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Diesel fuel with improved cetane number and containing polynitrate esters and stabilizers.

Mixtures of polynitrate esters and selected amines are effective in improving the cetane number of diesel and alcohol fuels.
This invention is concerned with improved diesel fuel. More particularly it is concerned with improving the cetane number thereof by adding polynitrate esters and stabilizers for the esters.

Cetane number improvers have been used in the form of additives to upgrade marginal diesel fuels to meet specifications for ignition quality. Examples of these materials are the commercially marketed octyl nitrates, cyclohexyl nitrate, disclosed in German Offenlegungschrift DE3233834A1, primary alkyl nitrate esters such as 2-methyl-2-nitropropyl nitrate (U.S. Patent 4,417,903) and 3-tetrahydrofuranyl nitrate (U.S. Patent 4,406,665). More recently U.S. Patent 4,522,630 disclosed the use of tetrahydro-2,5-furandimethanol nitrate as a cetane improver for diesel fuels. Although many of these polynitrate esters will function well as cetane improvers, their use is hazardous in that they are explosives and are difficult to handle safely.

This invention comprises the addition of polynitrate esters in admixture with certain stabilizing amine compounds to diesel fuel, thereby increasing the cetane rating of diesel fuel, and lessening the hazard of working with these polynitrate esters. This invention provides a liquid fuel composition for use in a diesel engine comprising liquid diesel fuel boiling within the range of 93 to 454°C and containing a cetane number-increasing amount of a mixture of fuel-soluble polynitrate esters and a stabilizer selected from diphenyl amine, diethyl diphenylurea and 2-dinitro-diphenylamine.

This invention also provides a method of improving the cetane rating of a liquid diesel fuel comprising adding to the fuel a cetane-number-increasing amount of a fuel-soluble polynitrate ester and a stabilizer selected from diphenyl amine, diethyl diphenylurea, 2-dinitro-diphenylamine and mixtures thereof.

In its most preferred embodiment this invention is a liquid additive for diesel fuels to improve their cetane number by adding polynitrate esters and stabilizers.

The preferred polynitrate esters are selected from ethylene glycol dinitrate (EGD), diethylene glycol dinitrate (DEGN), triethylene glycol dinitrate (TEGN), 2-methyl-2[(nitr oxy)methyl]-1,3-propanediol dinitrate (PDN). These polynitrates can also be used in mixtures. Other polynitrate esters useful are nitroglycerin, cellulose tri, di, and mononitrate and their mixtures.

These polynitrates are found to be effective but are generally considered to be explosive and dangerous to handle. The safety of handling these polynitrates is assured by use of a proper amount of stabilizer. The stabilizers are amine compounds selected from diphenyl amine, diethyl diphenylurea and 2-dinitro-diphenylamine.

The polynitrate esters are mixed with the stabilizers at a concentration level of 0.01 to 5% of stabilizer by weight, preferably 0.1 to 1%, based on the polynitrate esters. Too much stabilizer will render the cetane improver ineffective and too little stabilizer will make it unsafe to use. For example, a mixture of 99% DEGN and 1% diphenylamine is an excellent cetane improver.

To improve the safety of handling the polynitrate esters they are diluted in a liquid diluent in admixture with a stabilizer to form stock solutions. Preferably the diluent is a diesel fuel. The stock solutions are made up to contain 10 to 50 percent by weight of the mixture of polynitrate ester and stabilizer.

The mixture of polynitrate ester and stabilizer, preferably in the stock solution form, is mixed in the diesel oil to be treated for cetane improvement and used for fuel in sufficient quantity to result in a concentration of between about 0.05% and about 1% by weight of the polynitrate ester in the diesel oil.

The polynitrates are more effective than the commercial mono-nitrates, such as octyl nitrates commercially used, because of their higher potential for generating reactive species, RO and NO₂ to ignite oxidation. The polynitrates are generally more effective than mono-nitrates by a factor of 2 to 5, i.e., the dosage requirement for polynitrates for similar cetane number improvement is 1/2 to 1/5 that required for mononitrates.

These cetane improvers are especially useful for low quality diesel fuel such as coal derived diesel fuel or ethanol. The cetane number of ethanol is about 8. For example, to increase the cetane number of ethanol to 52, 18% by weight of a commercial cetane improver (DII-3) is required but only 5% of (diethylene glycol trinitrate) (DEGN), is required to achieve the same effect. This result shows that DEGN is more effective than octyl nitrate (DII-3) by a factor of 3.2. For similar improvement, the dosage required for triethylene glycol nitrate (TEGN) is 4%, indicating that TEGN is more effective than DII-3 by a factor of 4.

Claims

1. A liquid fuel composition adapted for use in a diesel engine, which composition comprises (a) ethanol or diesel fuel boiling within the range of
93° to 454° C containing a cetane number-increasing amount of (b) at least one fuel-soluble polynitrate ester and (c) at least one fuel-soluble stabilizer which is an aromatic amine or aromatic urea.

2. A composition according to claim 1 wherein (c) comprises at least one of diphenylamine, 2-dinitrodiphenylamine, or diethyl diphenylurea.

3. A composition according to claim 1 or 2 wherein (b) comprises at least one of ethylene glycol dinitrate, diethylene glycol dinitrate, triethylene glycol dinitrate, 2-methyl-2[(nitroxy)methyl]-1,3-propanediol dinitrate, butanetriol trinitrate, 1,3-propanediol dinitrate, nitroglycerin, cellulose tri-, di-, and mono-nitrate.

4. A composition according to any preceding claim wherein (b) comprises a mixture of mono-, di- and polynitrates.

5. A composition according to claim 4 wherein (b) comprises a mixture of two or more of ethylene glycol dinitrate, diethylene glycol dinitrate, triethylene glycol dinitrate, 2-methyl-2[(nitroxy)methyl]-1,3-propanediol dinitrate, and nitroglycerin.

6. A composition according to any preceding claim wherein the concentration of (c) is between about 0.01 percent and about 5 percent of the weight of polynitrate ester present.

7. A composition according to claim 6 wherein the concentration of (c) is between about 0.1 percent and about 1 percent of the weight of polynitrate ester present.

8. A composition according to any preceding claim wherein the concentration of (b) in the liquid fuel composition is between about 0.05 percent and about 1 percent of the weight of liquid fuel.

9. A composition according to any preceding claim wherein (a) comprises a coal derived diesel fuel.

10. A method of improving the cetane-rating of a liquid fuel composition adapted for use in a diesel engine, which method comprises adding to (a) ethanol or diesel fuel boiling within the range of 93° to 454° C a cetane-number-increasing amount of (b) at least one fuel-soluble polynitrate ester and (c) at least one fuel-soluble stabilizer which is a an aromatic amine or aromatic urea.

11. A method of handling and transporting a liquid fuel composition adapted for use in a diesel engine and comprising (a) ethanol or diesel fuel boiling within the range of 93° to 454° C and containing (b) at least one fuel-soluble unstable polynitrate ester, which method comprises adding to the fuel (c) at least one fuel-soluble stabilizer which is an aromatic amine or aromatic urea.

12. A method according to claim 10 or 11 wherein (a), (b) of (c) are defined in any of claims 1 to 9.
**EUROPEAN SEARCH REPORT**

**Application Number**

**EP 87 30 924**

**DOCSMENTS CONSIDERED TO BE RELEVANT**

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<th>Category</th>
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<tr>
<td>X</td>
<td>EP-A-0 711 134 (BAYER AG) * Claims; page 2, lines 23-25; page 3, lines 9-18; page 4, line 16 - page 5, line 18; page 6, lines 11-26; page 10 *</td>
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**TECHNICAL FIELDS SEARCHED (Int. Cl.)**

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**The present search report has been drawn up for all claims**

**Place of search**

**THE HAGUE**

**Date of completion of the search**

**27-04-1988**

**Examiner**

**DE LA MORINERIE B.M.S.B.**

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**CATEGORY OF CITED DOCUMENTS**

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**EUROPEAN SEARCH REPORT**

**DOCUMENTS CONSIDERED TO BE RELEVANT**

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