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An American National Standard

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

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## 1. Scope

1.1 This specification covers nominally anhydrous denatured fuel ethanol intended to be blended with unleaded or leaded gasolines at 1 to 10 volume % for use as a spark-ignition automotive engine fuel. The significance of this specification is shown in Appendix X1.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

## 2. Referenced Documents

2.1 *ASTM Standards:*

D 86 Test Method for Distillation of Petroleum Products at Atmospheric Pressure[2]

D 381 Test Method for Gum Content in Fuels by Jet Evaporation[2]

D 512 Test Methods for Chloride Ion in Water[3]

D 891 Test Methods for Specific Gravity, Apparent, of Liquid Industrial Chemicals[4]

D 1152 Specification for Methanol (Methyl Alcohol)[5]

D 1193 Specification for Reagent Water[6]

D 1613 Test Method for Acidity in Volatile Solvents and Chemical Intermediates Used in Paint, Varnish, Lacquer, and Related Products[5]

D 1688 Test Methods for Copper in Water[6]

D 3505 Test Method for Density or Relative Density of Pure Liquid Chemicals[5]

D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter[7]

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products[7]

D 4814 Specification for Automotive Spark-Ignition Engine Fuel[7]

D 5453 Test Method for Determination of Total Sulfur in Light Hydrocarbons, Motor Fuels, and Oils by Ultraviolet Fluorescence[8]

D 5501 Test Method for the Determination of Ethanol Content of Denatured Fuel Ethanol by Gas Chromatography[8]

D 5580 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[8]

D 6423 Test Method for Determination of pHe of Ethanol, Denatured Fuel Ethanol, and Fuel Ethanol (Ed75–Ed85)[9]

D 6550 Test Method for Determination of Olefin Content of Gasolines by Supercritical-Fluid Chromatography[9]

E 203 Test Method for Water Using Volumetric Karl Fischer Titration[4]

E 300 Practice for Sampling Industrial Chemicals[4]

E 1064 Test Method for Water in Organic Liquids by Coulometric Karl Fischer Titration[4]

2.2 *Other Standards:*

United States Code of Federal Regulations, Title 27, Parts 20 and 21[10]

United States Federal Specification O-E-760b Ethyl Alcohol (Ethanol): Denatured Alcohol: and Proprietary Solvent[11]

## 3. Terminology

3.1 *Definitions:*

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

3.1.2 *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. **D 4814**

3.1.3 *gasoline-ethanol blend*, *n*—a fuel consisting primarily of gasoline along with a substantial amount (more than 0.35

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[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] 1986 *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Annual Book of ASTM Standards*, Vol 15.05.

[5] *Annual Book of ASTM Standards*, Vol 06.04.

[6] *Annual Book of ASTM Standards*, Vol 11.01.

[7] *Annual Book of ASTM Standards*, Vol 05.02.

[8] *Annual Book of ASTM Standards*, Vol 05.03.

[9] *Annual Book of ASTM Standards*, Vol 05.04.

[10] Order as Code of Federal Regulations Title 27 Parts 200-End: from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401.

[11] Order from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401.

mass % oxygen) of denatured fuel ethanol. **D 4814**

3.1.4 *oxygenate, n*—an oxygen-containing, ashless, organic compound, such as an alcohol or ether, which may be used as a fuel or fuel supplement. **D 4814**

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *denaturants*—natural gasoline, gasoline components, unleaded gasoline, or toxic or noxious materials added to fuel ethanol to make it unsuitable for beverage use but not unsuitable for automotive use.

3.2.2 *denatured fuel ethanol*—fuel ethanol made unfit for beverage use by the addition of denaturants.

3.2.3 *fuel ethanol*—ethanol with impurities common to its production (including water but excluding denaturants).

3.2.4 *impurities*—in commercially produced fuel ethanol, compounds other than ethanol or denaturants present, such as methanol and fusel oil (for example, amyl and isoamyl alcohols).

3.2.5 *pHe*—a measure of the acid strength of alcohol fuels.

## 4. Performance Requirements

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

| | |
|---|---|
| Ethanol, volume %, min | 92.1 |
| Methanol, volume %, max | 0.5 |
| Solvent-washed gum, mg/100 mL, max | 5.0 |
| Water content, volume %, max | 1 (Note 1) |
| Denaturant content, volume %, min volume %, max | 1.96<br>4.76 |
| Inorganic Chloride content, mass ppm (mg/L), max | 40 (32) |
| Copper content, mg/kg, max | 0.1 |
| Acidity (as acetic acid $CH_3COOH$), mass % (mg/L), max | 0.007 (56) (Note 3) |
| pHe | 6.5 to 9.0 |
| Appearance | Visibly free of suspended or precipitated contaminants (clear and bright) |

NOTE 1—In some cases, a lower water content may be necessary to avoid phase separation of a gasoline-ethanol blend at very low temperatures. This reduced water content, measured at the time of delivery, shall be agreed upon between the supplier and purchaser.

NOTE 2—If denatured fuel ethanol is prepared by the addition of denaturants to undenatured fuel ethanol after it has been produced rather than during the dehydration process, the 15.56/15.56°C (60/60°F) specific gravity in air of the undenatured fuel ethanol shall be in the range from 0.7937–0.7977.

NOTE 3—Denatured fuel ethanol may contain additives such as corrosion inhibitors and detergents that may affect the titratable acidity (acidity as acetic acid) of the finished fuel ethanol. Although the base fuel ethanol may meet the acidity specification, the effect of these additives may produce an apparent high titratable acidity of the finished product. Contact the ethanol supplier if there is a question regarding the titratable acidity of your denatured fuel ethanol to verify that the base ethanol meets the acidity requirements of 4.1.

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.

## 5. Denaturants

5.1 The only denaturants used for fuel ethanol shall be natural gasoline, gasoline components, or unleaded gasoline at a minimum concentration of two parts by volume per 100 parts by volume of fuel ethanol. One denatured formula specifically designed for fuel use by the Bureau of Alcohol, Tobacco, and Firearms (BATF) of the U.S. Treasury Department is Formula C.D.A. 20. It requires that for every 100 gal of ethanol of not less than 195 proof, a total of 2.0 gal of denaturant be added. Another fuel alcohol rendered unfit for beverage use and manufactured at an alcohol fuel plant requires the addition of 2 gal or more of materials listed by the director to each 100 gal of ethanol. The fuel ethanol formulas approved by the U.S. Treasury Department include materials, which are not allowed by this ASTM specification. This specification prohibits the use of hydrocarbons with an end boiling point higher than 225°C (437°F) as determined by Test Method D 86, although they may be permitted by BATF regulations. Some kerosines, for instance, promote piston scuff in automotive engines. The denaturants permitted by this specification may be included as part of the 10 volume % denatured fuel ethanol blended with a gasoline if they do not exceed five parts by volume per 100 parts by volume of fuel ethanol. This is permitted in the United States by law. Any part of these denaturants that are present at concentrations higher than five parts by volume per 100 parts by volume of fuel ethanol are considered as part of the base gasoline.

NOTE 4—BATF regulations concerning the preparation, use, and handling of denatured ethanols are published in the United States Code of Federal Regulations, Title 27, Parts 19, 20, and 21. 27 CFR 19.1005 contains regulations for rendering fuel alcohol unfit for beverage use. 27 CFR 21.24 contains the formula for manufacturing completely denatured alcohol, C.D.A. 20.

5.2 *Prohibited Denaturants*—Although this specification permits only hydrocarbons in the gasoline boiling range to be used as denaturants, 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 which does not meet Specification D 1152, pyrroles, turpentine, ketones, and tars (high-molecular weight pyrolysis products of fossil or nonfossil vegetable matter). While any significant amount of methanol will lower the water tolerance and increase the vapor pressure of a gasoline-ethanol blend, these effects become more serious when methanol is present at more than 2.5 parts by volume per 100 parts by volume of fuel ethanol. Also, methanol which does not meet Specification D 1152 frequently contains impurities such as turpentine and tars. Similarly, 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, but unless a denaturant, such as a higher aliphatic alcohol or ether, is known to have no adverse effect on a gasoline-ethanol blend or on automotive engines or fuel systems, it shall not be used.

## 6. Sampling

6.1 Samples may be obtained by an appropriate procedure of Practice D 4057 or Practice E 300, except that water displacement (in section on Sampling for Specific Tests in D 4057) must not be used. Where practical, fuel ethanol should be sampled in glass containers. If samples must be collected in metal containers, do not use soldered metal containers, although they are specified in the Sampling Equipment section in Practice E 300, because the soldering flux in the containers may contaminate the sample.

6.2 *Sample Size*—A minimum of about 1 L or 1 U.S. qt 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.

6.3 *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 of Practice E 300 for a detailed discussion of the statistics of sampling.

## 7. Test Methods

7.1 The scope of some of the test methods specified in 7.2 to 7.10 do not include denatured fuel ethanol. The precisions of those test methods may differ from the reported precisions when testing denatured fuel ethanol.

7.2 *Water Content*—Test Methods E 203 or E 1064.

7.3 *Solvent-Washed Gum Content*—Test Method D 381, air jet apparatus.

7.4 *Acidity*—Test Method D 1613.

7.5 *pHe*—Test Method D 6423.

7.6 *Appearance*—The product shall be visibly free of suspended or precipitated contaminants (clear and bright). This shall be determined at indoor ambient temperature unless otherwise agreed upon between the supplier and the purchaser.

7.7 *Specific Gravity*—Test Method D 891, Procedure B or Test Method D 4052. For Test Method D 891, Procedure B (hydrometer), no formal precision statement is available, but practical experience indicates that precision is no better than 0.0005. Test Method D 891 Procedure C (pycnometer), with an interlaboratory precision (reproducibility) of 0.0002, should be used as a referee method.

7.8 *Inorganic Chloride Content*—Modification of Test Method D 512–81(1985)$^{\epsilon 1}$, Method C.

7.8.1 The modification of Test Method D 512–81(1985)$^{\epsilon 1}$, Method C consists of using 5 mL of sample diluted with 20 mL of water in place of the 25 mL sample specified in the standard procedure. The water shall meet Specification D 1193, Type II. The volume of the sample prepared by this modification will be slightly larger than 25 mL. To allow for the dilution factor, report the chloride ion present in the fuel ethanol sample as the chloride ion present in the diluted sample multiplied by five.

7.8.2 The precision of this modified method has not been determined, but for the actual amount of chloride ion found in the diluted sample, it is expected to be similar to the precision of Test Method D 512–81(1985)$^{\epsilon 1}$, Method C.

7.9 *Copper Content*—Modification of Test Method D 1688, Test Method A.

7.9.1 The modifications of Test Method D 1688, Test Method A (atomic absorption, direct) consists of mixing reagent grade ethanol (which may be denatured according to the U.S. Bureau of Alcohol, Tobacco, and Firearms (BATF) of the U.S. Treasury Department 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 11.1 of Test Method D 1688. Because a violent reaction may 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.

7.9.2 The precision of this modified method has not been determined, but it is expected to be similar to the precision of Test Method D 1688, Test Method A.

7.10 *Ethanol Content*—Test Method D 5501.

## 8. Keywords

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

## APPENDIXES

**(Nonmandatory Information)**

### X1. SIGNIFICANCE OF SPECIFIED PROPERTIES

### X1.1 Denatured Fuel Alcohol

X1.1.1 *Water Content*—Karl Fischer analysis is generally the only consistently reliable procedure for the determination of water in denatured ethanol. Test Method E 203 describes the modifications required to run the test in the presence of alcohols. Specific gravity methods such as Test Methods D 891 and D 3505, are generally unsuitable for the reasons given in X1.2.1. Blends of fuel ethanol and gasoline 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 volume % fuel ethanol with a gasoline containing 14 volume % aromatics and 0.6 mass % dissolved water (about 0.5 volume %), will separate into a lower alcohol-rich aqueous phase and an upper

hydrocarbon phase if cooled to about 7°C (45°F). As normal spark-ignition engines will not run on the aqueous phase material, such a separation is likely to cause serious operating problems. Because some degree of water contamination is practically unavoidable in transport and handling, and because gasoline-ethanol blends are hygroscopic, the water content of the denatured fuel ethanol must be limited when it is blended with gasoline to reduce the risk of phase separation.

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 fuel-insoluble gum and fuel-soluble 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 D 381 were developed using only data on hydrocarbons, they may not be applicable to denatured fuel ethanol.

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

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

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

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. The adverse effects are less when ethanol is used at 10 volume % in a blend with gasoline.

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

X1.1.8 *Ethanol Purity*—The presence of even small quantities of some organic oxygen compounds other than ethanol may adversely affect the properties of fuel ethanol-gasoline blends.

X1.2 *Undenatured Ethanol:*

X1.2.1 *Specific Gravity*—The density of a water-ethanol mixture is primarily a function of its water content. Normal U.S. industry practice and Federal regulations call for the use of the 15.56/15.56°C (60/60°F) specific gravity in air as the control method for water content of undenatured ethanol. Because the addition of denaturants will normally affect specific gravity, specific gravity methods are generally not suitable for determining the water content of denatured ethanols.

## X2. FUTURE CALIFORNIA AND FEDERAL ETHANOL REQUIREMENTS

### X2.1 California Ethanol Requirements

X2.1.1 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 become effective December 31, 2003.

X2.1.2 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 D 4806-99.

X2.1.3 California specifies that compliance with the sulfur standard shall be determined by testing the denatured ethanol using Test Method D 5453-93. California specifies that compliance with the standards for benzene, olefins, and aromatics contents shall be determined by testing a sample of the denaturant using the test methods specified for CARB gasoline and then calculating the content of those compounds in the denatured ethanol multiplying the test value by 0.0476 (except where it is demonstrated that the denatured ethanol contains less than 4.76 percent denaturant, then the test results are multiplied by the decimal fraction representing the percent denaturant).

X2.1.4 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 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.

X2.1.5 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.

X2.1.6 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 4.76 vol % and the limits in Table X2.1 are met.

**TABLE X2.1 California Denatured Ethanol Standards (In Addition to the Performance Requirements in ASTM D 4806-99)**

| Property | Specification Limit | Test Method |
|---|---|---|
| Sulfur, ppm, max. | 10 | D 5453-93 |
| Benzene, vol % max. | 0.06 | D 5580-95 test results of a sample of the denaturant multiplied by 0.0476 (see X2.1.3 for exceptions) |
| Olefins, vol % max. | 0.5 | D 6550-00 (modified) test results of a sample of the denaturant multiplied by 0.0476 (see X2.1.3 for exceptions) |
| Aromatics, vol % max. | 1.7 | D 5580-95 test results of a sample of the denaturant multiplied by 0.0476 (see X2.1.3 for exceptions) |

### X2.2 Federal Ethanol Sulfur Requirements

X2.2.1 The federal Tier 2 Motor Vehicle and Emissions Standards and Gasoline Sulfur Control Requirements establishes sulfur standards for refineries and importers producing reformulated gasoline, Reformulated Blendstock for Oxygenate Blending (RBOB), and conventional gasoline. Under the gasoline sulfur program, denatured ethanol to be blended with conventional or RBOB gasoline shall meet a maximum sulfur content of 30 ppm beginning January 1, 2004.

**TABLE X2.2 California Denaturant Standards**

| Property | Specification Limit | Test Method |
|---|---|---|
| Benzene, vol % max. | 1.1 | D 5580-95 |
| Olefins, vol % max. | 10 | D 6550-00 (modified) |
| Aromatics, vol % max. | 35 | D 5580-95 |