re-refiner (source A, sampling period B)	W024	5.83 , 5.78	0.88, 0.86
---	Used oil feedstock to re-refiner (source B)	W038	3.95^{d}, 2.45^{d}	0.75, 0.76

[a] Coagulated insolubles for this oil are lower than sediment (D 473) values (see text).

[b] Coagulated insolubles using 2X the coagulant concentration specified in D 893.

[c] Oily sludge; would not dry properly.

[d] Black tarry residue.

CONCLUSION

The water and sediment concentrations are important considerations for adequate fuel oil performance in service. Recycled oils used for fuel may contain substantial amounts of these impurities. ASTM method D 95-70, "Water in Petroleum Products and Bituminous Materials by Distillation," has been evaluated with recycled fuel oils and used lubricating oils, and is a satisfactory method for determination of the water content in recycled oils used as fuel. with the modification that the sample volume taken for analysis be reported. Also, ASTM method D 473-69 (reapproved in 1974), "Sediment in Crude and Fuel Oils by Extraction," has been evaluated with recycled oils, used oils, and virgin fuel oils. This test is recommended as a satisfactory test procedure for the determination of larger particles in a recycled fuel oil, with the modification that a new refractory thimble be used for each determination.

It has also been shown that centrifugation techniques which determine water and sediment simultaneously are not satisfactory for all types of used and recycled oils. This means that water must be measured (by volume) separate from sediment, which is measured by weight. Thus, there are three ways to report the values: together by volume, together by weight, or separately. The first one requires the density of the sediment. In the ASTM procedure (see page 86, this report), an arbitrary relative density value of 2.0, close to that of sand, was selected. We suspect that the

sediment in used and recycled oils is much more dense than sand. Consequently, a combined value based upon volume is not recommended. Since the density of water is well established, it would be satisfactory to report a combined value for water and sediment _on a weight basis_. Reporting the water and sediment values separately, the third way, is also satisfactory.

5.3.2 Carbon Residue

The carbon residue of a petroleum product is the amount of carbonaceous residue formed during evaporation and pyrolysis of that product. It provides an indication of the relative coke-forming propensity of a fuel oil. The carbon residue test is generally applicable to relatively nonvolatile petroleum products which partially decompose on distillation at atmospheric pressure, and it is used primarily to predict the performance of distillate fuels, grade numbers 1 and 2 [25]. A high carbon residue value for a distillate fuel oil would indicate a tendency to form excessive carbon and/or deposits on burning, thereby greatly reducing the efficiency of vaporizing pot-type and sleeve-type burners or fouling nozzles in small residential-type burners.

The available virgin oil test procedures for carbon residue are ASTM D 524-76, "Ramsbottom Carbon Residue of Petroleum Products," and ASTM D 189-76, "Conradson Carbon Residue of Petroleum Products" [2]. The usual test procedure for determining carbon residue of virgin fuel oils is the Ramsbottom carbon residue test, which is identical to Method 5002 - Federal Test Method Standard 791B and to the British Institute of Petroleum test method IP 14/65 (British standard 4451). The method D 189 (Conradson carbon residue) was not evaluated for this report since existing fuel oil specifications do not call for this method and because in note 2 of method D 189 it is stated that, "In general, Ramsbottom Carbon Residue is the preferred method for samples that are mobile below

90°C. The Conradson Carbon Residue is finding use to characterize heavy residue fuel coker feed stocks, etc., which cannot readily be loaded into a Ramsbottom coker bulb, and when it is desirable to examine or further test the residue." It should be noted that all grades of fuel oil are mobile at 90° C or below.

The Ramsbottom D 524-76 test procedure requires, "The sample, after being weighed into a special glass bulb having a capillary opening, is placed in a metal furnace maintained at approximately 1020°F (550°C). The sample is thus quickly heated to the point at which all volatile matter is evaporated out of the bulb with or without decomposition while the heavier residue remaining in the bulb undergoes cracking and coking reactions. In the latter portion of the heating period, the coke or carbon residue is subject to further slow decomposition or slight oxidation due to the possibility of breathing air into the bulb. After a specified heating period, the bulb is removed from the bath, cooled in a desiccator, and again weighed. The residue remaining is calculated as a percentage of the original sample, and reported as Ramsbottom carbon residue" [2].

For virgin oils, the carbon residue is normally specified only for distillate fuel oil, grade numbers 1 and 2, and is measured on the 10-percent residue after distillation (see section 7 of ASTM D 524-76). Petroleum products containing ash-forming constituents will provide a value which includes both the carbonaceous residue and the ash. Normally, the ash content of a distillate fuel oil would be very low and is

not separately determined for existing specifications. However, if ash-forming constituents are present in a distillate fuel oil, they would be expected to contribute to the carbon residue value. If desired, or if large amounts of ash-forming constituents are suspected, the ash content of the fuel oil may be determined separately using ASTM method D 482-74 or, for a recycled fuel oil, method D 874-77 (see Section 5.3.3, Ash, this report). (Note: The ash included in the carbon residue test should not be assumed to be similar in composition to other ashing tests.)

The Ramsbottom carbon residue test can also be applied to residual fuel oils and lubricating base oils, although not normally used as part of specifications. With these heavier oils, the test procedure is applied to 100-percent samples as received, rather than on the 10-percent residuum specified for distillate fuel oils. For such oils, the carbon residues usually range from a few percent up to approximately 15 percent.

The precision of the carbon residue test procedure for virgin oils is given graphically in the ASTM test method, and examples taken from this figure are given in table 27. These precision data are applicable to both distillate and residual petroleum oils.

The Ramsbottom carbon residue test procedure (D 524-76) was evaluated for recycled oil used as burner fuel. As part of this evaluation the D 524 test procedure was applied to a number of recycled and used oils, virgin distillate fuel oils, virgin distillate fuel oil/used oil

Table 27. Precision of Carbon Residue Test Procedure for Virgin Fuel Oils[a]

Ramsbottom carbon residue average percent	Difference, percent carbon residue	
	Repeatability	Reproducibility
0.10	0.026	0.036
0.30	0.040	0.061
1.0	0.082	0.15
3.0	0.22	0.38
10	0.80	1.4

[a] Data taken from ASTM D 524-76, "Ramsbottom Carbon Residue of Petroleum Products," figure 4.

blends, and virgin residual oil/used oil blends. Typical data are shown in tables 28 and 29. All of our results indicated that the repeatability of the carbon residue test for recycled oils and virgin oil/recycled oil blends falls within that of virgin fuel oils, as shown in table 27.

As a result of the test procedure evaluation, it became apparent that some additives and contaminants normally found in used lubricating oils would increase the carbon residue test results as determined by D 524. These additives and contaminants include both organics such as long-chain polymeric molecules (e.g., viscosity index improvers, pour point depressants), and inorganics (e.g., ash-forming constituents such

Table 28. Repeatability of the Carbon Residue Test Procedure on Distillate Fuel/Used Oil Blends (on 10-Percent Distillation Residue) - D 524 (% Wt.)

		Added Automotive Used Oil (% v/v)[a]					
Grade	Sample	0.0	0.1	0.2	0.5	1.0	5.0
No. 1	F132	0.11	0.18		0.26		2.21
		0.14	0.16		0.28		2.20
No. 2	F131	0.20		0.23	0.36	0.47	1.78
		0.20		0.24	0.37	0.51	1.73

[a] For used oil W022 with carbon residue of 3.81, 3.78, 3.73, the average equals 3.77 percent (not distilled; standard deviation of the mean is 0.02%, n=3).

Table 29. Repeatability of the Carbon Residue Test Procedure for Recycled Oil and Virgin Fuel Oil/Used Oil Blends - D 524

			Fuel oil/used oil blend	
Fuel oil	Sample number	Virgin oil carbon residue (%)	Used oil concentration (w/w)	Carbon residue (%)
No. 4	8-2-273	-----	100% (recycled distillate fuel oil)	1.26[a]
				1.25[b]
				1.30[b]
				Avg. = 1.27
				Std. Dev. = 0.03
No. 6	F022	14.72	16.7% W022[c]	12.67
		14.88		12.86
		14.92		12.97
		14.71		
		14.94		Avg. = 12.83
				Std. Dev. = 0.15
		Avg. = 14.83		
		Std. Dev. = 0.11		
No. 6	F130	5.53	16.7% W022	5.50
		5.39		5.35
		5.63		5.66
		5.45		5.09
		Avg. = 5.50		Avg. = 5.40
		Std. Dev. = 0.10		Std. Dev. = 0.24

[a] Measurement by operator a.

[b] Measurement by operator b.

[c] W022 carbon residue is 3.77 percent (standard deviation of the mean is 0.02%, n=3).

as zinc, lead and calcium compounds, wear metals). Our results indicate that the carbon residue test procedure is a useful indicator of the total residue-forming potential of a recycled distillate fuel oil.

CONCLUSION

The carbon residue test is a useful indicator of performance for distillate fuel oils. The Ramsbottom carbon residue test procedure, ASTM D 524-76, has been evaluated with recycled fuel oils and blends of virgin fuel oil with used oil. This test may be used to establish that a product meets the specified values of carbon residue, limited to distillate fuels on the 10-percent residuum. Method D 524 can also be used with the heavier residual oils in order to determine the carbon residue of these products.

5.3.3 Ash

The ash content of a fuel oil is defined as that residue, free from carbonaceous matter, remaining after ignition in air at a specified high temperature [3,19]. The ash in virgin fuel oils results from a variety of inorganic and metal-containing compounds present in the crude oil, from contaminants acquired during transportation and storage, and from additives which are used to improve particular fuel properties [3]. The ash in recycled fuel oils results primarily from the additives and contaminants found in used lubricating oils. Particular ash-forming constituents may include lead (from leaded gasoline); wear metals; silica from dust and dirt; and calcium, zinc, and magnesium additives.

Depending on the use of the fuel, the amount of ash has a considerable bearing on whether or not detrimental effects will occur. Ash in virgin heavy fuel oils can cause clogging or deposits and high-temperature corrosion in boilers; it may attack refractory materials (e.g. bricks) used in the construction of high-temperature furnaces, kilns, etc.; and it may affect the finished product in certain industrial processes such as ceramic and glass manufacture [3]. There are also certain environmental restrictions on the emission of ash particulates from stacks. For a recycled fuel oil, the ash content can reasonably be expected to have effects similar to those described above for virgin fuel oils. It is also known that many residual recycled fuel oils and used lubricating oils have ash levels considerably higher than virgin fuel oils [5,7].

Since the ash forming constituents of crude oil generally have low-volatility, they ultimately concentrate in the residue from distillation and therefore, distillate fuel oils tend to contain only negligible amounts of ash-forming constituents [3]. However, both distillate and residual fuels may pick up ash contributors during transportation from the refinery. Fuel oil specifications usually include ash content for residual fuels only, with the ash content of distillate fuels included in the carbon residue specification (see also Section 5.3.2, Carbon Residue, this report). Specifications for grade No. 6 residual fuel oil do not have a limiting value for ash.

Two test procedures are available for the determination of ash in petroleum products. The first method is ASTM D 482-74, "Ash from Petroleum Products" [2]. This method is also found as Method 5421 - Federal Test Method Standard No. 791B, Institute of Petroleum Designation 4/65, British Standard 4450, and Deutsche Norm DIN 51575. This test procedure is usually called for in specifications for virgin residual fuel oils. However, method D 482, in note 2, states that, "This method is not intended for the analysis of unused lubricating oils containing additives; for such samples use ASTM Method D 874-IP 163, Test for Sulfated Ash from Lubricating Oils and Additives,... neither is it intended for the analysis of lubricating oils containing lead nor for used engine crankcase oils" [2]. Since recycled oils used as fuel often contain both lubricating oil additives and lead and are often made from used engine crankcase oils, the "regular ash" method (D 482) was considered to be less promising and a second ash method was considered.

This second method is ASTM D 874-77, "Sulfated Ash from Lubricating Oils and Additives" [2]. This test procedure is also found as Method 5422 - Federal Test Method Standard No. 791B, Institute of Petroleum Designation 163/65, British Standard 4716, and Deutsche Norm DIN 51575. The term "sulfated ash" is defined as "...the residue remaining after the sample has been carbonized, and the residue subsequently treated with sulfuric acid and heated to constant weight" [2]. A summary of the D 874 test procedure is as follows: "The sample is ignited and burned until only ash and carbon remain. After cooling, the residue is treated with sulfuric acid and heated at 775°C until oxidation of carbon is complete. The ash is then cooled, re-treated with sulfuric acid, and heated at 775°C to constant weight" [2]. This test procedure also has a precautionary note stating that it was "... not intended for the analysis of used engine oils or oils containing lead" and a cautionary statement regarding possible problems with magnesium and phosphorus [2]. However, the D 874 test procedure was examined further because (1) it is stated to be usable for the determination of residues from calcium, zinc, magnesium (probably), barium, potassium, sodium, and tin [2]; and (2) a preliminary examination suggested that the test may also retain lead from used lubricating oils. While it is recognized that the sulfated ash test procedure will provide test results which are somewhat higher than the regular ash procedure, due in part to the incorporation of sulfate into the ash residue, it is necessary to provide a test procedure which can reliably indicate the maximum level of ash-forming constituents which may be found in a recycled oil used for burner fuel.

The repeatability of the D 874 test procedure for virgin petroleum oils is stated as follows: "The difference between successive test results, obtained by the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in 1 case in 20:

$$0.047\ X^{0.85}$$

where: X = average of the two test results in units of percent sulfated ash" [2]. For example, with an oil having a 0.1-percent sulfated ash (by weight), the repeatability is given as 0.006 weight percent sulfated ash, or 6 percent; for a 1.0-percent sulfated ash, the repeatability is 0.047 weight percent sulfated ash, or 4.7 percent.

The reproducibility of the D 874 test procedure for virgin petroleum oils is stated as follows: "The difference between two, single and independent results, obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in 1 case in 20:

$$0.189\ X^{0.85}$$

where: X = average of the two test results in units of percent sulfated ash" [2]. This reproducibility works out to 0.027 weight percent sulfated ash, or 27 percent at the 0.1-percent sulfated ash level, and 0.189 weight percent sulfated ash, or 18.9 percent at the 1.0-percent sulfated ash level.

The D 874-77 sulfated ash test procedure was evaluated for use with recycled oils to be used as burner fuel. As a part of the evaluation, the D 874 test was applied to a number of used oils, recycled oils, virgin fuel oils, and a blend of virgin residual fuel oil with used oil. The results of these analyses are shown in table 30. In general, the results indicate that the repeatabilities obtained for D 874 with used and recycled oils are consistent with the ASTM criteria. This table also includes some results for the D 482 (regular ash) procedure, and it may be seen that the standard deviations obtained for that method are similar to those for the D 874 method. (Note: D 482 precision statement does not cover ash values above 0.15 percent). However, chemical analyses of the D 482 ash from two used automotive oils (W022 and W011) indicated lead recoveries of only 59.9 percent and 62.2 percent, respectively.

In order to establish that the D 874 sulfated ash test procedure can reliably indicate the primary ash-forming constituents in a recycled fuel oil, it was necessary to further evaluate the three possible problems mentioned in the test procedure; phosphorus, lead and magnesium.

For phosphorus, the D 874 test procedure states that "when phosphorus is present with metals, it remains partially or wholly in the sulfated ash as metal phosphates" [2]. This statement was confirmed, and it was further reported that the phosphorus would most likely be found in the final ash as the phosphate (PO_4^{-3}) or pyrophosphate ($P_2O_7^{-4}$) [27]. In order to establish the magnitude of the problem, phosphorus concentrations were determined in two recycled fuel oils and four used automotive lubricating oils, and these averaged 880 µg/g (range = 716 to 1035 µg/g,

Table 30. Repeatability of the D 482 and D 874 Ash Test Procedures

Fuel oil grade	Sample description	Sample number	Ash, weight percent					
			D 482			D 874		
			Average	Std. Dev.	n[a]	Average	Std. Dev.	n[a]
4	Virgin fuel oil	F126	0.0203	.0003	(3)	0.0215		(1)
5	Virgin fuel oil	F125	0.0294	.0006	(3)	0.0268		(1)
6	Virgin fuel oil	F022	0.0487	.0006	(3)	0.0507		(1)
---	Virgin formulated motor oil	M011	0.840	.005	(3)	1.09	.03	(6)
---	Used automotive crankcase oil	W011	1.42	.05	(16)	1.84	.04	(11)
---	Used automotive crankcase oil	W004	2.16	.04	(3)	3.06	.06	(3)
---	Composite used automotive crankcase oil	W022	1.81	.03	(6)	2.68	.07	(11)
---	Above sample centrifuged to remove large to moderate particulates[b]	W022	1.25	.03	(3)	1.43	.02	(6)
---	Re-refiner's feedstock used oil	W023	1.27	.01	(2)	1.423	.003	(2)
---	Service station used oil	W033	0.64	.02	(2)	0.66	.03	(2)
5	Recycled fuel oil (source A)	F133	4.58	.02	(2)	4.70		(1)
5	Recycled fuel oil (source B)	F134	0.95	.01	(2)	1.25	.02	(2)
---	Fuel oil/used oil blend (20% W022)	(F022)		---		0.581	.005	(2)

[a] Numbers in parentheses are n (= number of determinations).

[b] Centrifuged for 20 minutes at 20,000 x gravity.

n=6). These results are consistent with the phosphorus concentrations reported for 30 used lubricating oils obtained throughout the country (average = 901 μg/g, range = 81 to 1393 μg/g, n=30) [28]. The potential gravimetric effect (i.e., substitution of phosphate or pyrophosphate for oxide and/or sulfate) of a phosphorus impurity at the above concentrations on the sulfated ash result was calculated. These calculations indicate that for the six used and recycled fuel oils described earlier, the maximum potential gravimetric effect on the sulfated ash values is only slightly larger than the ASTM repeatability.[11] Therefore, for the purposes of this report, i.e., indicating the maximum level of ash-forming constituents in a recycled fuel oil, the phosphorus problem should not be considered important.

For lead, the D 874 test procedure states that it is "...not intended for the analysis of used engine oils or oils containing lead" [2]. Although the above statement may be interpreted to mean that lead is lost during the test procedure, discussions with persons originally involved with the test procedure suggest that the statement was included to eliminate errors in estimation of the additive levels for used motor oils, based on the sulfated ash result. Regardless, it was felt important to establish whether lead is in fact retained in the sulfated ash, and

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[11] For example, the worst case is F 134 which has a sulfated ash value of 1.25% (table 30) and a phosphorus concentration of 823 μg/g. If this phosphorus is assumed to quantitatively remain in the ash as the phosphate, and to substitute <u>only</u> for the oxide (no sulfate substitution), this maximum gravimetric effect is calculated to be 6.0 percent, only slightly higher than the ASTM repeatability of 5.6 percent for that ash level. If substitution of phosphorus for sulfate occurs, the gravimetric effect will be affected in the opposite direction, but never more than the ASTM repeatability (at these phosphorus concentrations).

this question was evaluated through analysis of the sulfated ash residue as described below.[12]

For magnesium, the D 874 test procedure states that it may not react the same as other alkali metals, and the magnesium data "...should be interpreted with caution" [2]. For this element also, an investigation was made of the amount recovered in the sulfated ash (compared to the amount in the original oil sample), and is described below. In addition to lead and magnesium, an elemental balance was obtained for calcium and zinc. These four elements are the major inorganic constituents in many recycled fuel oils and used oils.

For this investigation, samples of two used automotive lubricating oils (W022 and W011) were ashed using D 874, and the sulfated ash residues removed from the crucibles and analyzed by atomic absorption spectroscopy. The amounts of the four elements found in the ash were then compared to the amounts expected from analyses of the starting materials, i.e., the used oils, and the percentages of the elements recovered in the ash are shown in table 31. No assumptions were made as to the chemical form of the element in the ash.

The data in table 31 show average recoveries for all four elements of greater than 85 percent. In order to evaluate whether some of the elements were retained on the walls of the silica crucible, one set of ash samples was dissolved <u>in situ</u> (in their original crucibles). These "dissolution recovery" values were higher than the average recovery values

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[12] There is some evidence to suggest that the compounds of lead retained in the sulfated ash, while apparently reproducible, are not stochiometrically lead sulfate.

in every case except for calcium, which remained the same. For lead, the average dissolution recovery (one value for each oil sample) was 97.1 percent, and for zinc that the average dissolution recovery was 94.0 percent. Reference 29 also indicates that both lead and zinc can form stable, insoluble silicates on the surface of silica crucibles, which may not be completely removed even with acid dissolution. [It should be noted that formation of silicates or an insoluble residue in the crucible is not a problem for the sulfated ash procedure since the final weight of the ash is determined in the crucible, but only for the evaluation of that procedure.] The results indicate that these four elements, lead, calcium, zinc and magnesium, are substantially retained in the sulfated ash procedure, and confirm that this test is a useful indicator of the maximum level of ash-forming constituents in recycled oils used as fuel.

One additional concern in this test procedure involves the crucible material. The D 874 method specifies that porcelain, fused silica, or platinum crucibles may be used, "...except for samples containing elements injurious to platinum" [2]. It further states that phosphorus may attack the platinum under the conditions of the test procedure. Also, reference 29 indicates that lead can form an alloy with platinum. Both of these elements are present in many recycled fuel oils. Therefore, it is recommended that the sulfated ash test procedure be modified to indicate that platinum dishes or crucibles should not be used with recycled fuel oils or used automotive lubricating oils.

Table 31. Elemental Recovery in Sulfated Ash (D 874) for the Major Constituents in Recycled Fuel Oils.

	Average percent recovery of specified element in the sulfated ash[a]	
Element	Used Oil W022[b]	Used Oil W011[c]
Lead	85.6 ± 5.8%	94.2 ± 1.6%
Calcium	99.4 ± 1.6%	96.5 ± 1.7%
Zinc	88.1 ± 3.7%	90.2 ± 6.8%
Magnesium	105 ± 3%	90.8 ± 7.3%

[a] Uncertainty values are the standard deviation of the mean, $s/\sqrt{n}$.

[b] Sample W022 is a composite used automotive oil; number of determinations for each element (n) = 4.

[c] Sample W011 is a used automotive crankcase oil; number of determinations for each element (n) = 3.

CONCLUSION

The ash content of a fuel oil is an important indicator of performance for residual fuel oils, including recycled oils used as fuel. ASTM method D 874-77, "Sulfated Ash from Lubricating Oils and Additives," has been evaluated with recycled fuel oils, a virgin fuel oil/used oil blend, and used automotive oils and is a satisfactory method for indicating the maximum level of ash-forming constituents in these petroleum products, with the modification that platinum vessels should not be used.

5.3.4 Total Sulfur

The sulfur content of a fuel oil is of concern for the control of corrosion in combustion and exhaust systems and for the reduction of environmentally important emissions. In both industrial and Federal fuel oil specifications, the sulfur is covered under two categories, total sulfur and corrosive sulfur. This section discusses test procedures for total sulfur, while Section 5.2.6, Copper Corrosion, discusses a test procedure for corrosive sulfur. It should be noted that the test for total sulfur is important for both corrosion (especially of exhaust systems) and for emissions, while the test for corrosive sulfur considers only copper corrosion [18].

It is important that petroleum products be noncorrosive and remain so during service [19]. Crude petroleum usually contains a variety of sulfur compounds, most of which are removed during refining to reduce the corrosive tendencies of the refined product. Particular attention is given to the control of sulfur content in distillate fuel oils used in various household and industrial heating systems. In addition, the products of fuel oil combustion may contain sulfur compounds that are corrosive or become corrosive in the presence of moisture [19]. Low-temperature corrosion can become significant due to condensation of sulfuric acid if the temperature of the stack gas is below the "dew point" of the gas. Stack gas temperatures can be considerably lowered when more efficient energy-saving equipment is used, possibly causing

severe corrosion problems [25]. A test for total sulfur is also important to assure that the fuel meets legal requirements (if any) for sulfur content, as well as applicable sulfur oxide emission standards. Any test procedure should be accurate in order to minimize unnecessary cost in reducing the sulfur levels of the fuel oils to meet these legal requirements.

A number of test procedures for total sulfur are used with virgin fuel oils. These are ASTM D 129-64, "Sulfur in Petroleum Products (General Bomb Method)"; D 1266-70, "Sulfur in Petroleum Products (Lamp Method)"; D 1551-68 (reapproved in 1973), "Sulfur in Petroleum Oils (Quartz-Tube Method)"; D 1552-64 (reapproved in 1973), "Sulfur in Petroleum Products (High-Temperature Method)"; and D 2622-77, "Sulfur in Petroleum Products (X-Ray Spectrographic Method)." Except for the x-ray method, these test procedures involve the combustion of the sample and determination of the resulting oxides of sulfur by an appropriate chemical method.

Method D 1552, the high-temperature method, was selected for further evaluation with recycled oils because it is currently in common use and appears to be least affected by the contaminants usually found in used oils recycled for use as fuel. In the D 1552 method, "The sample is burned in a stream of oxygen at a sufficiently high temperature to convert about 97 percent of the sulfur to sulfur dioxide. A standardization factor is employed to obtain accurate results" [2].

This standardization factor is obtained "using an oil sample of similar type to the unknown sample and of accurately known sulfur content . . . ." [2]. The combustion products are passed into an absorber containing an acid solution of potassium iodide and starch indicator. A slight blue color is developed in the absorber solution by the addition of standard potassium iodate solution. As combustion proceeds, the sulfur oxides bleach the blue color, and more iodate is added. The amount of standard iodate consumed during the combustion is a measure of the sulfur content of the sample [2].

In D 129, "The sample is oxidized by combustion in a bomb containing oxygen under pressure. The sulfur, as sulfate in the bomb washings, is determined gravimetrically as barium sulfate" [2]. This test procedure was not evaluated for use with recycled oils because, as stated in note 1 of the test, "This method is not applicable to samples containing elements that give residues, other than barium sulfate, which are insoluble in dilute hydrochloric acid and would interfere in the precipitation step. These interfering elements include iron, aluminum, calcium, silicon, and lead which are sometimes present in greases, lube oil additives, or additive oils. Other acid insoluble materials that interfere are silica, molybdenum disulfide, asbestos, mica, etc. The method is not applicable to used oils containing wear metals, and lead or silicates from contamination. Samples that are excluded can be analyzed by ASTM Method D 1552, Test for Sulfur in Petroleum Products (High-Temperature Method)" [2]. Recycled oils for use as fuel almost always contain one or more of these interfering elements or materials.

In method D 1266, "Sulfur in Petroleum Products (Lamp Method)," the fuel oil sample is burned in a prescribed lamp placed in a closed system having an artificial atmosphere; the sulfur oxides formed during combustion are absorbed in a hydrogen peroxide solution; and, finally, the sulfuric acid formed is titrated with a standard sodium hydroxide solution and the amount of sulfur in the original sample is calculated [2]. This method is not often used for determination of sulfur in fuel oils, and, in addition, reference 18 states that "Method D 1266 is not applicable to samples that contain halogens, phosphorus, nitrogen, or other acid-forming compounds." Since many recycled oils often contain halogens, phosphorus, and other acid-forming contaminants, this method was not evaluated for use with recycled oils used as fuel.

In method D 1551, "Sulfur in Petroleum Oils (Quartz-Tube Method)," "The sample is vaporized and burned in a stream of air, and the oxidation completed by passing over quartz particles maintained at a temperature of 950 to 1000°C. The combustion products are passed through hydrogen peroxide which absorbs the sulfur as sulfuric acid and the chlorine as hydrochloric acid. The absorbent is then analyzed for total acidity and for chloride ion" [2]. This method was not evaluated for use with recycled oil because it is stated in the method that it gives erroneous results when applied to materials containing phosphorus and many organometallic compounds, both of which are often present in used oils, and because the method was discontinued by the ASTM in 1976.

Method D 2622, "Sulfur in Petroleum Products (X-Ray Spectrographic Method)," covers the determination of total sulfur in liquid petroleum products. In this method, the sample is placed in the x-ray beam, and the intensity of the sulfur Kα line at 5.373 Å is measured. The intensity of a corrected background is subtracted, and the resultant net counting rate is compared to previously prepared calibration curves to obtain the concentration of sulfur in weight percent. For sulfur concentrations between 0.015 to 5.0 percent, the ASTM repeatability is 0.05 x percent S and the ASTM reproducibility is 0.16 x percent S. This method is a possible alternative for D 1552; however, it was not the primary method evaluated for recycled oils because it requires expensive and highly specialized instrumentation, and because the method may require corrections for elements commonly found in recycled oils (phosphorus, zinc, barium, lead, calcium, and chlorine) [2]. However, since both the instrumentation and operators with appropriate experience and expertise were available to us, this method was used to analyze for sulfur in selected oil samples in an attempt to estimate the accuracy of the ASTM D 1552 method, the one selected for extensive evaluation in this report. These data are found in table 32, and the results are discussed below.

For ASTM method D 1552, the repeatabilities and reproducibilities for judging the acceptability of results as stated in the ASTM method are shown in table 33. An NBS virgin fuel oil Standard Reference Material (SRM 1623) having a certified sulfur concentration of 0.268 percent was analyzed 12 times using D 1552 during 2 different days and using 3 different operators, and the repeatability of the method for

Table 32. Sulfur Data for Fuel Oils and Recycled Oils

Sample number	Grade/source	% Recycled oil	% Sulfur, D 1552		% Sulfur, D 2622[a]	
			Operator 1	Operator 2	Original sample	Centrifuged sample[b]
F125	No. 5 virgin fuel oil	0	1.19 1.17	1.24 1.12	N.D.[c]	N.D.
F022	No. 6 virgin fuel oil	0	3.06 3.22 3.17	3.06 3.17 3.14	2.96 2.92 2.91	N.D.
F134	No. 5 recycled fuel oil (source A)	100	0.51 0.45 0.45	0.50 0.52	0.44 0.49	0.48
F133	No. 5 recycled fuel oil (source B)	100	0.49 0.47	0.55 0.54	0.42 0.35 0.43	
F133	Above sample, centrifuged[b]	100	N.D.	0.48 0.51		0.47 0.49
W022	Composite used automotive crankcase oil	(100)[d]	0.38 0.38	0.38 0.44 0.43	0.36 0.40	0.38
----	Fuel oil/used oil blend (80% No. 6, F022; 20% used oil, W022)	(20)[d]	2.36 2.58 2.63	N.D.	2.52 2.59 2.57	N.D.

[a] X-ray fluorescence method; see text for discussion of results between methods.

[b] Centrifuged for 20 minutes at 20,000 x gravity.

[c] N.D. = not determined.

[d] Used oil not processed beyond collection and storage.

this fuel oil was calculated. The standard deviation of these 12 values was 0.042-percent sulfur. The values obtained did not vary from the average by more than 0.038-percent sulfur, indicating acceptable repeatability of the D 1552 method for virgin fuel oil.

Table 33. Precision of D 1552 Test Procedure for Sulfur [2]

Sulfur, (wt. % range)	Repeatability	Reproducibility
0.0 to 0.5	0.05	0.08
0.5 to 1.0	0.07	0.11
1.0 to 2.0	0.10	0.17
2.0 to 3.0	0.16	0.26
3.0 to 4.0	0.22	0.40
4.0 to 5.0	0.24	0.54

Method D 1552, the high-temperature method, was evaluated for use with recycled oils. Since this is a comparative analytical technique, it requires fuel oils with known sulfur contents for calibration and standardization of the instrumentation, and two NBS SRM's having certified sulfur concentrations were routinely used for calibration. The usual procedure was to establish the standardization factor each day. As a part of the evaluation of D 1552, a number of virgin fuel oils, recycled oils, and a virgin fuel oil/recycled oil blend were analyzed for sulfur content. The results of these analyses are shown in table 32 and are discussed further, below.

Contaminants normally found in recycled oils do not significantly interfere in this test procedure. The test procedure states that alkali

and alkaline earth metals, zinc, phosphorus, and lead do not interfere, and chlorine in concentrations less than 1 weight percent does not interfere [2]. In the D 1552 procedure, it is stated that nitrogen present in excess of 0.1 weight percent may interfere, depending upon the type of nitrogen compound present in the oil and the combustion conditions of the test [2]. It is known from published surveys that most used automobile crankcase oils contain nitrogen compounds around the 0.1 weight percent (1000 ppm) level: analyses of 30 composite used oils averaged 814 ppm nitrogen, with a range of 530 to 1770 ppm (w/w) [28]. A potential nitrogen interference may be eliminated by the addition of about 250 mg of dry sodium azide to the iodometric titration vessel before initiation of the combustion process. The sodium azide reacts rapidly and preferentially with the oxides of nitrogen, but does not participate in or interfere with the sulfur determination [30]. (Reference 30 should also be consulted regarding hazards in the use of sodium azide. This chemical can react to form explosive compounds unless neutralized in a suitable manner.) However, reference 30 also indicates that the nitrogen interference will be very small at low concentrations of nitrogen. For example, for a sulfur concentration of approximately 2 wt.%, the presence of one-half wt. percent nitrogen caused an error of 0.06 wt.% sulfur on the low side, or about 3% relative. Our experimental data comparing the D 1552 results with an independent analytical method which does not suffer from nitrogen interference (X-ray fluorescence, D 2622) indicates that an error, if present, is small and within the expected ASTM repeatability and reproducibility (table 32). Consequently, we do not recommend any test modification such as sodium azide addition to the titration vessel.

The results of analyses for sulfur using this test (table 32) exhibit the repeatability of D 1552 for determining the sulfur content for virgin fuel oils, recycled and used oils, and blends of virgin fuel oils with used oils.

As described above, X-ray fluorescence (XRF) analyses (D 2622) were carried out on many of the fuel oil samples shown in table 32 in order to obtain an independent verification of the actual sulfur content of these oils. The results of these analyses indicated that, except for one sample (F 133), the XRF values for sulfur agreed with the high-temperature method (D 1552) in view of the latter's stated reproducibility.

It was noted that during the D 2622 measurements some of the recycled oil and used oil samples showed a decrease in sulfur signal with time, possibly due to settling of lead and perhaps other types of particles to the bottom of the sample cell. (This "settling" decreased the sulfur signal by 10 percent in 100 seconds for the worst case, sample F133.) In an attempt to understand this behavior and explain the F 133 result, three oils were centrifuged for 20 minutes at 20,000 x gravity to remove larger particles, and were then reanalyzed. The results of these analyses, also shown in table 32, demonstrate that for sample F133 the removal of larger particles by centrifuging led to analytical results by D 2622 which agreed very well with the D 1552 values, while the D 1552 results did not change after this treatment. For the other two oils for which no discrepancy had been noted, centrifuging did not appreciably

change the D 2622 sulfur results.

As a final check for the D 1552 test procedure, a sulfur balance was calculated for the virgin fuel oil/used oil blend shown in table 32. The D 1552 analytical results for the fuel oil, F022 (80 percent), and the used automotive crankcase oil, W022 (20 percent), provided a calculated blend concentration of 2.59-percent sulfur. This value is consistent with the D 1552 results for the blended sample as shown in table 32.

CONCLUSION

The sulfur content of fuel oil is an important characteristic that is controlled by law in most areas. ASTM method D 1552, "Sulfur in Petroleum Products (High-Temperature Method)," has been evaluated with recycled fuel oils, used oils, and a blend of virgin fuel oil with used oil and is a satisfactory, rapid method for the determination of sulfur in these petroleum products.

5.3.5 Acidity

Some petroleum products are routinely treated with mineral acid as part of a refining procedure. Any residual mineral acid in a petroleum product is stated to be "obviously...undesirable" [2]. The general requirements of a burner fuel oil as described in the ASTM D 396-76 specification include the statement, "The grades of fuel oil specified herein shall be...free from inorganic acid...." [2] (see also page 21 of section 5, Test Procedures, this report).

The word "acid" is a chemical term, and can be defined as a substance that in water solution ionizes with the formation of hydronium as one of its ions (Arrhenius definition of an acid). [Note: hydronium ions are hydrated hydrogen ions, $H^+(H_2O)_\chi$]. One acid is characterized as being stronger or weaker than another, depending on its degree of ionization, i.e., whether a larger or smaller concentration of hydronium ions are present in a solution at a specific total concentration of acid. The concentration of hydronium ions in a solution is usually determined by use of a color indicator dye (which changes color over a certain specific concentration range of hydronium ions, e.g., methyl orange), by electrical measurements (potentiometry), or by titrating the acid with a base to neutrality as determined using a suitable indicator. The common practice is to express hydronium ion concentrations in terms of a system known as the pH scale. The pH value of a solution is the logarithm of the reciprocal of the activity (effective concentration) of hydronium ion which it contains, or

$$pH = \log \frac{1}{[H^+]} = -\log [H^+] \qquad (1)$$

For pure water or a neutral solution, the hydronium ion concentration is 1×10^{-7} moles per liter, and the pH = 7. For a strong acid, the hydronium ion concentration may be 1×10^{-3} moles per liter, and then the pH = 3. (Note: where the activity coefficient of the acid is less than 1.0, the actual pH value will vary between, say 3.0 and 3.5).

While a test procedure for acidity is not likely to be needed for virgin fuel oils because of the many check tests made during various stages of refinery operations [18], there is a possibility of acid contamination of a recycled fuel oil due to improper disposal practices, or due to use of mineral acid in the reprocessing procedure during recycling into the fuel oil. Any mineral acid present in significant amounts in a fuel oil could result in serious corrosion problems, especially for storage, transfer and burner systems.

In practice, the statement "...fuel oil... shall be...free from inorganic acid..." [2] is impossible to confirm and only an upper bound can be determined from any test method. Also, both recycled and virgin fuel oils usually contain weak organic acids and other components which may be involved in chemical reactions and/or buffering effects which neutralize or mask the presence of small amounts of an inorganic acid. (Note: Solutions of weak acids and their salts or of weak bases and their salts are called "buffers" since they resist a change in hydronium ion activity upon addition of small amounts of strong acids or bases [31]). Further, with regard to acidity, the

important characteristic of a recycled fuel oil is the hydronium ion activity, not the source of the ions. Therefore, the overall hydronium ion activity, or pH, appears to be the appropriate measurement rather than the inorganic acid content.

There are two test procedures which can be used for the determination of acidity in recycled petroleum oils. The first procedure is ASTM method D 1093-65 (reapproved in 1975), "Acidity of Distillation Residues or Hydrocarbon Liquids." This test is similar to Method 5101.6 - Federal Test Method Standard No. 791B. The second test procedure is ASTM D 664-58 (reapproved in 1975), "Neutralization Number by Potentiometric Titration." This test is identical to Method 5106 -Federal Test Method Standard No. 791B, to the Institute of Petroleum Designation 177/64, and to the British Standard 4457. A third test procedure, ASTM method D 974-64 (reapproved in 1977), "Neutralization Number by Color-Indicator Titration," cannot be used with most recycled fuel oils due to their dark coloration.

The D 1093 test procedure is a very simple qualitative test, in which "The sample of...hydrocarbon liquid is shaken with water and the aqueous layer tested for acidity to methyl orange" [2]. Preliminary review of this method indicated it should be adequate for testing of fuel oil acidity, and therefore D 1093 was selected for further evaluation.

Test procedure D 664, neutralization number by potentiometry, covers procedures for determination of acidic and/or basic constituents in petroleum products, and resolves these constituents into groups

having weak-acid, strong-acid, weak-base, and strong-base ionization properties [2]. This procedure involves dissolving the sample in a mixture of toluene and isopropyl alcohol containing a small amount of water, and titrating it potentiometrically with alcoholic potassium hydroxide or hydrochloric acid solution. The meter readings are plotted against the respective volumes of titrating solution, and the end points taken at the inflections in the resulting curve [2]. Since the D 664 method can differentiate between strong and weak acids, it can indicate whether a petroleum product contains a mineral (inorganic) acid contaminant (strong acid), or an organic acidic constituent (weak acid), or both. However, if a very small amount of strong acid is present in the sample in addition to weak acid(s), the quantitation of that strong acid may be somewhat obscured by the weak acid titration curve.

Method D 1093 can be used to test for acidity directly in a hydrocarbon liquid, or in the distillation residue from a gasoline or petroleum solvent. For a recycled fuel oil, the sample of hydrocarbon liquid can be used without distillation. The D 1093 method uses 50 mL of the petroleum sample, which is placed in a clean centrifuge tube along with 15 mL of water and three drops of methyl orange indicator solution. (Note: Methyl orange indicator is a 0.1 percent water solution, and changes to a red color at approximately pH = 3.1 to 4.4 [32]). The stoppered tube is thoroughly shaken (caution: reference 2 should be consulted for appropriate venting procedures), and then centrifuged for a specified period of time in order to separate the water layer. A red or pink color in the aqueous layer indicates the presence of "acidity" in

the petroleum product and the sample is considered to fail the test [2]. There is no precision indicated for this test procedure.

The D 1093 test procedure for acidity was evaluated for recycled oils used as burner fuel. As part of this evaluation, the D 1093 test was applied to a number of recycled oils, used automotive lubricating oils, and virgin fuel oils. Two problems identified with this test procedure were: 1) inadequate separation of the water layer, and 2) use of the methyl orange indicator. These problems are discussed further below.

During the evaluation, it was found that sufficient amounts of free water could not be separated under the conditions of the D 1093 test for some of the recycled and used oils samples which contained high levels of detergents and dispersants. After additional investigation, the test procedure was modified to use 50 mL of water (instead of 15 mL) with the 50 mL sample of oil. This modification assures separation of a sufficient quantity of free water (even with high additive motor oils) so that the test procedure can be completed. The effect of this modification on the pH (hydronium ion concentration) would be to make the solution to be tested more dilute, thus somewhat diluting any acid which may be present from the oil sample. This dilution effect can be calculated from equation (1) above, and a pH = 3.00 would result in pH = 3.52 for the modified procedure, and a pH = 4.00 would result in a pH = 4.52 for the modified procedure. This dilution effect would be reduced by any buffering which might take place in the system due to the presence of one or more weak acids, approaching zero dilution effect for a strongly buffered system.

Data are shown in table 34 for the several petroleum oils for which 15 mL of water could be separated, compared with results from the modified D 1093 procedure on the same oils. The results using methyl orange indicator as specified in the test agree for both of the procedures. The pH measurements shown in the table were made on the separated water sample after removal from the centrifuge tube using a capillary syringe, and were made using a pH meter. These pH results are similar for two of the samples, the paraffin oil and sample number F134, due to buffering effects of water (for the paraffin oil), and residual additives and/or organic acids (for F134). [Note: Potentiometric titration with potassium hydroxide (KOH) on sample F134 using ASTM method D 664 verified the presence of this buffering effect, and required an average of 4.34 mg KOH per gram of F 134 for neutralization.] Recycled distillate fuel oil sample 7L24 had a much smaller buffering effect, and the modified D 1093 test procedure results showed an average pH change of 3.13 to 3.56, which is close to the calculated effect due to dilution.

The second problem identified was use of methyl orange indicator as the detector for establishing the hydronium ion activity. In addition to the rather wide range of pH covered by most indicators (e.g. methyl orange range is 3.1 to 4.4 [32]), the pH range of indicators also may be affected by factors such as temperature, electrolyte concentration, the presence of organic solvents, and the presence of colloidal particulates [33]. These effects can cause a shift in the color range of one or more pH units [33]. The use of a potentiometric determination of the hydronium ion activity, such as a pH meter, would eliminate this problem.

Table 34. Comparability of the D 1093 and Modified D 1093 Test Procedures

Fuel oil grade	Description	Sample number	50 mL oil + 15 mL water[a]		50 mL oil + 50 mL water[b]	
			Methyl orange indicator	pH	Methyl orange indicator	pH
---	Paraffin oil	---	Neutral	6.89	Neutral	6.78
---	Paraffin oil	---	Neutral	6.82	Neutral	6.80
---[c]	Recycled distillate fuel oil	7L24	Acid	3.14	Acid	3.60
---[c]	Recycled distillate fuel oil	7L24	Acid	3.12	Acid	3.52
5	Recycled fuel oil	F134	Acid[d]	4.28	Acid[d]	4.30
5	Recycled fuel oil	F134	----[e]	----	Acid[d]	4.22
5	Recycled fuel oil	F134	N.D.[f]	N.D.	Acid[d]	4.24

[a] Conditions for D 1093 test procedure.

[b] Conditions for modified D 1093 test procedure (see text).

[c] Viscosity measurements on this oil place the fuel oil grade between 2 and 4.

[d] Water after centrifugation was only slightly pink.

[e] Insufficient water separated for color observation or pH measurement.

[f] N.D. = Not determined.

The modified D 1093 test procedure was then applied to a variety of recycled fuel oils, used oils, and virgin fuel oil samples, and the results are shown in table 35. This table contains both the colorimetric results as obtained from the methyl orange indicator, as well as pH measurements made on the separated water layer using a potentiometric determination (pH meter). The data in table 35 indicate that, while most of the oil samples tested neutral to methyl orange, the two recycled oil samples discussed earlier (7L24 and F134) were the only samples tested which gave positive tests for acidity. In addition, the pH measurements on these two oils indicated that the hydronium ion activities were definitely higher than the other samples. [Note: Separate tests demonstrated that the presence of the methyl orange indicator has no detectable influence on the resulting pH measurement.]

In order to investigate the nature of the acidity for the oil which tested strongly positive to the modified D 1093 test procedure, sample 7L24 (recycled distillate fuel oil) was evaluated further using potentiometric titration (ASTM method D 664) to determine whether a detectable amount of a strong acid (i.e., inorganic acid) was present. In this experiment, a strong base (potassium hydroxide, KOH) used to titrate the acidic components of the oil sample, and the resulting electrode potential plotted against volume of titrant (Figure 5). In D 664, the strong acid is calculated from the volume of titrant required to take the sample to the appropriate electrode potential (see D 664 for specific details; for examples used in D 664, values of approximately - 200 millivolts were used).

Table 35. Repeatability of the Acidity Test Procedure for Petroleum Oils Using the Modified ASTM D 1093[a]

Fuel oil grade	Description	Sample number	Acidity: Methyl orange indicator	Acidity: pH[b]
2	Virgin distillate fuel oil	F131	Neutral Neutral	6.48 6.58
4	Virgin residual fuel oil	F126	Neutral Neutral	6.42 6.35
5	Virgin residual fuel oil	F125	Neutral Neutral	6.48 6.33
6	Virgin residual fuel oil (source A)	F022	Neutral Neutral	7.03 7.01
6	Virgin residual fuel oil (source B)	F130	Neutral Neutral	5.93 6.04
---[c]	Recycled distillate fuel oil	7L24	Acid Acid	3.60 3.52
5	Recycled residual fuel oil	F134	Acid[d] Acid[d] Acid[d]	4.30 4.22 4.24
---	Composite used automotive oil	W022	Neutral Neutral	5.80 5.92
---	Used oil feedstock to re-refiner	W023	Neutral Neutral	6.32 6.42
---	Used oil from service station	W033	Neutral Neutral	5.64 5.62
---	Used industrial oil[e]	W037	Neutral Neutral	5.20 5.18

[a] In order to obtain adequate separation of the water layer, the ASTM D 1093 test procedure was modified to add 50 mL of water to the 50 mL oil sample, instead of the normal 15 mL of water (see text).

[b] Water added to fuel oil had a pH = 7.00.

[c] Viscosity measurements on this oil place the fuel oil grade between 2 and 4.

[d] Water after centrifugation only slightly pink.

[e] Used oil from an industrial wastewater treatment plant.

The results of this potentiometric evaluation, are found in figure 5. The titration curve of sample 7L24 did not indicate the presence of a strong acid, only weak acids. The presence of the sulfuric acid in the second sample was easily detected.

The above results suggest that the ASTM D 1093 test procedure may be used with modifications to indicate the hydronium ion activity (acidity) of recycled fuel oils. The recommended modifications to this procedure are: 1) increasing the volume of water used from 15 mL to 50 mL, and 2) removal of the separated water layer from the centrifuge tube and determination of the hydronium ion activity with a pH meter. An appropriate hydronium ion activity which appears to be essentially equivalent to the methyl orange indicator (including the effect of dilution with the larger volume of water) would be a pH of 4.5.[12] Thus, a pH value less acid than pH = 4.5 would indicate a "neutral" result (e.g., pH = 5.0), while a pH value more acid than 4.5 would provide a "positive" indication of acidity (e.g., pH = 4.0).

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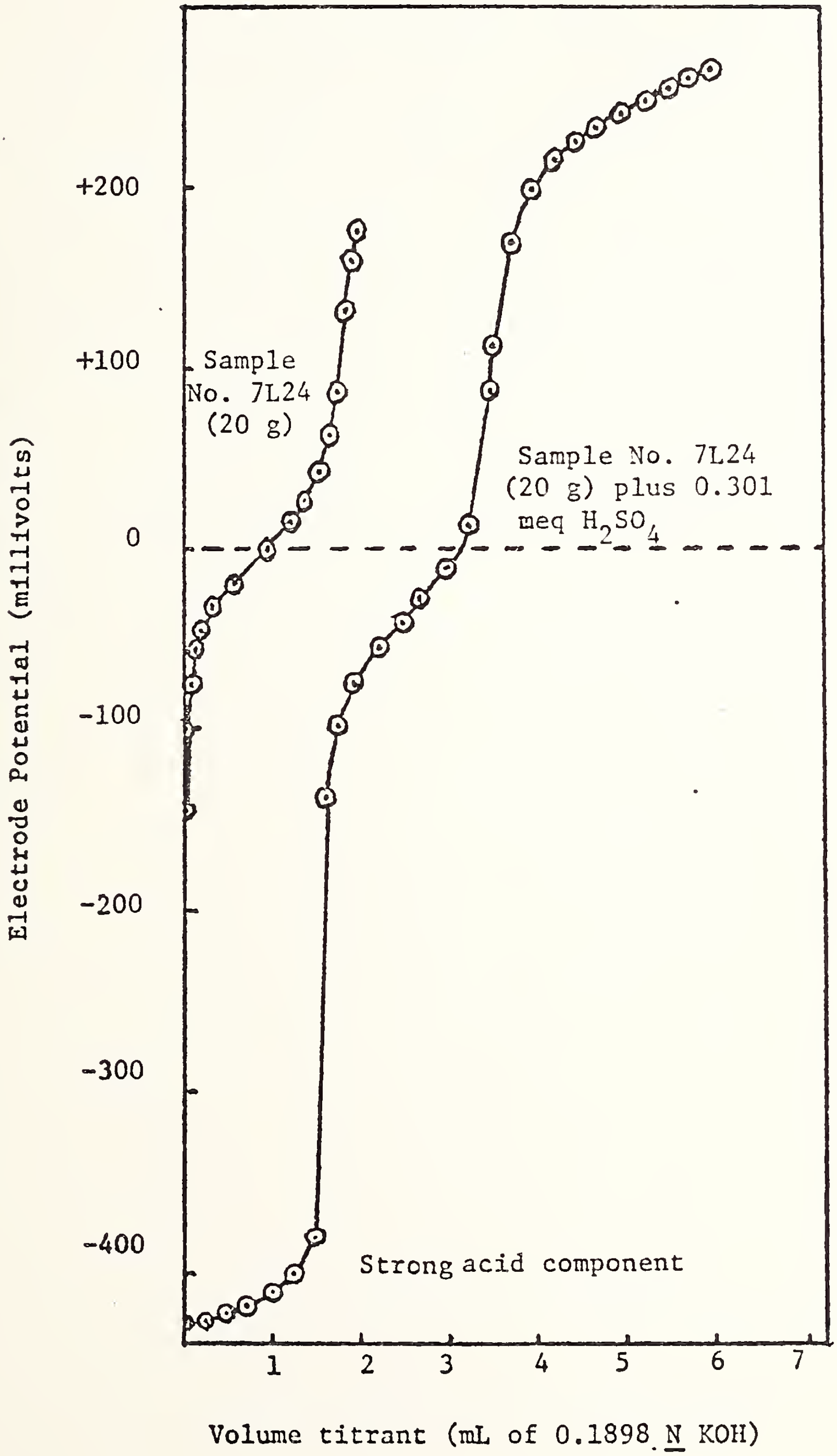
[12] The selection of a pH = 4.5 for the determination of a "positive" vs. "neutral" result appears appropriate due to comparability with the methyl orange results. However, there is some evidence to indicate that, in the absence of other influences, the corrosion of ferrous materials is possible at hydronium ion activities of 10^{-5} (pH = 5) or higher [34].

Figure 5. Potentiometric Titration of Recycled Distillate Fuel Oil Sample 7L24



CONCLUSION

The presence of high hydronium ion activity (acidity) in a recycled oil to be used for fuel would be expected to have a deleterious effect upon the storage-transfer-burner system. The ASTM method D 1093-65 (reapproved in 1975), "Acidity of Distillation Residues or Hydrocarbon Liquids," may be used to indicate the hydronium ion activity (acidity) of recycled fuel oils, with the modifications that the amount of water initially added to the oil sample be increased to 50 mL, and that potentiometric detection be used to determine the hydronium ion activity (acidity) of the separated water. A pH = 4.5 would be approximately equivalent to the methyl orange indicator color change as specified in the original ASTM test procedure.

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Finally, the authors especially wish to thank Mrs. Helen Anne Hurd for her untiring efforts in the preparation of this report and for her diligent endeavors as program secretary which have significantly contributed to making the Recycled Oil Program more efficient and effective.

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APPENDIX A

Energy Policy and Conservation Act
Section 383

the agency determines has the effect of requiring, permitting, or inducing the inefficient use of petroleum products, coal, natural gas, electricity, and other forms of energy, together with a statement of the need, purpose, or justification of any such requirement or such action. Each such report shall be submitted to the Congress within one year after the date of enactment of this Act.

Report to Congress. Energy impact statement.

(b) Except as provided in subsection (c), each of the agencies specified in subsection (a)(1) shall, where practicable and consistent with the exercise of their authority under other law, include in any major regulatory action (as defined by rule by each such agency) taken by each such agency, a statement of the probable impact of such major regulatory action on energy efficiency and energy conservation.

(c) Subsection (b) shall not apply to any authority exercised under any provision of law designed to protect the public health or safety.

FEDERAL ACTIONS WITH RESPECT TO RECYCLED OIL

42 USC 6363.

SEC. 383. (a) The purposes of this section are—

(1) to encourage the recycling of used oil;

(2) to promote the use of recycled oil;

(3) to reduce consumption of new oil by promoting increased utilization of recycled oil; and

(4) to reduce environmental hazards and wasteful practices associated with the disposal of used oil.

Definitions.

(b) As used in this section:

(1) the term "used oil" means any oil which has been refined from crude oil, has been used, and as a result of such use has been contaminated by physical or chemical impurities.

(2) The term "recycled oil" means—

(A) used oil from which physical and chemical contaminants acquired through use have been removed by re-refining or other processing, or

(B) any blend of oil, consisting of such re-refined or otherwise processed used oil and new oil or additives,

with respect to which the manufacturer has determined, pursuant to the rule prescribed under subsection (d)(1)(A)(i), is substantially equivalent to new oil for a particular end use.

(3) The term "new oil" means any oil which has been refined from crude oil and has not been used, and which may or may not contain additives. Such term does not include used oil or recycled oil.

(4) The term "manufacturer" means any person who re-refines or otherwise processes used oil to remove physical or chemical impurities acquired through use or who blends such re-refined or otherwise processed used oil with new oil or additives.

(5) The term "Commission" means the Federal Trade Commission.

(c) As soon as practicable after the date of enactment of this Act, the National Bureau of Standards shall develop test procedures for the determination of substantial equivalency of re-refined or otherwise processed used oil or blend of oil, consisting of such re-refined or otherwise processed used oil and new oil or additives, with new oil for a particular end use. As soon as practicable after development of such test procedures, the National Bureau of Standards shall report such procedures to the Commission.

Rules.

(d)(1)(A) Within 90 days after the date on which the Commission receives the report under subsection (c), the Commission shall, by rule, prescribe—

(i) test procedures for the determination of substantial equivalency of re-refined or otherwise processed used oil or blend of oil, consisting of such re-refined or otherwise processed used oil and new oil or additives, with new oil distributed for a particular end use; and

(ii) labeling standards applicable to containers of recycled oil in order to carry out the purposes of this section.

(B) Such labeling standards shall permit any container of recycled oil to bear a label indicating any particular end use for which a determination of substantial equivalency has been made pursuant to subparagraph (A)(i).

(2) Not later than the expiration of such 90-day period, the Administrator of the Environmental Protection Agency shall, by rule, prescribe labeling standards applicable to containers of new oil, used oil, and recycled oil relating to the proper disposal of such oils after use. Such standards shall be designed to reduce, to the maximum extent practicable, environmental hazards and wasteful practices associated with the disposal of such oils after use.

Rules.

(e) Beginning on the effective date of the standards prescribed pursuant to subsection (d)(1)(A)—

(1) no rule or order of the Commission, other than the rules required to be prescribed pursuant to subsection (d)(1)(A), and no law, regulation, or order of any State or political subdivision thereof may apply, or remain applicable, to any container of recycled oil, if such law, regulation, rule, or order requires any container of recycled oil, which container bears a label in accordance with the terms of the rules prescribed under subsection (d)(1)(A), to bear any label with respect to the comparative characteristics of such recycled oil with new oil which is not identical to that permitted by the rule respecting labeling standards prescribed under subsection (d)(1)(A)(ii); and

(2) no rule or order of the Commission may require any container of recycled oil to also bear a label containing any term, phrase, or description which connotes less than substantial equivalency of such recycled oil with new oil.

(f) After the effective date of the rules required to be prescribed under subsection (d)(1)(A), all Federal officials shall act within their authority to carry out the purposes of this section, including—

(1) revising procurement policies to encourage procurement of recycled oil for military and nonmilitary Federal uses whenever such recycled oil is available at prices competitive with new oil procured for the same end use; and

(2) educating persons employed by Federal and State governments and private sectors of the economy of the merits of recycled oil, the need for its use in order to reduce the drain on the Nation's oil reserves, and proper disposal of used oil to avoid waste of such oil and to minimize environmental hazards associated with improper disposal.

TITLE IV—PETROLEUM PRICING POLICY AND OTHER AMENDMENTS TO THE ALLOCATION ACT

PART A—PRICING POLICY

OIL PRICING POLICY

SEC. 401. (a) The Emergency Petroleum Allocation Act of 1973 is amended by adding at the end thereof the following new sections: 15 USC 751 note.

APPENDIX B

Fuel Oil Specifications

AMERICAN NATIONAL STANDARD ANSI/ASTM D 396 – 76$^{\epsilon}$

Standard Specification for
FUEL OILS[1]

This Standard is issued under the fixed designation D 396; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

$^{\epsilon}$ Note—The Fahrenheit equivalent in Column 7 of Table 1 was corrected editorially in January 1977.

1. Scope

1.1 This specification (Note) covers grades of fuel oil intended for use in various types of fuel-oil-burning equipment under various climatic and operating conditions.

Note—For information on the significance of the terminology and test methods used in this specification, see the Appendix.

1.2 This specification is for the use of purchasing agencies in formulating specifications to be included in contracts for purchases of fuel oils and for the guidance of consumers of fuel oils in the selection of the grades most suitable for their needs.

2. General Requirements

2.1 The grades of fuel oil specified herein shall be homogeneous hydrocarbon oils, free from inorganic acid, and free from excessive amounts of solid or fibrous foreign matter likely to make frequent cleaning of suitable strainers necessary.

2.2 All grades containing residual components shall remain uniform in normal storage and not separate by gravity into light and heavy oil components outside the viscosity limits for the grade.

3. Detailed Requirements

3.1 The various grades of fuel oil shall conform to the limiting requirements shown in Table 1.

3.2 Modifications of limiting requirements to meet special operating conditions agreed upon between the purchaser, the seller, and the supplier shall fall within limits specified for each grade, except as stated in supplementary footnotes for Table 1.

4. Test Methods

4.1 The requirements enumerated in this specification shall be determined in accordance with the following ASTM Methods,[2] except as may be required under 4.1.1.

4.1.1 *Flash Point*—Method D 93, Test for Flash Point by Pensky-Martens Closed Tester,[3] except where other methods are prescribed by law for the determination of minimum flash point. For Grades No. 1 and No. 2, Method D 56, Test for Flash Point by Tag Closed Tester[3] may be used as an alternative with the same limits, provided the flash point is below 79.4°C (175°F) and the viscosity is below 5.8 cSt (45 SUS) at 38°C (100°F). This method will give slightly lower values. In cases of dispute, Method D 93 shall be used as the referee method.

4.1.2 *Pour Point*—Method D 97, Test for Pour Point of Petroleum Oils.[3] Alternative test methods that indicate flow point properties may be used for low sulfur residual fuels by agreement between purchaser and supplier.

4.1.3 *Water and Sediment*—The water and sediment in Grades Nos. 1, 2, 4, and 5 shall be determined in accordance with Method D 1796, Test for Water and Sediment in Fuel

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[1] This specification is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants.

Current edition approved Aug. 27, 1976. Published October 1976. Originally published as D 396 – 34 T. Last previous edition D 396 – 75.

[2] For information on the precision of the ASTM methods of test for fuel oils refer to "An Evaluation of Methods for Determination of Sulfur in Fuel Oils" by A. R. Crawford, Esso Mathematics & Systems Inc. and G. V. Dyroff, Esso Research and Engineering Co., 1969. This document is available from the Publications Section, American Petroleum Institute, 2101 L. St., N.W., Washington, D.C. 20037.

[3] *Annual Book of ASTM Standards*, Part 23.

Oils by Centrifuge:[3] and Grade No. 6 by Method D 95, Test for Water in Petroleum and Other Bituminous Materials,[3] and Method D 473, Test for Sediment in Crude and Fuel Oils by Extraction.[3]

4.1.4 *Carbon Residue*—Method D 524, Test for Ramsbottom Carbon Residue of Petroleum Products.[3]

4.1.5 *Ash*—Method D 482, Test for Ash from Petroleum Oils.[3]

4.1.6 *Distillation*—Distillation of Grade No. 1 and No. 2 oils shall be determined in accordance with the Method D 86, Test for Distillation of Petroleum Products.[3]

4.1.7 *Viscosity*—Viscosity of Grade No. 1 and 2 shall be determined in accordance with Method D 445, Test for Kinematic Viscosity of Transparent and Opaque Liquids and the Calculation of Dynamic Viscosity[3] and of Grades Nos. 4, 5, and 6 in accordance with Method D 88, Test for Saybolt Viscosity.[3]

4.1.8 *Gravity*—Method D 287, Test for API Gravity of Crude Petroleum and Petroleum Products (Hydrometer Method).[3]

4.1.9 *Corrosion*—Method D 130, Test for Copper Corrosion by Petroleum Products, Copper Strip Test,[4] 3 h test at 50°C (122°F).

4.1.10 *Sulfur*—The sulfur content of any grade may be determined by any of the following methods: Method D 129, Sulfur in Petroleum Products by the Bomb Method,[2, 3] Method D 1552, Sulfur in Petroleum Products, High-Temperature Method,[2, 3] or Method D 2622, Sulfur in Petroleum Products (X-Ray Spectrographic Method).[2, 4] In addition, the sulfur of Grade No. 1 may be determined by Method D 1266, Sulfur in Petroleum Products (Lamp Method).[2, 3]

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[4] *Annual Book of ASTM Standards*, Part 24.

TABLE 1 Detailed Requirements for Fuel Oils^{A}

Grade of Fuel Oil	Flash Point, °C (°F)	Pour Point, °C (°F)	Water and Sediment, vol %	Carbon Residue on 10 % Bottoms, %	Ash, weight %	Distillation Temperatures, °C (°F)			Saybolt Viscosity, s^{D}				Kinematic Viscosity, cSt^{D}				Specific Gravity 60/60°F (deg API)	Copper Strip Corrosion	Sulfur, %
						10% Point	90% Point		Universal at 38°C (100°F)		Furol at 50°C (122°F)		At 38°C (100°F)		At 50°C (122°F)				
	Min	Max	Max	Max	Max	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Max	Max	Max
No. 1 A distillate oil intended for vaporizing pot-type burners and other burners requiring this grade of fuel	38 or legal (100)	−18^{C} (0)	0.05	0.15	...	215 (420)	...	288 (550)	...	...	...	...	1.4	2.2	...	...	0.8499 (35 min)	No. 3	0.5 or legal
No. 2 A distillate oil for general purpose heating for use in burners not requiring No. 1 fuel oil	38 or legal (100)	−6^{C} (20)	0.05	0.35	...	...	282^{C} (540)	338 (640)	(32.6)	(37.9)	...	...	2.0^{C}	3.6	...	...	0.8762 (30 min)	No. 3	0.5^{E} or legal
No. 4 Preheating not usually required for handling or burning	55 or legal (130)	−6^{C} (20)	0.50	...	0.10	...	...	...	(45)	(125)	...	...	5.8	26.4^{F}	...	...	...	...	legal
No. 5 (Light) Preheating may be required depending on climate and equipment	55 or legal (130)	...	1.00	...	0.10	...	...	...	(>125)	(300)	...	...	>26.4	65^{F}	...	...	...	...	legal
No. 5 (Heavy) Preheating may be required for burning and, in cold climates, may be required for handling	55 or legal (130)	...	1.00	...	0.10	...	...	...	(>300)	(900)	(23)	(40)	>65	194^{F}	(42)	(81)	...	...	legal

TABLE 1 *Continued*

Grade of Fuel Oil	Flash Point, °C (°F)	Pour Point, °C (°F)	Water and Sediment, vol %	Carbon Residue on 10 % Bottoms, %	Ash, weight %	Distillation Temperatures, °C (°F)			Saybolt Viscosity, s[D]				Kinematic Viscosity, cSt[D]				Specific Gravity 60/60°F (deg API)	Copper Strip Corrosion	Sulfur, %
						10% Point	90% Point		Universal at 38°C (100°F)		Furol at 50°C (122°F)		At 38°C (100°F)		At 50°C (122°F)				
	Min	Max	Max	Max	Max	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Max
No. 6 Preheating required for burning and handling	60 (140)	[G]	2.00[E]	...	...	...	...	...	(>900)	(9000)	(>45)	(300)	...	...	>92	638[F]	...	...	legal

[A] It is the intent of these classifications that failure to meet any requirement of a given grade does not automatically place an oil in the next lower grade unless in fact it meets all requirements of the lower grade.

[B] In countries outside the United States other sulfur limits may apply.

[C] Lower or higher pour points may be specified whenever required by conditions of storage or use. When pour point less than −18°C (0°F) is specified, the minimum viscosity for Grade No. 2 shall be 1.8 cSt (32.0 SUS) and the minimum 90 % point shall be waived.

[D] Viscosity values in parentheses are for information only and not necessarily limiting.

[E] The amount of water by distillation plus the sediment by extraction shall not exceed 2.00 %. The amount of sediment by extraction shall not exceed 0.50 %. A deduction in quantity shall be made for all water and sediment in excess of 1.0 %.

[F] Where low sulfur fuel oil is required, fuel oil falling in the viscosity range of a lower numbered grade down to and including No. 4 may be supplied by agreement between purchaser and supplier. The viscosity range of the initial shipment shall be identified and advance notice shall be required when changing from one viscosity range to another. This notice shall be in sufficient time to permit the user to make the necessary adjustments.

[G] Where low sulfur fuel oil is required, Grade 6 fuel oil will be classified as low pour +15°C (60°F) max or high pour (no max). Low pour fuel oil should be used unless all tanks and lines are heated.

APPENDIX

X1. SIGNIFICANCE OF ASTM SPECIFICATION FOR FUEL OILS

X1.1 Scope

X1.1.1 ASTM Specification D 396, for Fuel Oils, divides fuel oils into grades based upon the types of burners for which they are suitable. It places limiting values on several of the properties of the oils in each grade. The properties selected for limitation are those that are believed to be of the greatest significance in determining the performance characteristics of the oils in the types of burners in which they are most commonly used.

X1.2 Classes

X1.2.1 Because of the methods employed in their production, fuel oils fall into two broad classifications: distillates and residuals. The distillates consist of overhead or distilled fractions. The residuals are bottoms remaining from the distillation, or blends of these bottoms with distillates. In Specification D 396, Grades No. 1 and No. 2 are distillates and the grades from No. 4 to No. 6 are usually residual, although some heavy distillates may be sold as Grade No. 4.

X1.3 Grades

X1.3.1 *Grade No. 1* is a light distillate intended for use in burners of the vaporizing type in which the oil is converted to a vapor by contact with a heated surface or by radiation. High volatility is necessary to ensure that evaporation proceeds with a minimum of residue.

X1.3.2 *Grade No. 2* is a heavier distillate than grade No. 1. It is intended for use in atomizing type burners which spray the oil into a combustion chamber where the tiny droplets burn while in suspension. This grade of oil is used in most domestic burners and in many medium capacity commercial-industrial burners where its ease of handling and ready availability sometimes justify its higher cost over the residual fuels.

X1.3.3 *Grade No. 4* is usually a light residual, but it sometimes is a heavy distillate. It is intended for use in burners equipped with devices that atomize oils of higher viscosity than domestic burners can handle. Its permissible viscosity range allows it to be pumped and atomized at relatively low storage temperatures. Thus, in all but extremely cold weather it requires no preheating for handling.

X1.3.4 *Grade No. 5* (*Light*) is residual fuel of intermediate viscosity for burners capable of handling fuel more viscous than grade No. 4 without preheating. Preheating may be necessary in some types of equipment for burning and in colder climates for handling.

X1.3.5 *Grade No. 5* (*Heavy*) is a residual fuel more viscous than Grade No. 5 (light) and is intended for use in similar service. Preheating may be necessary in some types of equipment for burning and in colder climates for handling.

X1.3.6 *Grade No. 6*, sometimes referred to as "Bunker C," is a high-viscosity oil used mostly in commercial and industrial heating. It requires preheating in the storage tank to permit pumping, and additional preheating at the burner to permit atomizing. The extra equipment and maintenance required to handle this fuel usually preclude its use in small installations.

X1.3.7 Residual fuel oil supplied to meet regulations requiring low sulfur content may differ from the grade previously supplied. It may be lower in viscosity (and fall into a different grade number). If it must be fluid at a given temperature, Method D 97 may not accurately reflect the pour point which can be expected after a period of storage. It is suggested that the purchaser and supplier discuss the proper handling and operating techniques for a given low-sulfur residual fuel oil in the installation where it is to be used.

X1.4 Significance of Test Methods

X1.4.1 The significance of the properties of fuel oil on which limitations are placed by the specification is as follows:

X1.4.1.1 *Flash Point*—The flash point of a fuel oil is an indication of the maximum temperature at which it can be stored and handled without serious fire hazard. The minimum permissible flash point is usually regulated by federal, state, or municipal laws and is based on accepted practice in handling and use.

X1.4.1.2 *Pour Point*—The pour point is an indication of the lowest temperature at which a fuel oil can be stored and still be capable of flowing under very low forces. The pour point is prescribed in accordance with the conditions of storage and use. Higher pour point fuels are permissible where heated storage and adequate piping facilities are provided. An increase in pour point may occur when residual fuel oils are subjected to cyclic temperature variations that may occur in the course of storage or when the fuel is preheated and returned to storage tanks. To predict these properties, test methods such as British Admiralty Method VII, Shell-Amsterdam 2148-1, Method D 3245-IP 230/69, Test for Pumpability of Industrial Fuel Oils.[3] or Method D 1659, Test for Maximum Fluidity Temperature of Residual Fuel Oil.[3] may be required.

X1.4.1.3 *Water and Sediment*—Appreciable amounts of water and sediment in a fuel oil tend to cause fouling of facilities for handling it, and to give trouble in burner mechanisms. Sediment may accumulate in storage tanks and on filter screens or burner parts, resulting in obstruction to flow of oil from the tank to the burner. Water in distillate fuels may cause corrosion of tanks and equipment and it may cause emulsions in residual fuels.

X1.4.1.4 *Carbon Residue*—The carbon residue of a fuel is a measure of the carbonaceous material left after all the volatile components are vaporized in the absence of air. It is a rough approximation of the tendency of a fuel to form deposits in vaporizing burners, such as pot-type and sleeve-type burn-

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[3] *Annual Book of ASTM Standards*, Part 25.

ers, where the fuel is vaporized in an air-deficient atmosphere.

To obtain measurable values of carbon residue in the lighter distillate fuel oils, it is necessary to distill the oil to remove 90 percent of it in accordance with ASTM Method D 86, Test for Distillation of Petroleum Products,[7] and then determine the carbon residue concentrated in the remaining 10 percent bottoms.

X1.4.1.5 *Ash*—The amount of ash is the quantity of noncombustible material in an oil. Excessive amounts may indicate the presence of materials that cause high wear of burner pumps and valves, and contribute to deposits on boiler heating surfaces.

X1.4.1.6 *Distillation*—The distillation test shows the volatility of a fuel and the ease with which it can be vaporized. The test is of greater significance for oils that are to be burned in vaporizing type burners than for the atomizing type. For example, the maximum 10 percent and 90 percent distilled temperatures are specified for grade No. 1 fuel. The limiting 10 percent value assures easy starting in vaporizing type burners and the 90 percent limit excludes heavier fractions that would be difficult to vaporize.

The limits specified for grade No. 2 heating oil define a product that is acceptable for burners of the atomizing type in household heating installations. Distillation limits are not specified for fuel oils of grades Nos. 4, 5, and 6.

X1.4.1.7 *Viscosity Limits for Grades Nos. 1 and 2*—The viscosity of an oil is a measure of its resistance to flow. In fuel oil it is highly significant since it indicates both the relative ease with which the oil will flow or may be pumped, and the ease of atomization.

Viscosity limits for No. 1 and No. 2 grades are specified to help maintain uniform fuel flow in appliances with gravity flow, and to provide satisfactory atomization and constant flow rate through the small nozzles of household burners. For the heavier grades of industrial and bunker fuel oils, viscosity is of major importance, so that adequate preheating facilities can be provided to permit them to be pumped to the burner and to provide good atomization. However, it is equally important that the maximum viscosity under the existing conditions be such that the oil can be pumped satisfactorily from the storage tank to the preheater.

X1.4.1.8 *Gravity*—Gravity alone is of little significance as an indication of the burning characteristics of fuel oil. However, when used in conjunction with other properties, it is of value in weight-volume relationships and in calculating the heating value of an oil.

X1.4.1.9 *Corrosion*—The corrosion test serves to indicate the presence or absence of materials that might corrode copper, brass, and bronze components of the fuel system. This property is specified only for No. 1 distillate fuel.

X1.4.1.10 Limited sulfur content of fuel oil may be required for special uses in connection with heat treatment, nonferrous metal, glass, and ceramic furnaces or to meet federal, state or local legislation or regulations.

VV-F-815C
July 10, 1972
SUPERSEDING
VV-F-815B
16 December 1969

FEDERAL SPECIFICATION

FUEL OIL, BURNER

This specification was approved by the Commissioner, Federal Supply Service, General Services Administration, for the use of all Federal agencies.

1. SCOPE AND CLASSIFICATION

1.1 Scope. This specification covers fuel oil for stationary oil-burning, heat-generating equipment (see 6.1).

1.2 Classification. Burner fuel oil covered by this specification shall be of the following grades as specified (see 6.2):

Grade No. 1 - Distillate
Grade No. 2 - Distillate
Grade No. 4 - Light residual or heavy distillate
Grade No. 5 (Light) - Residual
Grade No. 5 (Heavy) - Residual
Grade No. 6 - Residual (Bunker C)

2. APPLICABLE DOCUMENTS

2.1 Specifications and standards. The following specifications and standards of the issue in effect on date of invitation for bids or request for proposal, form a part of the specification to the extent specified herein.

Federal Standards:

Fed. Test Method Std. No. 791 - Lubricants, Liquid Fuels and Related Products; Methods of Testing

(Activities outside the Federal Government may obtain copies of Federal Specifications and Standards and Handbooks as outlined under General Information in the Index of Federal Specifications and Standards, and at the prices indicated in the Index. The Index, which includes cumulative monthly supplements as issued, is for sale on a subscription basis by the Superintendent of Documents, U. S. Government Printing Office, Washington, D. C. 20402

FSC 9140

(Single copies of this specification and other product specifications required by activities outside the Federal Government for bidding purposes are available without charge at the General Services Administration Regional Offices in Boston, New York, Washington, D. C., Atlanta, Chicago, Kansas City, Mo., Fort Worth, Denver, San Francisco, Los Angeles, and Auburn, Washington.

(Federal Government activities may obtain copies of Federal Specifications and Standards and the Index of Federal Specifications and Standards from established distribution points in their agencies.)

Military Standards:

MIL-STD-105 - Sampling Procedures and Tables for Inspection by Attributes
MIL-STD-290 - Packaging, Packing and Marking of Petroleum and Related Products

(Copies of Military Specifications and Standards required by suppliers in connection with specific procurement functions should be obtained from the procuring activity or as directed by the contracting officer.)

2.2 Other publications. The following documents form a part of this specification to the extent specified herein. Unless otherwise indicated, the issue in effect on date of invitation for bids or request for proposals shall apply.

American Society for Testing and Materials (ASTM)

Standards:

D 56 - Flash Point by Tag Closed Tester
D 86 - Distillation of Petroleum Products
D 88 - Saybolt Viscosity
D 93 - Flash Point by Pensky-Martens Closed Tester
D 95 - Water in Petroleum and Other Bituminous Materials
D 97 - Pour Point
D 129 - Sulfur in Petroleum Products by the Bomb Method
D 130 - Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test
D 270 - Sampling Petroleum and Petroleum Products
D 287 - API Gravity of Crude Petroleum and Petroleum Products (Hydrometer Method)
D 445 - Viscosity of Transparent and Opaque Liquids (Kinematic and Dynamic Viscosities)
D 473 - Sediment in Crude and Fuel Oils by Extraction
D 482 - Ash from Petroleum Products
D 524 - Ramsbottom Carbon Residue of Petroleum Products
D 611 - Test for Aniline Point in Petroleum Products

D 1551 - Sulfur in Petroleum Products (Quartz Tube Method)
D 1552 - Sulfur in Petroleum Products (High Temperature Method)
D 1796 - Water and Sediment in Crude Oils and Fuel Oils by Centrifuge
D 2161 - Conversion of Kinematic Viscosity to Saybolt Universal or to Saybolt Furol Viscosity
D 2622 - Sulfur in Petroleum Product (X-Ray Spectrographic Method)

(The ASTM methods listed above are included in Part 17 or Part 18 of the Annual Book of ASTM Standards and are available individually. Application for copies should be addressed to the American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103.)

(Technical Society specifications and standards are generally available for reference from libraries. They are also distributed among using Federal agencies.)

3. REQUIREMENTS

3.1 Material. Burner fuel oil shall consist of petroleum-derived products. In the procurement of new fuel oils, suppliers are prohibited from adulterating either Grade No. 5 or Grade No. 6 fuel oil with waste crankcase lubricants or with similar products. Blending of various compatible grades of the material to produce an intermediate grade is permitted; however, such blending shall be accomplished by mechanical mixing or agitation in a tank, or by in-line blending prior to loading the product into transport equipment. The product formed by such blending shall comply with all the requirements of the grade produced.

3.2 Physical and chemical requirements. Burner fuel oil shall conform to the physical and chemical requirements given in Table I and in 3.2.1, 3.2.2, and 3.2.3.

3.2.1 Sulfur content.

3.2.1.1 In the U.S.A. For all grades of fuel, sulfur limits shall be as specified by the applicable contract, the Environmental Protection Agency, or the state or community where the fuel is to be used, whichever is more restrictive.

3.2.1.2 Outside the U.S.A. For procurement outside the U.S.A., the maximum sulfur content shall be 0.5 percent for No. 1 fuel and 1.0 percent for No. 2 fuel or as may be imposed by a foreign country or local community where the fuel is to be used, whichever is more restrictive.

3.2.2 Copper strip corrosion. For grades 1 and 2 fuel oil, the copper strip corrosion shall be a maximum of No. 3 per ASTM D 130.

3.2.3 Workmanship. The fuel oil shall be homogeneous in appearance, free from visible foreign matter such as grit or fiber.

TABLE I. Physical and chemical requirements

Grade of fuel oil		Flash Point °F. (°C.)	Pour1/2/ Point °F. (°C.)	Water and Sediment, % by volume	Carbon Residue on 10% residuum %	Ash % by weight	Distillation temperature °F. (°C.)			
							10% point	50% point	90% point	
No.	Description	Min.	Max.	Max.	Max.	Max.	Max.		Min.	Max.
1	Distillate	100 (38) or legal	0 (-18)	Trace	0.15	--	420 (215)	Report	--	550 (288)
2	Distillate	100 (38) or legal	20 (-7)	0.05	0.35	--	4/	Report	5402/ (282)	640 (338)
4	Light residual or Heavy distillate	130 (55) or legal	20 (-7)	0.50	--	0.10	--	--	--	--
5 (Light)	Residual	130 (55) or legal	--	1.00	--	0.10	--	--	--	--
5 (Heavy)	Residual	130 (55) or legal	--	1.00	--	0.10	--	--	--	--
6	Residual (Bunker C)	150 (65)	7/	2.005/	--	--	--	--	--	--

1/ Pour points other than those shown may be specified whenever required by conditions of storage and use, if agreed upon by purchaser and seller. For cold weather use, the specified pour point normally should not be more than 10°F. (5.6°C.) below the lowest expected ambient temperature.

2/ When pour point less than 0°F. (-18°C.) is specified the minimum viscosity shall be 1.8 centistokes (32 seconds Saybolt Universal) and the minimum 90% point shall be waived.

3/ Viscosity values in parentheses are for information only and not necessarily limiting.

4/ The 10 percent distillation point may be specified at 440°F. (226°C.) maximum for use in other than atomizing burners.

TABLE I. Physical and chemical requirements - (continued)

Grade of fuel oil		Saybolt viscosity[3] seconds				Kinematic viscosity centistokes				Gravity degrees API Min.	Aniline point °F.
		Universal at 100°F. (38°C.)		Furol at 122°F. (50°C.)		at 100°F. (38°C.)		at 122°F. (50°C.)			
No.	Description	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.		
1	Distillate	--	--	--	--	1.4	2.2	--	--	35	Report
2	Distillate	(32.6)	(37.9)	--	--	2.0[2]	3.6	--	--	30	Report
4	Light residual or Heavy distillate	(45)	(125)	--	--	5.8	26.4	--	--	--	--
5 (Light)	Residual	(150)	(300)	--	--	32[6]	65[6]	--	--	--	--
5 (Heavy)	Residual	(350)	(750)	(23)	(40)	75[6]	162[6]	42[6]	81[6]	--	--
6	Residual (Bunker C)	(900)	(9000)	(45)	(300)	--	--	92[6]	638[6]	--	--

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[5] The amount of water by distillation plus the sediment by extraction shall not exceed 2.00 percent. The amount of sediment by extraction shall not exceed 0.50 percent.

[6] Where low sulfur fuel oil is required, fuel oil in the viscosity range of a lower numbered grade, down to and including No. 4, may be supplied. By agreement between the receiving activity and supplier, the viscosity range of the initial shipment shall be identified and advance notice required when changing from one viscosity range to another. This notice shall be in sufficient time to permit the user to make necessary adjustments.

[7] Where low sulfur fuel oil (1.0 percent max. or less) is required, Grade No. 6 fuel oil shall be classified as low pour point (60°F. max.) or high pour point (no max.). Low pour point fuel oil should be used unless all tanks and lines are heated.

4. QUALITY ASSURANCE PROVISIONS

4.1 Responsibility for inspection. Unless otherwise specified in the contract or purchase order, the supplier is responsible for the performance of all inspection requirements as specified herein. Except as otherwise specified in the contract or order, the supplier may use his own or any other facilities suitable for the performance of the inspection requirements specified herein, unless disapproved by the Government. The Government reserves the right to perform any of the inspections set forth in the specification where such inspections are deemed necessary to assure supplies and services conform to prescribed requirements.

4.2 Lot.

4.2.1 Bulk lot. An indefinite quantity of a homogeneous mixture of one grade of fuel oil offered for acceptance in a single, isolated container; or manufactured in a single plant run (not exceeding 24 hours), through the same processing equipment, with no change in the ingredient materials.

4.2.2 Packaged lot. An indefinite number of 55-gallon drums or smaller unit containers of identical size and type, offered for acceptance, and filled with a homogeneous mixture of one grade of fuel oil from a single, isolated container; or filled with a homogeneous mixture of one grade of fuel oil, manufactured in a single plant run (not exceeding 24 hours), through the same processing equipment, with no change in the ingredient materials.

4.3 Sampling.

4.3.1 Sampling for examination of packed containers. Take a randon sample of packed containers from each packaged lot in accordance with MIL-STD-105 at inspection level II and acceptable quality level (AQL) = 2.5 percent defective.

4.3.2 Sampling for tests. Take samples for tests in accordance with ASTM method D 270.

4.4 Inspection. Perform inspection in accordance with method 9601 of Fed. Test Method Std. No. 791.

4.4.1 Examination of packed containers. Examine samples taken in accordance with 4.3.1 for compliance with MIL-STD-290 with regard to fill, closure, sealing, leakage, packaging, packing, and marking requirements. Reject any container having one or more defects or under the required fill. If the number of defective or underfilled containers exceeds the acceptance number for the appropriate plan of MIL-STD-105, reject the lot represented by the sample.

4.5 Classification of tests. All tests are quality conformance tests.

4.6 Test methods. Perform tests in accordance with the applicable methods listed in Table II.

TABLE II. Test methods

Test	ASTM test method number
Flash point[1]	D 93 or D 56
Pour point	D 97
Water and sediment (grades No. 1, 2, and 4)	D 1796
Water (grades No. 5 and 6)	D 95
Sediment (grades No. 5 and 6)	D 473
Carbon residue, Ramsbottom	D 524
Ash	D 482
Distillation temperature	D 86
Viscosity, Kinematic	D 445
Viscosity, Saybolt[2]	D 2161 or D 88
Gravity, API	D 287
Copper strip corrosion[3]	D 130
Sulfur[4]	D 1552, D129, D 1551 or D 2622
Aniline point	D 611

[1] ASTM D 93 is the preferred method. D 56 may be used as an alternate for grade No. 1 with the same limits. In case of dispute, D 93 shall be used as the referee method.

[2] ASTM D 2161 is the preferred method.

[3] The test shall be run for 3 hours at 212°F. (100°C.).

[4] ASTM method D 1552 is the preferred method. D 129, D 1551 and D 2622 may be used as alternate methods.

5. PREPARATION FOR DELIVERY

5.1 Packaging, packing, and marking. Unless otherwise specified in the contract or purchase order (see 6.2), packaging, packing, and marking shall be performed in accordance with MIL-STD-290.

6. NOTES

6.1 Intended use. Burner fuel oils covered by this specification fall into two broad classes, distillates and residuals. The oils are intended for use in various types of fuel-burning equipment under various climatic and operating conditions, for the generation of heat in furnaces for heating buildings, for the generation of steam, or for other purposes. The grades covered by this specification are intended for specific applications as indicated below:

6.1.1 Grade No. 1. A light distillate oil intended for use in burners of the vaporizing type in which the oil is converted to a vapor by contact with a heated surface or by radiation.

6.1.2 Grade No. 2. A heavier distillate than grade No. 1. It is intended for use in atomizing-type burners which spray the oil into a combustion chamber where the tiny droplets burn while in suspension. The grade of oil is used in most domestic burners and in many medium-capacity commercial-industrial burners where its ease of handling and ready availability sometimes justify its higher cost over the residual grades.

6.1.3 Grade No. 4. Usually a light residual but sometimes a heavy distillate. It is intended for use in burners equipped with devices that atomize oils of higher viscosity than domestic burners can handle. Its permissible viscosity range allows it to be pumped and atomized at relatively low storage temperatures. Thus, except in extremely cold weather, it requires no preheating for handling.

6.1.4 Grade No. 5 (light). A residual fuel of intermediate viscosity for burners capable of handling fuel more viscous than grade No. 4 without preheating. Preheating may be necessary in some types of equipment for burning and in colder climates for handling.

6.1.5 Grade No. 5 (heavy). A residual fuel more viscous than grade No. 5 (light). It is intended for similar service. Preheating may be necessary in some types of equipment for burning and in colder climates for handling.

6.1.6 Grade No. 6. A high-viscosity oil, sometimes referred to as "Bunker C", and used mostly in commercial and industrial heating. It requires preheating in the storage tank to permit pumping and additional preheating at the burner to permit atomizing. The extra equipment and maintenance required to handle this fuel usually preclude its use in small installations.

6.2 Ordering data. Procurement documents should specify the following:

(a) Title, number, and date of this specification.
(b) Grade of oil required (see 1.2).
(c) Quantity of oil required. The fuel oil should be purchased by volume, the unit being one U.S. gallon of 231 cubic inches at 60°F. (15.6°C). Outside the U.S.A., oil may be purchased in SI (metric) units if agreeable to purchaser and supplier.
(d) Whether bulk or packaged delivery is required.
(e) Type and size of containers if packaged delivery is required (see 5.1).
(f) Maximum permissible sulfur content (see 3.2.1 and 6.3).

6.3 Sulfur content (see 3.2.1). Sulfur content of burner fuel oils is being increasingly restricted because of air-pollution problems. Maximum limits for sulfur vary from one region or metropolitan area to another, and are likely to be reduced even further. Accordingly, it is not possible to set out specific requirements in this specification. Sulfur limits should be specified in all contracts or purchase orders, in compliance with the current legal requirements in the particular state or community, or with the standards of the Environmental Protection Agency.

> NOTE: The provisions for sulfur limits in this paragraph and in 3.2.1 are in consonance with Executive Order 11282, Control of Air Pollution Originating from Federal Installations.

MILITARY CUSTODIANS:

Army - MR
Navy - YD
Air Force - 68

Review activities:

Army - WC
Navy - YD, SA
Air Force - 68
DSA - PS

User activities:

Navy - MC, SH

Preparing activity:

Army - MR

(Project No. 9140-0040)

CIVIL AGENCY INTEREST:

GSA

☆U. S. GOVERNMENT PRINTING OFFICE : 1972 O - 514-169 (32)

Orders for this publication are to be placed with General Services Administration, acting as an agent for the Superintendent of Documents. See section 2 of this specification to obtain extra copies and other documents referenced herein. Price 15 cents each.

[illegible]

MIL-F-859E
22 SEPTEMBER 1965

SUPERSEDING
MIL-F-859D
21 DECEMBER 1956
(SEE 6.5)

MILITARY SPECIFICATION

FUEL OIL, BURNER

This specification is mandatory for use by all Departments and Agencies of the Department of Defense.

1. SCOPE

1.1 Scope. This specification covers burner fuel oil for steam powered vessels of the Navy and for other steam powered vessels of the Government service.

1.2 Classification. Burner fuel oil shall be the following grade (see 6.2):

Burner fuel oil—Navy special
(NATO symbol F-77).

2. APPLICABLE DOCUMENTS

2.1 The following documents of the issue in effect on date of invitation for bids or request for proposal, form a part of the specification to the extent specified herein.

STANDARDS

FEDERAL

FED-STD-791 — Lubricants, Liquid-Fuels, and Related Products; Methods of Testing.

MILITARY

MIL-STD-290 Packaging, Packing and Marking of Petroleum and Related Products.

(Copies of specifications, standards, drawings, and publications required by suppliers in connection with specific procurement functions should be obtained from the procuring activity or as directed by the contracting officer.)

2.2 Other publications. The following documents form a part of this specification to the extent specified herein. Unless otherwise indicated, the issue in effect on date of invitation for bids or request for proposal shall apply.

AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM)

ASTM Part 17— Petroleum Products-Fuels, Solvents, Engine Tests, Lubricating Oils, Cutting Oils, Grease.

D-88 — Viscosity, Saybolt.

D-92 — Flash and Fire Points by Cleveland Cup Open.

D-93 — Flash Point by Pensky - Martens Closed Tester.

D-95 — Water in Petroleum Products and Oth-

0/10

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177

	er Bituminous Materials.
D-97	— Cloud and Pour Points.
D-129	— Test for Sulfur in Petroleum Products by the Bomb Method.
D-189	— Test for Conradson Carbon Residue of Petroleum Products.
D-270	— Method of Sampling Petroleum and Petroleum Products (Tentative).
D-287	— Test for API Gravity of Crude Petroleum and Petroleum Products (Hydrometer Method).
D-473	— Test for Sediment In Crude Petroleum and Fuel Oil By Extraction.
D-482	— Test for Ash From Petroleum Products.
D-1659	— Method of Test for Maximum Fluidity Temperature of Residual Fuel Oil (Tentative).
D-1796	— Test for Water and Sediment in Fuel Oils by Centrifuge.

(Application for copies should be addressed to the American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pa. 19103.)

INTERSTATE COMMERCE COMMISSION

Code of Federal Regulations

(Application for copies should be addressed to the Superintendent of Documents, Government Printing Office, Washington, D.C. 20402).

(Technical society and technical association specifications and standards are generally available for reference from libraries. They are also distributed among technical groups and using Federal agencies.)

3. REQUIREMENTS

3.1 Material.

3.1.1 The burner fuel oil shall consist of a hydrocarbon oil. Additives are not permitted.

3.2 Chemical and physical requirements. The fuel oil shall conform to the chemical and physical requirements of table I.

TABLE I. *Chemical and physical requirements*

		Limits	Test method number[1]	ASTM method number
Flash point, closed cup (min.)	°F.	150	1102	D-93
Fire point (min.)	°F.	[2]200	1103	D-92
Viscosity, at 122°F. (max.)	SSF	....	304	D-88

TABLE I. *Chemical and physical requirements*—Continued

		Limits	Test method number[1]	ASTM method number
Viscosity, at 122°F. (max.)	SSU	225	304	D-88
Viscosity, at 85°F. (min.)	SSU	[3] 225	304	D-88
Ash (max.)	percent	0.10	5421	D-482
Water, by distillation (max.)	percent	0.5	3001	D-95
A.P.I. gravity (min.)		11.5	401	D-287
Pour point, upper (max.) [4]	°F.	15	[6] 201	D-97
Fluidity at 32°F. [5]		Pass		D-1659 Appendix
Carbon residue (max.)	percent	15	[7] 5001	D-189
Sediment by extraction (max.)	percent	0.12	3002	D-473
Water and sediment (max.)	percent	[8] 0.5	3000	D-1796
Thermal stability (NBTL heater)		[9] Pass	[10] 3461	....
Explosiveness (max.)	percent	50	1151	....
Sulphur (max.)		3.50	5202	D-129

[1] FED-STD-791.

[2] See 3.3.

[3] Equivalent to approximately 85 SSU at 122°F. If viscosity at 122°F. is greater than 100 SSU and less than 225 SSU the viscosity at 85°F. need not be measured.

[4] If the pour point is less than 15°F. the fluidity need not be performed.

[5] See 4.4.1.2.

[6] See 4.4.1.3 Pour test not required when fluidity test is performed and passes.

[7] See 4.4.1.1.

[8] Applicable only on samples taken at supp' r's refinery, tank farm, or pipe line.

[9] See 3.4 and 3.5.

[10] D-1661 is an optional method and may be used in lieu of NBTL heater.

3.3 Fire point. When the flash point of the fuel is 175°F. or higher, the fire point need not be determined. If the water content of the fuel prevents accurate determination of the fire point, the fuel oil will be acceptable if the foaming due to water starts below the fire point, and at a temperature not lower than 195°F.

3.4 Thermal stability. When subjected to the thermal stability test specified in table I fuel oil Navy special shall show a No. 1 tube or better.

3.5 Compatibility. Burner fuel oil Navy special, when tested in accordance with 4.4.2 shall show a No. 2 tube or better with each of Reference Fuels II and I. Compati-

bility need not be run on each blend of fuel unless the composition is altered to the extent that a total component change of 10 percent relative to the blend that passed the compatibility test has been made.

4. QUALITY ASSURANCE PROVISIONS

4.1 Responsibility for inspection. Unless otherwise specified in the contract or purchase order, the supplier is responsible for the performance of all inspection requirements as specified herein. Except as otherwise specified, the supplier may utilize his own facilities or any commercial laboratory acceptable to the Government. The Government reserves the right to perform any of the inspections set forth in the specification where such inspections are deemed to assure supplies and services conform to prescribed requirements.

4.2 Sampling.

4.2.1 *Bulk lot.* An indefinite quantity of material from one storage tank offered for acceptance. To establish homogeneity, upper, middle, and lower samples as prescribed in ASTM D-270 shall be taken from each lot and subjected to API gravity determinations in accordance with method 401 of FED-STD-791. To be considered homogeneous, those gravities shall not vary from the average more than 0.3°. If the lot is homogeneous, samples shall be composited for acceptance testing. If the lot is not homogeneous, acceptance tests shall be performed separately upon the upper, middle, and lower samples.

4.2.2 *Packaged lot.* An indefinite number of 55-gallon drums or smaller containers of identical size and type filled from one storage tank. Acceptance tests shall be performed upon a composite of samples taken in the number and as specified in ASTM D-270.

4.3 *Tests.*

4.3.1 Tests shall be conducted in accordance with the applicable methods of FED-STD-791 as specified in table I and the following:

4.3.1.1 *Carbon residue.* A 5-gm. sample shall be used. Other details of the test shall be in accordance with the specified method (see table I).

4.3.1.2 *Pour point.* In determining the pour point three consecutive tests of the same sample, using the same test jar, shall be conducted. The value to be reported, provided the results of the three tests check within 5°F., shall be the average of the three results to the nearest multiple of 5. All other details of the test shall be in accordance with the specified method (see table I).

4.3.1.3 *Fluidity test.* The object of the fluidity test is to ascertain if the oil will flow through a 1/2 inch pipe under slight pressure (such as it would be subjected to by a pump or by its own head from an overhead tank) at the specified temperature.

4.3.2 *Compatibility test.* The compatibility test shall consist of subjecting to the thermal stability test separate tests of Navy special fuel and reference fuel H and Navy special fuel and reference fuel I at a ratio of 1:1.

5. PREPARATION FOR DELIVERY

5.1 Packaging, packing, and marking. Packaging, packing, and marking shall be in accordance with MIL-STD-290.

5.2 Marking of shipments. Shipping containers shall be marked in accordance with MIL-STD-290. The nomenclature shall be as follows: Fuel Oil, Burner, Navy special (NATO symbol F-77), MIL-F-859. In addition, the information required by Code of Federal Regulations 49CFR 71-78 shall appear on each individual container and on all shipping containers.

6. NOTES

6.1 Intended use. Fuel oil Navy special is intended for use in all steam vessels of the Navy, and other Government vessels as required.

6.2 Ordering data. Procurement documents should specify the following:

- (a) Title, number, and date of this specification.
- (b) Quantity required (see 4.2.2).
- (c) Packaging, packing and marking required (see 5.1 and 5.2).

6.3 Certain provisions of this specification are the subject of an international standardization agreement (NATO). When amendment revision, or cancellation of this specification is proposed, the departmental custodians will inform their respective Departmental Standardization Office so that appropriate action may be taken respecting the international agreement concerned.

6.4 Information relative to obtaining H and I reference fuels may be obtained from the cognizant Military inspector.

6.5 Changes from previous issue. The extent of changes (deletions, additions, etc.) preclude the annotation of the individual changes from the previous issue of this document.

Custodians:
Army—MR
Navy—SH
Air Force—68

Review activities:
Army—MR
Navy—SH
Air Force—68

User activities:
Army—CE, GL, MU
Navy—YD

International (see section 6)

Preparing activity:
Navy—SH
(Project 9140-0015)

U714

09-23-79
04-25-19

MIL-F-859E
AMENDMENT-2
4 August 1967
SUPERSEDING[1]
Amendment-1
24 August 1966

MILITARY SPECIFICATION

FUEL OIL, BURNER

This amendment forms a part of Military Specification MIL-F-859E, dated 22 Septem 1966 and is mandatory for use by all Departments and Agencies of the Department Defense.

Page 2, paragraph 2.2, under AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM): "D-1661 - Thermal Stability of U. S. Navy Special Fuel Oil."

Page 3, Table I: Delete and substitute:

"Table I - Chemical and physical requirements (Continued)

		Limits	Test method number[1]	ASTM method number
Viscosity, at 122°F. (max.)	SSU	225	304	D-88
Viscosity, at 85°F. (min.)	SSU	[3] 225	304	D-88
Ash (max.)	percent	0.10	5421	D-482
Water, by distillation (max.)	percent	0.5	3001	D-95
A.P.I. gravity (min.)		11.5	401	D-287
Pour point, upper (max.)[6]		15	[5] 201	D-97
Fluidity at 32°F.[4]		Pass		D-1659 Appen
Carbon residue (max.)	percent	15	[7] 5001	D-189
Sediment by extraction (max.)	percent	0.12	3002	D-473
Water and sediment (max.)	percent	[8] 0.5	3000	D-1796
Thermal stability		[9] Pass		D-1661
Explosiveness (max.)	percent	50	1151	------
Sulphur (max.)		3.50	5202	D-129

See footnotes to table I on next page.

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[1] CHANGES FROM PREVIOUS ISSUE. THE OUTSIDE MARGINS OF THIS DOCUMENT HAVE BEEN MA "F" TO INDICATE WHERE CHANGES (DELETIONS, ADDITIONS, ETC.) FROM THE PREVIOUS HAVE BEEN MADE. THIS HAS BEEN DONE AS A CONVENIENCE ONLY AND THE GOVERNMENT ASSUMES NO LIABILITY WHATSOEVER FOR ANY INACCURACIES IN THESE NOTATIONS. BIDI AND CONTRACTORS ARE CAUTIONED TO EVALUATE THE REQUIREMENTS OF THIS DOCUMENT B ON THE ENTIRE CONTENT AS WRITTEN IRRESPECTIVE OF THE MARGINAL NOTATIONS AND RELATIONSHIP TO THE LAST PREVIOUS ISSUE.

M

FSC 9140

MIL-F-859E
AMENDMENT - 1
24 August 1966

MILITARY SPECIFICATION

FUEL OIL, BURNER

This amendment forms a part of Military Specification MIL-F-859E, dated 22 September 1965 and is mandatory for use by all Departments and Agencies of the Department of Defense.

Page 2, paragraph 2.2, under AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM): Add "D-1661 - Thermal Stability of U.S. Navy Special Fuel Oil."

Page 3, Table I: Delete and substitute:

"Table I - Chemical and physical requirements (Continued)

		Limits	Test method number[1]	ASTM method number
Viscosity, at 122°F. (max.)	SSU	225	304	D-88
Viscosity, at 85°F. (min.)	SSU	[3]225	304	D-88
Ash (max.)	percent	0.10	5421	D-482
Water, by distillation (max.)	percent	0.5	3001	D-95
A.P.I. gravity (min.)		11.5	401	D-287
Pour point, upper (max.)[6]	°F.	15	[4]201	D-97
Fluidity at 32°F.[5]		Pass		D-1659 Appendix
Carbon residue (max.)	percent	15	[7]5001	D-189
Sediment by extraction (max.)	percent	0.12	3002	D-473
Water and sediment (max.)	percent	[8]0.5	3000	D-1796
Thermal stability		[9]Pass		D-1661
Explosiveness (max.)	percent	60	1151	----------
Sulphur (max.)		3.50	5202	D-129

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[1] FED-STD-791.

[2] See 3.3.

[3] Equivalent to approximately 65 SSU at 122°F. If viscosity at 122°F. is greater than 100 SSU and less than 125 SSU the viscosity at 84°F. need not be measured.

[4] If the pour point is less than 15°F. the fluidity need not be performed.

[5] See 4.3.1.2.

[6] See 4.3.1.3. Pour test not required when fluidity test is performed and passes.

[7] See 4.3.1.1

[8] Applicable only on samples taken at supplier's refinery, tank farm, or pipe line.

[9] See 3.4 and 3.5."

FSC 9140

Custodians:
  Army—MR
  Navy—SH
  Air Force—68

Review activities:
  Army—MR
  Navy—SH
  Air Force—68

User activities:
  Army—CE, GL, MU
  Navy—YD

Preparing activity:
  Navy—SH
(Project 9140-0024)

MIL-F-16884G
7 March 1973
SUPERSEDING
MIL-F-16884F
3 November 1965
(See 6.4)

MILITARY SPECIFICATION

FUEL OIL, DIESEL, MARINE

This specification is approved for use by all Departments and Agencies of the Department of Defense.

1. SCOPE

1.1 This specification covers one grade of marine Diesel fuel (NATO symbol F-76).

2. APPLICABLE DOCUMENTS

2.1 The following documents, of the issue in effect on date of invitation for bids or request for proposal, form a part of the specification to the extent specified herein.

STANDARDS

FEDERAL
FED-STD-791 - Lubricants, Liquid Fuels, and Related Products; Method of Testing.

MILITARY
MIL-STD-290 - Packaging, Packing and Marking of Petroleum and Related Products.

(Copies of specifications, standards, drawings, and publications required by suppliers in connection with specific procurement functions should be obtained from the procuring activity or as directed by the contracting officer.)

2.2 Other publications. The following documents form a part of this specification to the extent specified herein. Unless otherwise indicated, the issue in effect on date of invitation for bids or request for proposal shall apply.

AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM)
D 86 - Distillation of Petroleum Products.
D 93 - Flash Point by Pensky-Martens Closed Tester.
D 97 - Pour Point.
D 129 - Sulfur in Petroleum Products by the Bomb Method.
D 130 - Copper Corrosion by Petroleum Products.
D 287 - API Gravity of Crude Petroleum and Petroleum Products (Hydrometer Method).
D 445 - Viscosity of Transparent and Opaque Liquids (Kinematic and Dynamic Vicosities).
D 482 - Ash from Petroleum Products.
D 524 - Ramsbottom Carbon Residue of Petroleum Products.
D 611 - Aniline Point and Mixed Aniline Point of Petroleum Products and Hydrocarbon Solvents.
D 613 - Ignition Quality of Diesel Fuels by the Cetane Method.
D 665 - Rust-Preventing Characteristics of Steam-Turbine Oil in the Presence of Water.
D 974 - Neutralization Number by Color-Indicator Titration.
D 976 - Calculated Cetane Index of Distillate Fuels.
D 1500 - ASTM Color of Petroleum Products (ASTM Color Scale).
D 1552 - Sulfur in Petroleum Products (High-Temperature Method), Test for.
D 2274 - Test for Stability of Distillate Fuel Oil (Accelerated Method).
D 2500 - Test for Cloud Point of Petroleum Oils.
D 2622 - Test for Sulfur in Petroleum Products (X-Ray Spectrographic Method).
D 2709 - Water and Sediment in Distillate Fuels by Centrifuge, Test for.
E 29 - Recommended Practice for Indicating Which Places of Figures Are to Be Considered Significant in Specified Limiting Values.

FSC 9140

(Application for copies should be addressed to the American Society For Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103.)

(Technical society and technical association specifications and standards are generally available for reference from libraries. They are also distributed among technical groups and using Federal agencies.)

3. REQUIREMENTS

3.1 Requirements contained herein are not subject to corrections for tolerance of test methods. If multiple determinations are made by the inspecting laboratory, average results will be used except for those test methods where repeatability data are given. In those cases, the average value derived from the individual results that agree within the repeatability limits given may be used at the discretion of the inspection authority, provided an indication is given of the total number or results obtained and the number falling outside the repeatability limits. For purposes of determining conformance with each requirement, and observed value or calculated value shall be rounded off "to the nearest unit" in the last right-hand place of figures used in expressing the limiting value, in accordance with the rounding-off procedure given in ASTM E 29.

3.2 Material. The fuel supplied under this specification shall be distillate fuel and may contain only those additives specified in 3.4.

3.3 Chemical and physical requirements. The diesel fuel shall conform to the physical and chemical requirements specified in table I.

Table I - Chemical and physical requirements.

Characteristics	Requirements	FED-STD-791 test method	ASTM test method
Ignition quality, cetane number (min) (see 4.3.1)	45		D 613
Appearance[1]	Clear, bright, and free from visible particulate matter.		
Distillation:			
50 percent point, °F	Record		
90 percent point, °F (max)	675°F (357.2°C)		D 86
End point, °F (max)[2]	725°F (385°C)		
Residue plus loss, percent (max)	3.0		
Flash point °F (min)	140°F (60°C)		D 93
Pour point, °F (max)	20°F (-6.7°C)		D 97
Cloud point, °F (max)	30°F (-1.1°C)		D 2500
Viscosity at 100°F (37.8°C) Kinematic, centistokes	1.8 - 4.5		D 445
Carbon residue, on 10 percent bottoms, percent (max) (see 4.6.2)	0.20		D 524
Sulfur, percent (max)	1.00		D 129[3]
Corrosion (max) at 212°F (100°C)	No. 1 ASTM		D 130
Color (max)	5		D 1500
Ash, percent (max)	0.005		D 482
Gravity (hydrometer)	Record		D 287
Demulsification, minutes (max) (see 4.6.3)	10	3201	-----
Acid number (max)	0.30		D 974
Neutrality	Neutral	5101	-----
Aniline point, °F	Record		D 611
Accelerated stability, total insolubles mg/100 ml (max)	2.5[4]		D 2274

[1] A slight haze is acceptable providing a maximum water and sediment of 0.01 percent is obtained using procedure ASTM D 2709.

[2] As the end point of the distillation is approached, if either a thermometer reading 725°F (385°C) or a decomposition point is observed, discontinue the heating and resume the procedure as directed in ASTM D 86.

[3] ASTM D 1552 and ASTM D 2622 may be used as alternate methods.

[4] Average of three determinations is acceptable.

3.4 Additives. The additives listed herein may be used singly or in combination in amounts not to exceed those specified.

3.4.1 Antioxidants. The following active inhibitors may be blended separately or in combination into the fuel in total concentration not in excess of 8.4 pounds of inhibitor (not including weight of solvent) per 1,000 barrels of fuel (9.1 grams (g)/100 gallons (gal) (U.S.), 24 milligrams (mg)/liter or 109 mg/gal (U.K.)) in order to prevent the formation of gum:

(a) N,N' - diisopropyl-para-phenylenediamine
(b) N,N' - disecondary butyl-para-phenylenediamine
(c) 2,6 - ditertiary butyl-4-methylphenol
(d) 2,4 - dimethyl-6-tertiary butylphenol
(e) 2,6 - ditertiary butylphenol
(f) 75 percent min. 2,6-ditertiary butylphenol
 25 percent min. tertiary and tritertiary butylphenols

3.4.2 Metal deactivator. A metal deactivator, N, N' - disalicyclidene-1, 2 propanediamine may be blended into the fuel in an amount not to exceed 2 pounds of active ingredient per 1,000 barrels of fuel (2.2g/100 gal (U.S.), 5.8 mg/liter or 25 mg/gal (U.K.)).

3.4.3 Ignition improver. The following additives, to raise the ignition quality of the fuel, may be used as required to conform to this specification:

Amyl nitrate (mixed primary nitrates).
Hexyl nitrate (N-hexyl nitrate).
Cyclohexyl nitrate.

4. QUALITY ASSURANCE PROVISIONS

4.1 Responsibility for inspection. Unless otherwise specified in the contract or purchase order, the supplier is responsible for the performance of all inspection requirements as specified herein. Except as otherwise specified in the contract or order, the supplier may use his own or any other facilities suitable for the performance of the inspection requirements specified herein, unless disapproved by the Government. The Government reserves the right to perform any of the inspections set forth in the specification where such inspections are deemed necessary to assure supplies and services conform to prescribed requirements.

4.2 Lot.

4.2.1 Bulk lot. Bulk lot shall be considered an indefinite quantity of a homogenous mixture of material offered for acceptance in a single isolated container.

4.2.2 Packaged lot. Packaged lot shall be considered an indefinite number of 55-gallon drums or smaller unit containers of identical size and type, offered for acceptance, and filled with a homogenous mixture of material from one isolated container; or filled with a homogenous mixture of material manufactured in a single plant run (not exceeding 24 hours) through the same processing equipment, with no change in ingredient material.

4.3 Sampling.

4.3.1 Sampling for examination of the preparation for delivery.

4.3.1.1 Packaged lot. A random sample of packed containers shall be taken from each lot in accordance with MIL-STD-105, at inspection level II, and acceptable quality level (AQL) equals 2.5 percent defective. Examine the sample in accordance with 4.4.1.

4.3.2 Sampling for tests. Take samples for tests in accordance with ASTM D 270. Test the samples in accordance with table I and 4.6.

4.4 Inspection. Perform inspection in accordance with method 9601 of FED-STD-791.

4.4.1 Examination of the preparation for delivery. Samples taken in accordance with 4.3.1 shall be examined for compliance with MIL-STD-290 with regard to fill, closure, sealing, leakage, packaging, packing, and marking requirements. Reject any container having one or more defects, or under the required fill. If the number of defective or underfilled containers exceeds the acceptance number for the appropriate plan of MIL-STD-105, the lot represented by the sample shall be rejected.

4.5 Classification of tests. All tests are quality conformance tests.

4.6 Test methods.

4.6.1 Ignition quality. When the apparatus specified in ASTM D 613 is not available for product inspection purposes, the cetane index may be authorized in lieu of the cetane number, provided that sufficient data are available to establish the cetane index number correlation for a finished product or a blend of products from the same manufacturing process or processes and the same specific crude source. In all instances the product submitted shall be of sufficiently high cetane index to assure a cetane number at least as high as that shown in table I. In no case shall the cetane index be less than 45. The calculated cetane index shall not be used in determining the ignition quality of fuel containing ignition improvers. The cetane index shall be determined by ASTM D 976.

4.6.2 Carbon residue. When the finished fuel contains a cetane improver the carbon residue requirement specified in table I shall apply to the base fuel without the cetane improver.

4.6.3 Demulsification. The test for demulsification shall be conducted in accordance with method 3201 of FED-STD-791 with the following exceptions:

(a) Synthetic sea water prepared in accordance with ASTM D 665 shall be used as the emulsifying fluid.
(b) The test temperature shall be 77° ± 2°F (25° ± 1.1°C).
(c) The demulsification time shall be that required for separation into two layers with no cuff at the interface. A lacy emulsion which does not form a band or cuff on the wall of the cylinder shall be disregarded.

‡ 4.7 Inspection of preparation for delivery. The packaging, packing, and marking shall be inspected for compliance with section 5 of this specification.

5. PREPARATION FOR DELIVERY

‡ 5.1 Packaging, packing, and marking. Packaging, packing, and marking shall be in accordance with MIL-STD-290. The level of packaging, level of packing, type, and size shall be as specified (see 6.2).

6. NOTES

‡ 6.1 Intended use. This grade of marine Diesel fuel is intended for use in Diesel engines in submarines and for such other uses as may be specified at temperature above 30°F (-1.1°C).

6.2 Ordering data. Procurement documents should specify the following:

(a) Title, number, and date of this specification.
(b) Applicable level of packaging and packing required (see 5.1).
(c) Unit container quantity (see 5.1).

6.3 Certain provisions of this specification are the subject of international standardization agreement NATO STANAG-1135. When amendment, revision, or cancellation of this specification is proposed which will affect or violate the international agreement concerned, the preparation activity will take appropriate reconciliation action through international standardization channels including departmental standardization offices, if required.

6.4 THE MARGINS OF THIS SPECIFICATION ARE MARKED "‡" TO INDICATE WHERE CHANGES (ADDITIONS, MODIFICATIONS, CORRECTIONS, DELETIONS) FROM THE PREVIOUS ISSUE HAVE BEEN MADE. THIS WAS DONE AS A CONVENIENCE ONLY AND THE GOVERNMENT ASSUMES NO LIABILITY WHATSOEVER FOR ANY INACCURACIES IN THESE NOTATIONS. BIDDERS AND CONTRACTORS ARE CAUTIONED TO EVALUATE THE REQUIREMENTS OF THIS DOCUMENT BASED ON THE ENTIRE CONTENT IRRESPECTIVE OF THE MARGINAL NOTATIONS AND RELATIONSHIP TO THE LAST PREVIOUS ISSUE.

Custodians:
Army - MR
Navy - SH
Air Force - 68
Review activities:
Army - MR, ME
Navy - SH
Air Force - 68
DSA - PS, GS

Preparing activity:
Navy - SH
(Project 9140-0039)

International interest (see section 6)

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