Designation: D4806 – 17

Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel[1]

This standard is issued under the fixed designation D4806; 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*

1.1 This specification covers nominally anhydrous denatured fuel ethanol intended to be blended with unleaded or leaded gasolines at 1 % to 15 % by volume for use as automotive spark-ignition engine fuel covered by Specification D4814 as well as other fuel applications or specifications involving ethanol. The significance of this specification is shown in Appendix X1.

1.2 Jurisdictions may vary in their regulatory requirements for the allowable or prohibited types of denaturants, chemical composition of the denaturant or concentration of denaturant needed to denature the ethanol. The user is advised to check with the national and regional regulatory agencies where the ethanol is denatured and used.

1.2.1 Specific regulatory requirements for denatured fuel ethanol and acceptable denaturants from various jurisdictions are given in Appendixes for information.

1.3 The values stated in SI units are to be regarded as standard.

1.3.1 *Exception*—Values given in parentheses are provided for information only. Non-SI units are shown in the Appendix if they are in a direct quotation from government regulations. In most cases, U.S. federal regulations specify non-SI units.

1.4 The following safety hazards caveat pertains only to the method modification in 8.7 of this specification: *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 and health practices and determine the applicability of regulatory limitations prior to use.*

1.5 *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]

D86 Test Method for Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure

D381 Test Method for Gum Content in Fuels by Jet Evaporation

D1298 Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method

D1613 Test Method for Acidity in Volatile Solvents and Chemical Intermediates Used in Paint, Varnish, Lacquer, and Related Products

D1688 Test Methods for Copper in Water

D2622 Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry

D3120 Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry

D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D4306 Practice for Aviation Fuel Sample Containers for Tests Affected by Trace Contamination

D4814 Specification for Automotive Spark-Ignition Engine Fuel

D5453 Test Method for Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence

D5501 Test Method for Determination of Ethanol and Methanol Content in Fuels Containing Greater than 20%

[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.A0.02 on Oxygenated Fuels and Components.

Current edition approved July 1, 2017. Published August 2017. Originally approved in 1988. Last previous edition approved in 2016 as D4806 – 16a. DOI: 10.1520/D4806-17.

[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

Ethanol by Gas Chromatography
D5580 Test Method for Determination of Benzene, Toluene, Ethylbenzene, *p/m*-Xylene, *o*-Xylene, C_9 and Heavier Aromatics, and Total Aromatics in Finished Gasoline by Gas Chromatography
D5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products
D6423 Test Method for Determination of pHe of Denatured Fuel Ethanol and Ethanol Fuel Blends
D6550 Test Method for Determination of Olefin Content of Gasolines by Supercritical-Fluid Chromatography
D7039 Test Method for Sulfur in Gasoline, Diesel Fuel, Jet Fuel, Kerosine, Biodiesel, Biodiesel Blends, and Gasoline-Ethanol Blends by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry
D7318 Test Method for Existent Inorganic Sulfate in Ethanol by Potentiometric Titration
D7319 Test Method for Determination of Existent and Potential Sulfate and Inorganic Chloride in Fuel Ethanol and Butanol by Direct Injection Suppressed Ion Chromatography
D7328 Test Method for Determination of Existent and Potential Inorganic Sulfate and Total Inorganic Chloride in Fuel Ethanol by Ion Chromatography Using Aqueous Sample Injection
D7347 Test Method for Determination of Olefin Content in Denatured Ethanol by Supercritical Fluid Chromatography
D7576 Test Method for Determination of Benzene and Total Aromatics in Denatured Fuel Ethanol by Gas Chromatography
D7757 Test Method for Silicon in Gasoline and Related Products by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry
D7795 Test Method for Acidity in Ethanol and Ethanol Blends by Titration
D7923 Test Method for Water in Ethanol and Hydrocarbon Blends by Karl Fischer Titration
E29 Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications
E203 Test Method for Water Using Volumetric Karl Fischer Titration
E300 Practice for Sampling Industrial Chemicals
E1064 Test Method for Water in Organic Liquids by Coulometric Karl Fischer Titration

2.2 *Government Regulations:*
United States Code of Federal Regulations, Title 27, Parts 19, 20, and 21[3]
United States Code of Federal Regulations, Title 40, Part 80
California Code of Regulations, CCR Title 13, §2260 – §2298[4]

3. Terminology

3.1 For general terminology, refer to Terminology D4175.

NOTE 1—The user is advised that the definitions used by various industries, marketers, and regulatory bodies can differ from those specific to this specification. It is the responsibility of the user to ensure that the terms used in a particular context are clearly understood.

3.2 *Definitions:*

3.2.1 *denaturants, n*—materials added to ethanol to make it unsuitable for beverage use under a formula approved by a regulatory agency to prevent the imposition of beverage alcohol tax.

3.2.1.1 *Discussion*—Denaturants are only those materials added by the denaturer to comply with the approved formula; any materials absorbed later are not denaturants.

3.2.2 *denatured fuel ethanol, n*—fuel ethanol made unfit for beverage use by the addition of denaturants under formula(s) approved by the applicable regulatory agency to prevent the imposition of beverage alcohol tax.

3.2.3 *ethanol, n*—ethyl alcohol, the chemical compound C_2H_5OH.

3.2.4 *fuel ethanol, n*—a grade of undenatured ethanol with other components common to its production (including water) that do not affect the use of the product as a component for automotive spark-ignition engine fuels.

3.2.5 *gasoline, n*—a volatile mixture of liquid hydrocarbons, generally containing small amounts of additives, suitable for use as a fuel in spark-ignition, internal combustion engines. **D4814**

3.2.6 *gasoline blendstock, n*—a liquid hydrocarbon component suitable for use in spark-ignition engine fuels.

3.2.6.1 *Discussion*—Examples of gasoline blendstock include natural gasoline, raffinate, reformate, conventional gasoline blendstock for oxygenate blending (CBOB), and reformulated gasoline blendstock for oxygenate blending (RBOB).

3.2.7 *gasoline-ethanol blend, n*—a fuel consisting primarily of gasoline along with a substantial amount (more than 0.35 % by mass oxygen) of denatured fuel ethanol.

3.2.8 *oxygenate*—an oxygen-containing, ashless, organic compound, such as an alcohol or ether, which may be used as a fuel or fuel supplement. **D4814**

3.3 *Definitions of Terms Specific to This Standard:*

3.3.1 *pHe, n*—a measure of the acid strength of denatured fuel ethanol.

3.4 *Abbreviations:*

3.4.1 *CCR*—California Code of Regulations

3.4.2 *CFR*—U.S. Code of Federal Regulations

3.4.3 *DFE*—Denatured Fuel Ethanol

3.4.4 *EPA*—The U.S. Environmental Protection Agency

3.4.5 *IRS*—U.S. Internal Revenue Service

3.4.6 *RBOB*—reformulated blendstock for oxygenate blending

3.4.7 *RIN*—Renewable Identification Number

[3] A printed copy of the Code of Federal Regulations may be purchased from the U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401 or the online store at http://bookstore.gpo.gov/. The Code of Federal Regulations may be browsed online at http://www.gpoaccess.gov/cfr/index.html.

[4] California regulations are available online at http://government.westlaw.com.

TABLE 1 Performance Requirements

Property	Limit	Method
Ethanol, % by volume, min	92.1	D5501
Methanol, % by volume, max	0.5	D5501
Solvent-washed gum content, mg/100 mL, max	5.0	D381
Water, % by volume (% by mass), max	1.0 (1.26)	E203, E1064, or D7923
Inorganic Chloride, mg/kg (mg/L), max	6.7 (5)	D7319 or D7328
Copper, mg/kg, max	0.1	D1688
Acidity (as acetic acid CH_3COOH) mg/kg, (% by mass) [mg/L], max	70 (0.0070) [56] (Note 2)	D1613 or D7795
pHe	6.5 to 9.0	D6423
Sulfur, mg/kg, max	30.	D2622, D3120, D5453, or D7039
Existent sulfate, mg/kg, max	4	D7318, D7319, or D7328

3.4.8 *TTB*—The Alcohol and Tobacco Tax and Trade Bureau of the U.S Department of Treasury

4. Performance Requirements (Table 1)

4.1 *Denatured Fuel Ethanol*—After fuel ethanol is denatured as specified in Section 5, it shall conform to the following requirements at the time of blending with gasoline.

NOTE 2—Denatured fuel ethanol may contain additives, such as corrosion inhibitors and detergents, that can affect the titratable acidity (acidity as acetic acid) of the finished denatured fuel ethanol. Although the base fuel ethanol may meet the acidity specification, the effect of these additives can produce an apparent high titratable acidity of the finished product. Contact the ethanol supplier if there is a question regarding the titratable acidity of the denatured fuel ethanol to verify that the base fuel ethanol meets the acidity requirements in Table 1.

4.2 *Other Properties*—Limits more restrictive than those specified above, or the specification of additional properties such as color, may be agreed upon between the supplier and the purchaser.

4.3 For purposes of determining conformance with the specified limits in Table 1, an observed value or a calculated value shall be rounded "to the nearest unit" in the last righthand digit used in expressing the specification limit, in accordance with the rounding method of Practice E29, unless otherwise specified.

5. Denaturant and Regulatory Information

5.1 *General Requirements*—This specification provides general information for the denaturants to be used in denatured fuel ethanol and the concentration of denaturant to be added. Jurisdictions may vary in their regulatory requirements for the allowable or prohibited types of denaturants, chemical composition of the denaturant or concentration of denaturant needed to denature the ethanol.

5.1.1 *Allowable Denaturants*—The only denaturants allowed for the denatured fuel ethanol defined by this specification are natural gasoline, gasoline blendstocks, or unleaded gasoline. Small amounts of the same or similar hydrocarbons absorbed by the denatured fuel ethanol as it moves through the distribution system is not denaturant. A jurisdiction can maintain approved formulas to denature alcohol for fuel use.

5.1.1.1 This specification is specific to denatured fuel ethanol as a blendstock in spark-ignition engine fuel. Denaturants that could provide satisfactory performance for other uses could cause damage to spark-ignition engines. The fuel ethanol formulas approved by the alcohol regulatory agency for fuel use could include denaturing materials which are not allowed by this ASTM specification. It is the denaturer's responsibility to consult the regulations to ensure legal denaturing of the fuel ethanol and to ensure compliance with this specification with regard to allowed denaturants.

5.1.2 *Prohibited Denaturants*—This specification prohibits the use of hydrocarbons with an end boiling point higher than 225 °C as determined by Test Method D86, although they may be permitted by some regulations. Some kerosines, for instance, promote piston scuff in automotive engines. Specific mention must be made of some materials that have extremely adverse effects on fuel stability, automotive engines, and fuel systems. These materials shall not be used as denaturants for fuel ethanol under any circumstances. They are as follows: methanol, pyrroles, turpentine, ketones, and tars (high-molecular weight pyrolysis products of fossil or nonfossil vegetable matter). Ketone denaturants tend to degrade fuel stability or increase the tendency of a gasoline-ethanol blend to corrode metals and attack elastomers. These effects become more serious if the concentration of a ketone such as 4-methyl pentanone (methyl isobutyl ketone) exceeds one part by volume per 100 parts by volume of fuel ethanol. There is no information available on the effects of denaturants other than those mentioned above. Therefore, the only denaturants that shall be used are those listed in 5.1.1.

5.1.3 *Denaturant Level*—A buyer may ask the denaturer to denature within a specific range (for example, 1.96 % to 2.5 % by volume). A buyer may also ask the denaturer to certify the range used for the denaturant addition. A buyer or distributor may commingle receipts certified within the same range and provide a certification of conformance with the product from that commingling. The blender may use this certification of conformance for the product to demonstrate compliance with the denaturant limits. If the product is shipped directly from a denaturer to a blender, the initial certification from the denaturer may be used to demonstrate compliance. Compliance with the denaturant limit cannot be determined analytically. Compliance shall be based on the information from the original denaturer. The maximum concentration of denaturant allowed in this specification is 5 % by volume.

5.2 *Regulatory Information for Denaturants and Denatured Fuel Ethanol:*

5.2.1 Users of this specification are advised to consult with the applicable regulatory agency for specific requirements for denaturants (types, composition, and amounts) and denatured fuel ethanol in their jurisdictions. The requirements can be covered by regulations specific to a jurisdiction or by multiple

regulations due to overlapping jurisdictions. Appendixes have been developed to provide information for several jurisdictions describing the requirements within the designated jurisdiction:

5.2.1.1 Appendix X2, Regulatory Requirements for California.

5.2.1.2 Appendix X3, Regulatory Requirements for the United States.

6. Workmanship

6.1 At the point of custody transfer, the denatured fuel ethanol shall be visually free of sediment, suspended, or undissolved matter. It shall be clear and bright at the product temperature at the point of custody transfer or at a lower temperature agreed upon by the purchaser and seller.

NOTE 3—Fuel components should be resistant to phase separation or undissolved matter at the lowest temperatures to which it is likely to be subjected, dependent on the time and place of its intended use. See Specification D4814 Table X8.1 for guidance.

NOTE 4—Solubility is temperature dependent. As this fuel component cools, some high molecular weight additives can become insoluble.

6.2 The product shall be free of any adulterant or contaminant that can render the material unacceptable for its commonly used applications.

6.2.1 Manufacturers, importers, and others denaturing fuel ethanol shall avoid ethanol (for example, improperly recycled ethanol) or denaturants contaminated by silicon-containing materials, or both. Silicon contamination of gasoline-oxygenate blends has led to fouled vehicle components (for example, spark plugs, exhaust oxygen sensors, catalytic converters) requiring parts replacement and repairs. Test Method D7757 is a procedure for determining silicon content but no specification limits have been established for this silicon.

7. Sampling, Containers, and Sample Handling

7.1 The user is strongly advised to review all intended test methods prior to sampling to understand the importance and effects of sampling technique, proper containers, and special handling required for each test method.

7.2 Correct sampling procedures are critical to obtain a sample representative of the lot intended to be tested. Use appropriate procedures in Practice D4057 or Practice E300 for manual method sampling and in Practice D4177 for automatic method sampling, as applicable.

7.3 The correct sample volume and appropriate container selection are important decisions that can impact test results. Refer to Practice D4306 for aviation fuel container selection for tests sensitive to trace contamination. Refer to Practice D5854 for procedures on container selection and sample mixing and handling. All sampling and storage containers should be evaluated for durability, compatibility, and contamination of denatured fuel ethanol prior to use. If samples must be collected in metal containers, do not use soldered metal containers. Soldering flux in the containers and the lead in the solder can contaminate the sample.

7.4 *Sample Size*—A minimum of about 1 L is recommended. If specific gravity is to be determined by a hydrometer method, additional volume may be required. This depends on the size of the hydrometer.

7.5 *Lot Size*—A lot shall normally consist of the amount contained in a tanker compartment or other bulk container in which it is delivered. If this definition does not apply, the definition of a lot must be agreed upon between the supplier and purchaser.

NOTE 5—See Sections 5, 6, and 7 on Significance, Safety, and Statistical Considerations, respectively, of Practice E300 for a detailed discussion of the statistics of sampling.

8. Test Methods

8.1 The scope of some of the test methods listed below do not include denatured fuel ethanol. The precisions of those test methods can differ from the reported precisions when testing denatured fuel ethanol.

8.2 *Water*—Test Methods E203, E1064, or D7923.

8.3 *Solvent-Washed Gum Content*—Test Method D381, air jet apparatus.

8.4 *Acidity*—Test Method D1613 or D7795.

8.4.1 Dissolved carbon dioxide is a known interference and can cause a false high reading when using Test Method D1613. In the absence of dissolved CO_2, Test Method D1613 is an acceptable method. If a sample is known to have dissolved CO_2 or if dissolved CO_2 can be present, Test Method D7795 is the preferred method. In cases of differing results between the two test methods, D7795 shall be the referee method.

8.5 *pHe*—Test Method D6423.

8.6 *Inorganic Chloride*—Test Methods D7319 or D7328.

8.7 *Copper*—Modification of Test Methods D1688, Test Method A.

8.7.1 The modifications of Test Methods D1688, Test Method A (atomic absorption, direct) consists of mixing reagent-grade ethanol (which can be denatured in accordance with TTB Formula 3A or 30) in place of water as the solvent or diluent for the preparation of reagents and standard solutions. However, this must not be done to prepare the stock copper solution described in the section on Copper Solution, Stock in Test Method D1688. Because a violent reaction can occur between the acid and the ethanol, use water, as specified, in the acid solution part of the procedure to prepare the stock copper solution. Use ethanol for the rinse and final dilution only.

8.7.2 The precision of this modified method has not been determined, but it is expected to be similar to the precision of Test Method D1688, Test Method A.

8.8 *Ethanol and Methanol*—Test Method D5501.

8.9 *Sulfur*—Test Methods D2622, D3120, D5453, or D7039. California specifies that compliance with the California sulfur standard for denatured ethanol shall be determined using Test Method D5453 – 93. EPA allows Test Methods D3120 – 06$^{\varepsilon 1}$, D5453 – 08a, or D7039 – 07 for measuring sulfur in gasoline as long as these alternative test method results are correlated to the EPA designated Test Method D2622 – 05 when determining compliance with Federal EPA sulfur standards.

8.10 *Existent Sulfate*—Test Methods D7318, D7319, or D7328.

8.11 *Denaturant*—The denaturant content is determined by the ratio of (metered denaturant) to (metered denaturant and ethanol volumes) at the time of denaturing. There is no standardized test procedure or calculation to directly or indirectly determine the denaturant content in denatured fuel ethanol.

9. Keywords

9.1 acidity; automotive spark-ignition engine fuel; base gasoline; chloride ion; copper; corrosion inhibitors; denaturants; denatured fuel ethanol; ethanol; fuel; fuel ethanol; gasoline; gasoline-ethanol blend; oxygenate; solvent-washed gum content; sulfate ion; sulfur; water

APPENDIXES

(Nonmandatory Information)

X1. SIGNIFICANCE OF SPECIFIED PROPERTIES

X1.1 Denatured Fuel Alcohol

X1.1.1 *Water*—Karl Fischer analysis is generally the only consistently reliable procedure for the determination of water in denatured ethanol. Test Method E203 describes the modifications required to run the test in the presence of alcohols. Relative density or specific gravity is needed to convert the Karl Fischer water determination from E203 and E1064 from a percent by mass to a percent by volume. Methods D1298 and D4052 are recommended for determination of relative density.

X1.1.1.1 Methods and tables exist to determine the water content of ethanol/water mixtures based on the specific gravity of the mixture. These methods do not work for water determination after the denaturant has been added.

X1.1.1.2 Blends of denatured fuel ethanol and gasoline or similar hydrocarbons have a limited solvency for water. This solvency will vary with the ethanol content, the temperature of the blend, and the aromatic content of the base gasoline. A fuel made by blending 10 % by volume denatured fuel ethanol with a gasoline containing 14 % by volume aromatics and 0.6 % by mass dissolved water (about 0.5 % by volume), will separate into a lower alcohol-rich aqueous phase and an upper hydrocarbon phase if cooled to about 7 °C. As normal spark-ignition engines will not run on the aqueous phase material, such a separation is likely to cause serious operating problems. The phase separation of gasoline-ethanol blends is affected by the total water content of the mixture. This includes the water content from the ethanol and gasoline hydrocarbons blended at the rack and the water adsorbed from the transportation and storage infrastructure for the blended fuel. All water sources should be identified, monitored and controlled to prevent phase separation of the blended fuel. Denatured fuel ethanol is hygroscopic and can pick up water from the atmosphere during long-term storage. Prudent precautions to reduce water exposure and monitor the product should be considered if long term storage is expected.

X1.1.1.3 Test Method D7923 may be used to measure water content in denatured fuel ethanol in concentrations 0.05 % to 5.0 % by mass.

X1.1.2 *Solvent-Washed Gum Content:*

X1.1.2.1 The test for solvent-washed gum content measures the amount of residue after evaporation of the fuel and following a heptane wash. The heptane wash removes the heptane-soluble, nonvolatile material such as additives, carrier oils used with additives, and diesel fuels. Solvent-washed gum consists of heptane-insoluble gum. The fuel-insoluble portion can clog fuel filters. Both can be deposited on surfaces when the fuel evaporates.

X1.1.2.2 Solvent-washed gum can contribute to deposits on the surfaces of carburetors, fuel injectors, and intake manifolds, ports, valves, and valve guides. The impact of solvent-washed gum from pure alcohols such as ethanol on malfunctions of modern engines is not known. The test method is used essentially to detect the presence of high boiling, heptane-insoluble impurities.

X1.1.2.3 Because the precision statements for Test Method D381 were developed using only data on hydrocarbons, they are not applicable to denatured fuel ethanol.

X1.1.3 *Chloride Ion*—Low concentrations of chloride ions are corrosive to many metals.

X1.1.4 *Copper*—Copper is a very active catalyst for the low-temperature oxidation of hydrocarbons. Experimental work has shown that copper concentrations higher than 0.012 mg/kg in commercial gasolines can significantly increase the rate of gum formation.

X1.1.5 *Acidity*—Very dilute aqueous solutions of low-molecular weight organic acids such as acetic acid (CH_3COOH) are highly corrosive to many metals. It is therefore necessary to keep such acids at a very low level.

X1.1.5.1 The acidity method is intended to determine the concentration of organic acids in ethanol. However, carbon dioxide is very soluble in ethanol, and in the presence of water it converts to carbonic acid. Test Method D1613 has an option to use either water or alcohol as solvent. Since ethanol is completely soluble in water, water is added to the sample and the mixture is titrated with aqueous sodium hydroxide solution. Dissolved CO_2 converted to carbonic acid will be titrated as an "acid." The presence of dissolved CO_2 will thus create a high bias in the acidity results. If there is sufficient dissolved CO_2, Test Method D1613 can incorrectly indicate that the sample is above the maximum allowed acidity in the specification. In the absence of any dissolved CO_2, Test Method D1613 is an acceptable test method. If a sample is known to have dissolved

CO_2 or if dissolved CO_2 is expected to be present, Test Method D7795 is the preferred method. In cases of differing results between the two test methods, Test Method D7795 shall be the referee method.

X1.1.6 *pHe*—When the pHe of ethanol used as a fuel for automotive spark-ignition engines is below 6.5, fuel pumps can malfunction as a result of film forming between the brushes and commutator, fuel injectors can fail from corrosive wear, and excessive engine cylinder wear can occur. When the pHe is above 9.0, fuel pump plastic parts can fail.

X1.1.7 *Appearance*—Turbidity or evidence of precipitation normally indicates contamination.

X1.1.7.1 Fuel components can encounter conditions in the bulk distribution system that could cause the material to fail a workmanship visual evaluation. Some fuel components can contain dirt or rust particles during distribution. Terminals or bulk plants can address these issues with proper operating procedures; for example, by allowing sufficient time for the dirt or particles to settle in the tank, by filtration or by other means.

X1.1.8 *Ethanol*—The ethanol content is important in determining the blend ratios for adding denatured fuel ethanol into the finished gasoline. The ethanol content of denatured fuel ethanol will vary based on levels of denaturant, water and the minor components common to ethanol production.

X1.1.9 *Existent Sulfate*—The presence of small amounts of inorganic sulfates in denatured fuel ethanol under the right conditions can contribute to turbine meter deposits and the premature plugging of fuel dispensing pump filters in the fuel distribution system. The sulfates also have been shown to cause fuel injector sticking resulting in engine misfiring and poor driveability in automobiles.

X1.1.10 *Denaturant*—Section 5 discusses the denaturants that are allowed or prohibited and the denaturing levels for product meeting this specification. Denaturant is added in the specified concentration range to comply with TTB and IRS requirements. The content is set by volumetric addition during the denaturing process. Standard analytical methods do not exist to directly or indirectly determine the denaturant content or acceptability of the denaturant beyond that point.

X1.1.11 *Sulfur*—The Federal Tier 2 Motor Vehicle and Emissions Standards and Gasoline Sulfur Control Requirements establish sulfur standards for refineries and importers producing reformulated gasoline, Reformulated Blendstock for Oxygenate Blending (RBOB), and conventional gasoline. EPA has established gasoline sulfur content standards for gasoline and denatured fuel ethanol blended into gasoline. Sulfur contaminates the catalytic converter necessary for reducing emissions of hydrocarbons (HC), carbon monoxide (CO), and nitrogen oxides (NOx).

X1.1.12 *Methanol*—Small amounts of methanol can be produced in the ethanol production process. Methanol at high concentrations can be corrosive to components of the fuel system and has a greater effect on increasing vapor pressure than does ethanol. The limit is set to prevent methanol corrosion and the incremental effect on vapor pressure. The limit is also to prevent methanol from being used as a denaturant.

X2. CALIFORNIA ETHANOL REQUIREMENTS

X2.1 California Ethanol Requirements

X2.1.1 While the following requirements are believed to be accurate at the time of publication, users should consult the relevant authority to confirm the current regulations and requirements. The information provided about the regulations is for information only. In case of conflict, the text of current regulations takes precedence.

X2.1.2 The California Air Resources Board has approved standards for denatured ethanol to be field-blended with California Reformulated Gasoline Blendstock for Oxygenate Blending (CARBOB) to make California Phase 3 Reformulated Gasoline (CaRFG3). Standards also have been specified for the denaturant. These California standards for denatured ethanol and denaturant became effective Dec. 31, 2003, and were amended on Aug. 29, 2008.

X2.1.3 The California standards for denatured ethanol set maximum limits on sulfur, benzene, olefins, and aromatics contents as shown in Table X2.1, and also require the denatured ethanol to comply with the performance requirements in Specification D4806 – 99.

X2.1.4 California specifies that compliance with the sulfur standard shall be determined by testing the denatured ethanol using Test Method D5453 – 93. California specifies that compliance with the standards for benzene, olefins, and aromatics contents shall be determined by direct analysis of the denatured fuel ethanol (Table X2.1) or by testing a sample of the denaturant using the test methods specified for CARB gasoline (Table X2.2), and then calculating the content of those compounds in the denatured ethanol, multiplying the test value by 0.0500. However, where it is demonstrated that the denatured ethanol contains less than 5.00 % by volume denaturant, then the test results are multiplied by the decimal fraction representing the percent denaturant.

TABLE X2.1 California Denatured Ethanol Standards (In Addition to the Performance Requirements in ASTM D4806 – 99)

Property	Specification Limit	Test Method
Sulfur, mg/kg, max	10	D5453 – 93
Benzene, % by volume, max	0.06	D7576 – 10
Olefins, % by volume, max	0.5	D7347 – 07[1]
Aromatics, % by volume, max	1.7	D7576 – 10

X2.1.5 California allows an exception to the limits shown in Table X2.1 where the denatured ethanol supplier takes reasonably prudent precautions to ensure the denatured ethanol that exceeds these limits will only be added to a specially designed

TABLE X2.2 California Denaturant Standards

Property	Specification Limit	Test Method
Benzene, % by volume, max	1.10	D5580 – 02 (2007)
Olefins, % by volume, max	10.0	D6550 – 10
Aromatics,% by volume, max	35.0	D5580 – 02 (2007)

CARBOB which has been designated to be blended with such denatured ethanol. Documentation is required to support the transfer of denatured ethanol. All CaRFG3 requirements for the final blend shall be met.

X2.1.6 California specifies the standards for the denaturant used in denatured ethanol as shown in Table X2.2. Also shown are the test methods required to determine compliance.

X2.1.7 California standards allow higher amounts of benzene, olefins, and aromatics in the denaturant if the supplier takes necessary precautions to ensure that when added to the ethanol, the level is less than 5.00 % by volume and the limits in Table X2.1 are met.

X3. U.S. FEDERAL REQUIREMENTS FOR DENATURED FUEL ETHANOL

X3.1 While the following requirements are believed to be accurate at the time of publication, users should consult the relevant authority to confirm the current regulations and requirements. The information provided about the regulations is for information only. In case of conflict, the text of current regulations takes precedence.

X3.2 U.S. EPA Requirements for Denaturant in Denatured Fuel Ethanol

X3.2.1 There are two EPA regulations impacting the denaturant concentration in denatured fuel ethanol.

X3.2.1.1 In the definition for Renewable Fuel (40 CFR § 80.1401) the EPA states "(2) Ethanol covered by this definition shall be denatured as required and defined in 27 CFR parts 19 through 21. Any volume of denaturant added to the undenatured ethanol by a producer or importer in excess of 2 volume percent shall not be included in the volume of ethanol for purposes of determining compliance with the requirements under this subpart." The U.S. Environmental Protection Agency regulations stipulate that denaturant added in excess of 2 % by volume shall not be considered when determining volumes for the purposes of compliance with the Renewable Fuel Standard. This absolute limitation includes volumes for Renewable Identification Number (RIN) generation. The limits for the denaturant addition are shown in Table X3.1.

X3.2.1.2 The EPA also has a procedure to follow when determining compliance with this regulation. Regulation 40 CFR § 80.9, "Rounding a test result for determining conformance with a fuels standard," states "for purposes of determining compliance with the fuel standards of 40 CFR Part 80, a test result will be rounded to the nearest unit of significant digits specified in the applicable fuel standard in accordance with the rounding method described in the ASTM standard practice, ASTM E29 – $02^{\varepsilon 1}$, entitled, 'Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications'". The denaturant concentration in the denatured fuel ethanol is not determined by an analytical test method but is calculated from the metered volumes by the denaturer.

X3.2.1.3 The following portions of Practice E29 – 13 address the EPA denaturant limit.

6.4 *Rounding Procedure*—The actual rounding procedure shall be as follows:
6.4.1 When the digit next beyond the last place to be retained is less than 5, retain unchanged the digit in the last place retained.
6.4.2 When the digit next beyond the last place to be retained is greater than 5, increase by 1 the digit in the last place retained.
6.4.3 When the digit next beyond the last place to be retained is 5, and there are no digits beyond this 5, or only zeros, increase by 1 the digit in the last place retained if it is odd, leave the digit unchanged if it is even. Increase by 1 the digit in the last place retained, if there are non-zero digits beyond this 5.

X3.2.1.4 For rounding purposes only, if the records from the denaturant addition system indicate the denaturant concentration is between 1.5 % by volume to 2.5 % by volume, then using the rounding method in Practice E29 – $02^{\varepsilon 1}$, the denatured fuel ethanol is deemed to contain 2 % by volume denaturant for EPA purposes only.

X3.2.2 Beginning January 1, 2017, under the U.S. EPA Tier 3 fuel program, "the concentration of all denaturants used in DFE [denatured fuel ethanol] is limited to a maximum of 3.0 volume percent" (40 CFR 80.1610(a)(4)).

X3.2.3 Denatured fuel ethanol "must be composed solely of carbon, hydrogen, nitrogen, oxygen and sulfur" (40 CFR 80.1610(a)(2)), and "only previously certified gasoline (including previously certified blendstocks for oxygenate blending), gasoline blendstocks, or natural gas liquids may be used as denaturants" (40 CFR 80.1610(a)(3)).

X3.3 U.S. EPA Requirements for Sulfur in Denatured Fuel Ethanol

X3.3.1 Beginning January 1, 2017, under the U.S. EPA Tier 3 fuel program, "the sulfur content must not be greater than 10 ppm" (10 mg/kg) (40 CFR 80.1610(a)(1)).

X3.3.2 There are additional EPA federal requirements for producers and importers of certified denaturant to be used for the manufacture of denatured fuel ethanol: The sulfur content of the denaturant for use in the manufacture of denatured fuel ethanol "must not be greater than 330 ppm" (40 CFR 80.1611(a)(1)). "The ethanol denaturant "must be composed solely of carbon, hydrogen, nitrogen, oxygen and sulfur" (40 CFR 80.1611(a)(2)). "Only previously certified gasoline (including previously certified blendstocks for oxygenate blending), gasoline blendstocks, or natural gas liquids may be used as denaturants" (40 CFR 80.1611(a)(3)).

TABLE X3.1 U.S. Federal Limits on Denaturants and Denatured Fuel Ethanol

Limits on Denaturant Content of Denatured Fuel Ethanol		
Limit, volume %	Source	Requirement
1.96 min[A]	TTB[B]	TTB Formulas require a minimum of two parts of approved denaturant to 100 parts of ethanol with a minimum of 195 proof ethanol.
2 max[C,D]	EPA[D]	The maximum amount of denaturant the EPA allows for RIN generation in denatured fuel ethanol under the national Renewable Fuels Standard Program.
3.0 max[C]	EPA[E]	The maximum amount of denaturant the EPA allows in denatured fuel ethanol for use as a gasoline blendstock.
Chemical Limits on Denatured Fuel Ethanol		
Property	Specification Limit	Test Method
Sulfur, mg/kg, max	10[F]	D2622, D3120, D5453, D7039

[A] For purposes of determining conformance with this limit, the Absolute Method in Practice E29 should be used.
[B] See X3.4 for information on this TTB limit.
[C] For purposes of determining conformance with this limit, the Rounding Method in Practice E29 should be used.
[D] See X3.2.1.1 for additional information on this EPA limit.
[E] See X3.2.2 for additional information on this EPA limit.
[F] See X3.3.1 for additional information on this EPA limit.

X3.4 U.S. Alcohol and Tobacco Tax and Trade Bureau Requirements on Denatured Fuel Ethanol

X3.4.1 In the United States, ethanol is rendered unfit for beverage use by the addition of denaturants under formulas approved by the Alcohol and Tobacco Tax and Trade Bureau (TTB) of the U.S. Treasury Department that allow the denatured alcohol to ship from the denaturer free of beverage excise tax and to be distributed and used as a fuel component without TTB permits. TTB regulations concerning the preparation, handling, distribution and use of denatured ethanol formulas are published in the United States Code of Federal Regulations, Title 27, Parts 19, 20, and 21. The denatured fuel ethanol allowed by this specification shall contain a minimum of 1.96 % by volume denaturant.

X3.4.2 To avoid imposition of the beverage excise tax, TTB regulations require the denaturer to add specific quantities of approved denaturants to the ethanol prior to shipping. The denaturant content is determined by the ratio of metered denaturant and ethanol volumes at the time of denaturing. The TTB regulations stipulate the record keeping requirements for the denaturer. These regulations include records of the quantities of ethanol and denaturant added in the denaturing process. The TTB periodically audits the denaturing facilities and associated records for compliance with these regulations. The regulations do not require the receiver to analytically verify that the material added was an approved denaturant or that it was added within the necessary concentration range. Approved analytical methods or calculations do not exist to permit any the following: (*1*) to confirm compliance with this section of the specification after the denaturing process, (*2*) to determine that the denaturant used was approved by the TTB or allowed in this specification, (*3*) to quantify the ratio of denaturant added during the denaturing process, or (*4*) to distinguish between the hydrocarbons added as part of the denaturing process and those absorbed later in the distribution system. There is no ASTM approved test method for determining denaturant concentration in denatured fuel ethanol, although regulatory agencies may use non-ASTM methods for investigative purposes.

SUMMARY OF CHANGES

Subcommittee D02.A0 has identified the location of selected changes to this standard since the last issue (D4806 – 16a) that may impact the use of this standard. (Approved July 1, 2017.)

(1) Added Test Method D7923 to Referenced Documents.
(2) Revised Table 1 and subsection 8.2 to add Test Method D7923; added subsection X1.1.1.3 to discuss Test Method D7923.
(3) Revised subsection 1.2, 2.2, and added new subsection 4.3 (formerly Note 2).
(4) Added Abbreviations list to Terminology section.
(5) Updated regulatory information in Section 5, Appendix X2, and Appendix X3.

Subcommittee D02.A0 has identified the location of selected changes to this standard since the last issue (D4806 – 16) that may impact the use of this standard. (Approved Feb. 1, 2016.)

(1) Revised subsections 1.1 and X1.1.6; revised Table 1.
(2) Corrected SI formatting throughout.

Subcommittee D02.A0 has identified the location of selected changes to this standard since the last issue (D4806 – 15) that may impact the use of this standard. (Approved Jan. 1, 2016.)

(1) Revised subsection 6.1 and added Notes 3 and 4.
(2) Revised subsection X1.1.7.
(3) Added subsection X1.1.7.1.