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Standard Specification for Microemulsion Blendstock for Preparing Microemulsion Test Fuel Oils[1]

This standard is issued under the fixed designation D8181; 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. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. ~~Scope~~ Scope*

1.1 This specification describes an alcohol-carboxylic acid blendstock which is to be blended with fuel oils to produce a microemulsion of inverse micelles that is to be used as a test fuel oil.

NOTE 1—Microemulsion blendstocks shall not include substances such as raw vegetable oil triglycerides. Refer to Appendix X2.1.2, Composition, for details.

1.1.1 The microemulsion blendstock shall be stored in special facilities and drums or tanks that are suited for low flashpoint liquids and oxygenated products.

1.2 The microemulsion blendstock is to be blended with fuel oils to produce a microemulsion test fuel oil that is intended for testing and demonstration purposes in specialty applications such as compression-ignition engine and burner fuel applications.

NOTE 2—Typical fuel oils that could be used for blending with microemulsion blendstock are fuels that comply with Specifications D975 and D396 and may contain up to 5 % by volume biodiesel.

NOTE 3—Testing with test fuels containing 10 % microemulsion blendstock using B5 as a base fuel did not show any detrimental changes to specified fuel properties relative to B0 base fuels, but can impair measurement of microemulsion blendstock concentration.

1.2.1 The microemulsion test fuel oil (to be made from this blendstock) is to be used for demonstration purposes only in specific equipment and vehicles that are suited for use with low flashpoint fuels and oxygenated fuels such as ethanol.

NOTE 4—The low flash point of this blendstock relative to conventional diesel fuel increases certain hazards during storage and distribution.

1.3 Nothing in this specification shall preclude observance of federal, state, or local regulations, which may be more restrictive.

1.4 The values stated in SI units are to be regarded as standard. The values given in parentheses after SI units are provided for information only and are not considered standard.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D97 Test Method for Pour Point of Petroleum Products
D130 Test Method for Corrosiveness to Copper from Petroleum Products by Copper Strip Test
D396 Specification for Fuel Oils
D445 Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)
D664 Test Method for Acid Number of Petroleum Products by Potentiometric Titration
D665 Test Method for Rust-Preventing Characteristics of Inhibited Mineral Oil in the Presence of Water

[1] This specification is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.E0 on Burner, Diesel, Non-Aviation Gas Turbine, and Marine Fuels.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

***A Summary of Changes section appears at the end of this standard**

D974 Test Method for Acid and Base Number by Color-Indicator Titration
D975 Specification for Diesel Fuel Oils
D3242 Test Method for Acidity in Aviation Turbine Fuel
D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants
D4625 Test Method for Middle Distillate Fuel Storage Stability at 43 °C (110 °F)
D4806 Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel
D6584 Test Method for Determination of Total Monoglycerides, Total Diglycerides, Total Triglycerides, and Free and Total Glycerin in B-100 Biodiesel Methyl Esters by Gas Chromatography
D6751 Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels
D7042 Test Method for Dynamic Viscosity and Density of Liquids by Stabinger Viscometer (and the Calculation of Kinematic Viscosity)
D7545 Test Method for Oxidation Stability of Middle Distillate Fuels—Rapid Small Scale Oxidation Test (RSSOT)
D7862 Specification for Butanol for Blending with Gasoline for Use as Automotive Spark-Ignition Engine Fuel

3. Terminology

3.1 For definitions of terms used in this test method, refer to Terminology D4175.

3.2 *Definitions:*

3.2.1 *biodiesel, n*—fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100.

3.2.2 *higher alcohols, n*—aliphatic alcohols of the general formula $C_nH_{2n+1}OH$ with n being 2 to 8.

3.2.3 *surfactants, n*—surface active molecular species that exhibit both water-soluble and oil-soluble properties, and affect the physical behavior at the interface between water and oil phases.

3.3 *Definitions of Terms Specific to This Standard:*

3.3.1 *inverse micelle, n*—an aggregate of surfactant molecules dispersed in a non-polar liquid where the hydrophilic head groups are oriented at the center with the hydrophobic tails extending out.

3.3.2 *microemulsion blendstock, n*—a mixture of aqueous solution and surfactant(s) that when blended into hydrocarbon diesel fuel oil forms an isotropic and thermodynamically stable system with dispersed droplet diameters varying from 1 nm to 100 nm.

3.3.3 *microemulsion test fuel oil, n*—dispersion made of microemulsion blendstock in a liquid hydrocarbon fuel that is an isotropic and thermodynamically stable system with dispersed droplet diameter varying from 1 nm to 100 nm.

3.3.4 *oxygenate, n*—an oxygen-containing, ashless, organic compound, such as an alcohol or ester, which can be used as a fuel or fuel supplement.

3.3.4.1 *Discussion*—

Both alcohols such as ethanol and surfactants such as long-chain carboxylic acids are oxygenates.

3.3.5 *test fuel, n*—a homogeneous mixture of blendstocks and fuel additives meeting all specification and regulatory requirements for its intended use at the location where sold.

4. Requirements

4.1 Microemulsion blendstock shall be a mixture of aqueous alcohol solution and surfactants that conforms to the requirements in Table 1.

4.1.1 The alcohol component shall be alcohols containing two carbons and higher. Alcohols shall comply with existing standards, if any exist. For example, ethanol shall comply with the requirements of denatured fuel ethanol in Specification D4806, and butanol shall comply with the requirements of fuel butanol in Specification D7862.

4.1.2 The surfactant component shall have total glycerin less than 0.48 % by mass and free glycerin less than 0.04 % by mass, as determined by Specification ~~D6751~~D6584. See Appendix X2.1.2 for guidance.

5. Workmanship, Finish, and Appearance

5.1 The blendstock shall be visually free of undissolved water, sediment, and suspended matter. It shall be visually clear and bright.

5.2 If sediment or phase separation appears, the blendstock shall not be used.

6. Keywords

6.1 biofuel; blendstock; diesel alternative; inverse micelle; micelle; microemulsion; oxygenated diesel; renewable fuel; test fuel oils

TABLE 1 Requirements for Microemulsion Blendstock

Property	Limit	Test Method
Kinematic Viscosity, 40 °C, cSt	9.0 to 12.0	ASTM D7042[A]
Copper strip corrosion, max	No. 1	ASTM D130
Iron Corrosion, max	[A]	ASTM D665
Oxidation stability, 140 °C, 700 kPa, minutes	Report	ASTM D7545
Pour Point, °C	–13 to 15	ASTM D97
Blending Requirement		
~~(1) Formation of microemulsion test fuel—size of inverse micelles, nm, max~~	~~50~~	~~See Annex A1 and Annex A2~~
(1) Formation of microemulsion test fuel—size of inverse micelles, nm, max	50	See Annex A1 and Annex A2
(2) Stability of blendstock in certification fuel, days, min	60	See Annex A3

[A] Test Method D445 may also be used. Test Method D7042 is the referee test method.

ANNEXES

(Mandatory Information)

A1. VERIFICATION OF FORMATION OF MICROEMULSION TEST FUEL

A1.1 Scope

A1.1.1 Annex A1 specifies a method to test that the blendstock was made correctly and will behave as expected when blended into a fuel at a concentration of 5 % to 45 %.

A1.2 General Requirements

A1.2.1 Microemulsion blendstock shall be at room temperature (20 °C to 25 °C) for at least 1 h before testing.

A1.2.1.1 If microemulsion blendstock was at a reduced temperature prior to testing, the container shall be well mixed. Once any air bubbles settle, the microemulsion blendstock shall be clear.

A1.2.1.2 Diesel used for testing shall conform to Specification D975.

A1.3 Test Procedure

A1.3.1 Add 2 mL of microemulsion blendstock to a 50 mL conical tube.

A1.3.2 Add 2.5 mL of diesel to the tube.

A1.3.3 Agitate the tube to mix the sample.

A1.3.4 Allow the sample to sit for 5 min.

A1.3.5 Ensure the mixture is clear and bright. This represents blending at 44 %.

A1.3.6 Add an additional 2 mL of diesel to the tube.

A1.3.7 Agitate the tube to mix the sample.

A1.3.8 Allow the sample to sit for 5 min.

A1.3.9 Ensure the mixture is monophasic and the clarity of diesel. This represents blending at 31 %.

A1.3.10 Add an additional 6 mL of diesel to the tube.

A1.3.11 Agitate the tube to mix the sample.

A1.3.12 Allow the sample to sit for 5 min.

A1.3.13 Ensure the mixture is monophasic and the clarity of diesel. This represents blending at 16 %.

A1.3.14 Add an additional 26.5 mL of diesel to the tube.

A1.3.15 Agitate the tube to mix the sample.

A1.3.16 Allow the sample to sit for 5 min.

A1.3.17 Ensure the mixture is monophasic and the clarity of diesel. This represents blending at 5 %.

A1.3.18 Retain the 5 % blended test fuel for 24 h at room temperature.

A1.3.19 Ensure the mixture is monophasic and the clarity of diesel.

A1.4 Results

A1.4.1 If all of the above samples are monophasic and the clarity of diesel, the microemulsion blendstock passes and is confirmed to form micelles in a hydrocarbon solution.

A1.4.2 Appendix X1 provides information on correlating concentration of the blendstock to the inverse micelle size.

A2. VERIFICATION OF MICELLE FORMATION BY DYNAMIC LIGHT SCATTERING

A2.1 Scope

A2.1.1 Annex A2 specifies a method to test that the blendstock forms micelles.

A2.2 Apparatus

A2.2.1 Any dynamic light scattering (DLS) instrument capable of measuring in the 2 nm to 200 nm range shall be sufficient.

A2.2.2 Cuvettes shall be made of a material that is compatible with all components of the test fuel.

A2.3 Procedure

A2.3.1 A test fuel shall be made of 10 % microemulsion blendstock in diesel in sufficient quantity to fill the cuvette.

A2.3.2 Before adding the test fuel to the cuvette, add 0.5 % water by volume and mix well.

A2.3.2.1 If the sample becomes cloudy, the test fails.

A2.3.3 Sample shall retain the same clarity as the original test fuel.

A2.3.4 Samples shall be measured in triplicate and average values taken.

A2.4 Results

A2.4.1 The average size of the inverse micelles shall be recorded.

A2.4.2 Use Appendix X1 as guidance of typical sizes observed.

A3. VERIFICATION OF STABILITY OF BLENDSTOCK IN CERTIFICATION FUEL

A3.1 Scope

A3.1.1 Annex A3 specifies a method to test that long-term stability of a blendstock in certification fuel.

A3.2 Apparatus

A3.2.1 *Oven,* of adequate size to fit the samples. The oven should be adequately vented.

A3.2.2 *Thermometer*—Any temperature-measuring device may be used, provided it can accurately indicate the temperature to within 0.1 °C or 0.2 °F and properly be recorded.

A3.3 Accelerated Aging Theory

A3.3.1 Aging a sample at an elevated temperature is expected to expedite the aging process.

A3.3.2 According to Test Method D4625, 14 days at 43 °C should be equivalent to 60 days at room temperature.

A3.3.3 To expedite aging more, the temperature shall be held at 55 °C for 7 days.

A3.4 Procedure

A3.4.1 *Baseline*—Before the aging process is begun, the following should be measured:

A3.4.1.1 *Acid Number*—Test Method D664. Test Methods D3242 or D974 may also be used. Test Method D664 shall be the referee test method.

A3.4.1.2 Visual inspection of clarity.

A3.4.2 *Aging at 55 °C:*

A3.4.2.1 50 mL of test fuel shall be added to three glass vials whose caps provide adequate sealing at 55 °C.
(1) Glass vials should not be filled to the top and should be left with adequate headspace.

A3.4.2.2 Record the temperature of the oven and verify it is within 1 °C of 55 °C.

A3.4.2.3 Over the next 7 days, verify that the oven has remained within 1 °C of 55 °C.

A3.4.2.4 After 7 days at 55 °C, remove the vials from the oven.

A3.4.2.5 Allow to cool to room temperature before testing the aged samples.

A3.4.3 *Aged Samples*—After the samples have been aged for 7 days, the following tests shall be completed:

A3.4.3.1 *Acid Number*—Test Method D664. Test Methods D3242 or D974 may also be used. Test Method D664 shall be the referee test method.

A3.4.3.2 Visual inspection of clarity.

A3.4.4 *Results:*

A3.4.4.1 Changes of more than 5 % in the acid number results in a failed age-stability test for the blendstock in certification fuel.

A3.4.4.2 Formation of a precipitate or a decrease in visual clarity also result in a failed age-stability test.

APPENDIXES

(Nonmandatory Information)

X1. INVERSE MICELLE PROPERTIES

X1.1 *Micelle Structure and Morphology*—When splash-blended into diesel fuel oil at volumes ranging from 5 % to 45 % by volume, the resulting fuel blend forms a clear and thermodynamically stable homogeneous microemulsion consisting of ellipsoid micelles with geometric diameters that average approximately 3 nanometers. The geometric diameter is the diameter of a sphere of equal total volume as the ellipsoid. These samples can absorb additional water (roughly double initial concentrations), resulting in micelle swelling to nearly 15 nm diameter before the system starts to become unstable.[3] Micelle size and structure was characterized by dynamic light scattering (DLS), which measures the fluctuations in intensity of scattered light of diffusing particles, and small angle neutron scattering (SANS), which detects differences in neutron scattering densities between hydrogen and deuterium atoms, due to the lack or addition of a neutron.

X1.1.1 Table X1.1 shows the dimensions of inverse micelles that form when blended into hydrocarbon base fuels at different concentrations.

X1.1.2 Table X1.2 shows the dimensions of swollen inverse micelles as additional deuterated water (D_2O) is added to 10 % by volume blends. A relative D_2O level of 1.0 indicates the point at which the amount of water that is was initially present in the system has been doubled.

[3] Riiff, T. J., Webb, M. A., Orts, W., and Aramthanapon, K., "Small-Angle Neutron Scattering Studies on an Idealized Diesel Biofuel Platform," *Energy Fuels*, 2017, Vol 31, No. 4, pp. 3995–4002.