(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 116 197**
**A2**

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: **83303508.2**

(22) Date of filing: **17.06.83**

(51) Int. Cl.³: **C 10 L 1/02**

(30) Priority: **14.01.83 ZA 830264**

(43) Date of publication of application:
**22.08.84 Bulletin 84/34**

(84) Designated Contracting States:
**BE DE GB NL**

(71) Applicant: **AECI LIMITED**
**16th Floor Office Tower Carlton Centre Commissioner Street P.O. Box 1122**
**Johannesburg 2000 Transvaal(ZA)**

(72) Inventor: **Stiff, Anthony John**
**19 Lols Road Illiondale**
**Edenvale Transvaal(ZA)**

(74) Representative: **Martin, David Lincoln et al,**
**Imperial Chemical Industries PLC Legal Department: Patents PO Box 6 Bessemer Road**
**Welwyn Garden City Herts, AL7 1HD(GB)**

(54) **Ignition improver for an alcohol based fuel for compression ignition engines.**

(57) The invention concerns a composition of matter comprising a mixture of (A) at least one alcohol with an average molecular weight of less than 160 and (B) at least one organic compound of formula

$$NO_2-O-(CH_2CH_2O)_x-NO_2$$

wherein x = an integer greater than 3, and wherein the molecular weight (or average molecular weight) of the compound(s) is between 260 and 480. The composition may be used as a fuel for compression ignition engines.

EP 0 116 197 A2

Ignition improver for an alcohol based fuel for compression ignition engines.

This invention relates to a composition of matter, and its use, and is an improvement in or modification of the invention described and claimed in our co-pending application, published as European Patent Application No. 30429, hereinafter referred to as the parent application.

The lower alcohols, particularly methanol and ethanol, are desirable alternative fuels for internal combustion engines. They are, however, unsuitable (or less suitable than hydrocarbon diesel fuels) for use alone in compression-ignition (diesel) engines. This is primarily due to their poor compression-ignition characteristics, as is evidenced by their low cetane numbers (hereinafter referred to as "C.N."). Methanol has C.N. = 3, and methanol C.N. = 15, whereas the minimum C.N. for hydrocarbon diesel fuel is about 40. This problem can be overcome by using additives (ignition improvers) which improve the compression-ignition characteristics of such fuels, so that they are then suitable for use in commercial compression-ignition engines.

Alcohols up-rated in this way can be used as fuels in commercial compression-ignition engines without the need for additional energy inputs and/or aids such as heated air aspiration, turbo-charging, spark-ignition, abnormally high compression ratios or other additional energy sources and the like, although such additional energy sources and/or aids may be used, if desired.

The use of iginition improvers to upgrade conventional hydrocarbon diesel fuels is well established (Marks' Standard Handbook for Mechanical Engineers, 8th Edition, ed Baumeister et al, McGraw-Hill, page 7-19). However, although a wide range of materials have been used as ignition improvers for hydrocarbon diesel fuels, the majority of these are ineffective as ignition improvers for alcohol-based fuels. On the other hand, German Patent No. 2,701,588 disclosed the use of alkyl mononitrates and nitrites particularly ethyl nitrate and ethyl nitrite as ignition improvers for alcohol-based fuels.

The Applicant believes that although such materials are very effective in hydrocarbon diesel fuels, large quantities are required to improve the compression-ignition characteristics of alcohol fuels

sufficiently for these to be used as practical fuels for compression-ignition engines. For example, an addition of more than 25% by volume of ethyl nitrate to methanol or ethanol is required to produce a satisfactory compression-ignition fuel. Other alkyl nitrates are effective ignition improvers for the lower alcohols at addition levels of between 10% and 25% by volume.

The Applicants have invented a fuel comprising at least one alcohol and at least one nitrate. Thus the parent patent application claims a fuel comprising a mixture of (A) at least one alcohol with an average molecular weight of less than 160, and (B) at least one further organic compound which has a spontaneous ignition temperature of less than 450°C, said further organic compound being a compound which contains one nitrate group and at least two ether linkages or at least two nitrate groups and one or more ether linkages.

The parent patent application also claims a method of running an engine which comprises injecting into and/or inducting into the engine both A and B, defined in the paragraph immediately above.

Specific further organic compounds of the component B listed in the parent patent are 2' - butoxy - 2 - ethoxyethyl nitrate, diethylene glycol dinitrate (DEGDN), triethylene glycol dinitrate (TEGDN), and the dinitrate of polyethylene glycol of an average molecular weight of 400, (i.e. a compound of average molecular weight of 490).

These materials are particularly effective in alcohol-based fuels, since addition levels of about 5% by volume or less in methanol or ethanol are required to produce a satisfactory compression ignition fuel. TEDGN is one of the most effective ignition improvers for alcohols disclosed to date.

However, materials such as DEGDN and TEGDN possess explosive properties, which can be undesirable in some cases for an injection improver. For example, if the alcohol-based fuel contains 1% (by volume) or more of such ignition improvers, this problem of the explosive properties can be serious since evaporation of the volatile alcohol, for example in the case of fuel spillage, may leave a substantial quantity of residue with explosive properties.

The Applicant believes that it would be more desirable to use ignition improvers which exhibit ignition-improving properties

that are quantitatively similar to TEGDN when admixed with alcohols, but which do not possess explosive properties, and which do not require stabilising or desensitising agents to render them non-explosive.

In researching suitable ignition improvers, the Applicant has invented a composition of matter which may be used as a fuel.

According to the invention, there is provided a composition of matter comprising a mixture of (A) at least one alcohol with a molecular weight of less than 160 and (B) at least one an organic compound of the general formula

$$NO_2\text{-}O\text{-}(CH_2CH_2\text{-}O\text{-})_x\text{-}NO_2 \qquad (I)$$

wherein x = an integer greater than 3, and wherein the molecular weight (or average molecular weight) of the compound(s) is between 260 and 480. Such a composition of matter may be used as a fuel, as blending stock for a fuel, or the like.

Preferably, the component (B) is a mixture of compounds of Formula (I), such that the average molecular weight is between 280 and 350. Particular examples of component (B) are mixtures of average molecular weight about 292, 390 and 480. Component (B) conveniently can be present in an amount of between 0.01% by volume of the composition, e.g. about 2 to 5% by volume.

The component (B) has the ability, when admixed with the lower alcohol component (A) to improve the compression-ignition characteristics of the alcohol sufficiently to enable it to be used as a fuel for compression-ignition engines. It further has the inability to propagate an explosion initiated by a 150 g 'Pentolite' explosive booster when contained in a 50 mm diameter steel pipe.

The invention, therefore further provides a liquid fuel for a compression-ignition engine, said fuel, comprising (A) a mixture of at least one lower alcohol of molecular weight less than 160 and (B) an ignition improver which is at least one compound of general formula (I) above and which has a molecular weight between 260 and 480.

The liquid fuel may also contain at least one further combustible organic material.

In one embodiment, the composition may initially contain

between about 5% and about 99% (by volume) of the ignition improver, as it can then be used as a blending stock for preparing fuel for a compression-ignition engine.

Conveniently the liquid fuel contains between about 0.01% and about 10% (by volume) of the ignition improver (B) and it can then be used directly as a fuel for compression-ignition engines.

The alcohol component (A) may have a molecular weight of less than 90, and may be methanol and/or ethanol.

When further combustible organic materials are present, they may be one or more of the following: lubricants, stabilizers, corrosion inhibitors, ignition improvers, synergistic agents, other fuels, fuel additives, fuel diluents and fuel extenders. Such materials are of course, compatible with said alcohols.

According to yet another aspect of the invention, there is provided a method of operating a compression-ignition engine, which comprises supplying, to the engine, a fuel having a composition as hereinbefore described.

The invention will now be further described by way of the following non-limiting Examples.

EXAMPLE 1

Three ignition improvers comprising mixtures of compounds of Formula (I) and having average molecular weights of 292, 390 amd 480 respectively, (hereinafter referred to as '292', '390' and '480' respectively), were synthesised by nitration of the respective poly(oxyethylene)glycols. All three ignition improvers were a mixture of oligomers.

EXAMPLE 2

The ignition improvers of Example 1 exhibited insignificant explosive properties, as illustrated by a severe detonation test. Approximately 1100 ml of each improver were poured into a vertical steel pipe (50 mm internal diameter, length 600 mm) which was closed at the lower end. A 150 g explosive booster, available locally under the AECI Limited trade name 'Pentolite', was inserted in the upper end of the pipe. After detonation of the booster, the pipe was examined. Detonation of the material under test would have resulted in complete fragmentation of the pipe. However, in all three cases,

absence of such detonation was evidenced by the pipe only being splayed open at its upper end due to detonation of the booster only. The results are given in Table 1.

TABLE 1

SENSITIVITY OF IGNITION IMPROVERS TO DETONATION

| Ignition Improver | Results of Detonation Test |
|---|---|
| 292 | No detonation |
| 390 | No detonation |
| 480 | No detonation |
| triethylene glycol dinitrite (for comparison purposes | Complete detonation |

This test shows that the ignition improvers according to the invention are better than triethylene glycol dinitrate with regard to reduction of explosive hazard in use.

EXAMPLE 3

The effectiveness of the ignition improvers of the invention as ignition improvers was assessed by determining the concentration (designated "approximate effective concentration' in Table II) thereof required in methanol and ethanol to yield a fuel which will exhibit a similar ignition delay to hydrocarbon diesel fuel having a C.I. of 45, when used to operate a compression-ignition engine. The test engine was an instrumented single-cylinder direct-injection air-cooled diesel engine of 15,7:1 compression ratio, operated at 1500 rpm with a dynamic injection timing of 10° BTDC. Fuels which have adequate compression-ignition characteristics for satisfactory engine operation (such as hydrocarbon diesel fuel having a CI of 45) exhibit an ignition delay of between 6° and 7° C.A. (Crank Angle) under these conditions.

The results are given in Table II.

TABLE II

APPROXIMATE CONCENTRATIONS OF IGNITION IMPROVERS 292, 390 AND 480 REQUIRED IN METHANOL AND ETHANOL TO IMPART ADEQUATE COMPRESSION IGNITION CHARACTERISTICS THERETO FOR NORMAL ENGINE OPERATION.

| Ignition Improver | Approximate Effective Concentration (% by volume) | |
|---|---|---|
| | Methanol | Ethanol |
| 292 | 4.0 | 4.5 |
| 390 | 4.5 | 5.0 |
| 480 | 5.0 | - |
| Triethylene glycol dinitrate (molecular weight 240) for comparison | 4.0 | 4.5 |

This test shows the effectiveness of the ignition improvers of the invention in respect of methanol and ethanol as compared to triethylene glycol dinitrate.

EXAMPLE 4

Liquid compositions containing ignition improvers according to the invention were prepared by admixing the components as given in Table III. The components were placed in a screw-capped glass bottle which was closed and gently shaken to give a clear, homogeneous solution in each case. These compositions were used as a blending stock to prepare fuels (see Example 5).

TABLE III

| Composition | Ignition Improver | | Lubricant Quantity | Corrosion Inhibitor Quantity | Alcohol | |
|---|---|---|---|---|---|---|
| | Designation | Quantity | | | Type | Quantity |
| A | 292 | 400 ml | 100 ml | 2 g | Methanol | 500 ml |
| B | 390 | 450 ml | 100 ml | 2 g | Methanol | 450 ml |
| C | 480 | 500 ml | 100 ml | 2 g | Methanol | 450 ml |
| D | 292 | 450 ml | 100 ml | 2 g | Ethanol | 450 ml |
| E | 340 | 500 ml | 100 ml | 2 g | Ethanol | 500 ml |

EXAMPLE 5

Fuels for use in compression-ignition engines were prepared by mixing together 10 parts by volume of the compositions of Example 4 and 90 parts by volume of methanol or ethanol, to produce fuels having the compositions given in Table IV.

TABLE IV

| Fuel Designation | Ignition Improver | | Lubricant % by vol. | Corrosion Inhibitor | Alcohol | |
|---|---|---|---|---|---|---|
| | Designation | % by vol | | | Type | % by vol |
| AA | 292 | 4.0 | 1.0 | 0.02 | Methanol | 95.0 |
| BB | 390 | 4.5 | 1.0 | 0.02 | Methanol | 94.5 |
| CC | 480 | 5.0 | 1.0 | 0.02 | Methanol | 94.0 |
| DD | 292 | 4.5 | 1.0 | 0.02 | Ethanol | 94.5 |
| EE | 390 | 5.0 | 1.0 | 0.02 | Ethanol | 94.0 |

These fuels were used to operate the test engine described in Example 3. It was found that for all the fuels the engine started easily from cold, idled smoothly and ran normally under all speed and load conditions. Cylinder pressure readings indicated that the combustion characteristics, such as ignition delay, rate of pressure rise during combustion, and peak pressures, were satisfactory for normal operation of the engine.

Claims

1. A composition of matter comprising a mixture of (A) at least one alcohol with an average molecular weight of less than 160 and (B) at least one organic compound of the formula

$$NO_2\text{-}O\text{-}(CH_2CH_2O)_x\text{-}NO_2$$

wherein x = an integer greater than 3, and wherein the molecular weight (or average molecular weight) of the compound(s) is between 260 and 480.

2. A composition of matter as claimed in claim 1 wherein component (B) is a mixture of compounds of Formula I of average molecular weight between 280 and 350.

3. A composition of matter as claimed in claim 2 wherein the component (B) has an average molecular weight of about 292.

4. A composition of matter as claimed in claim 1 wherein component (B) has an average molecular weight of about 390.

5. A composition of matter as claimed in claim 1 wherein component (B) has an average molecular weight of about 480.

6. A composition of matter as claimed in any one of the preceding claims wherein component (B) is present in an amount of between 0.01% and 10% by volume of the composition.

7. A composition of matter as claimed in claim 6 wherein compound (B) is present in an amount of 2 to 5% by volume of the composition.

8. A composition of matter as claimed in any one of the preceding claims wherein the alcohol component (A) has a molecular weight of less than 90.

9. A liquid composition of matter as claimed in claim 8 wherein the alcohol is methanol and/or ethanol.

10. A fuel for a compression-ignition engine, said fuel comprising a composition as claimed in any one of the preceding claims, said composition being liquid at ambient temperatures.

11. A fuel as claimed in claim 10 wherein the fuel contains at least one further combustible organic material compatible therewith.

12. A method of operating a compression-ignition engine which comprises supplying to the engine a liquid fuel as claimed in claim 10 or 11.