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

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Description

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 ethanol 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 ignition 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 preceding paragraph.

Specific further organic compounds of the compound 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).

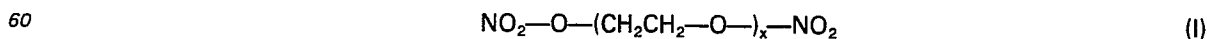
These materials are particularly effective in alcohol-based fuels, since addition levels of about 5% by volume or less in methanol or ethanol are required to produce a satisfactory compression ignition fuel. TEGDN is one of the most effective ignition improvers for alcohols disclosed to date.

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 organic compound of the formula



wherein x = an integer greater than 3, and wherein the molecular weight (or average molecular weight) of the compound(s) of the formula (I) is between 260 and about 390, with the proviso that no other compounds of the formula (I) other than the aforesaid are present. Such a composition of matter may be used as a fuel, as blending stock for a fuel, or the like.

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Preferably, the compound (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 and 390. Component (B) conveniently can be present in an amount of between 0.01% and 10% by volume of the composition, e.g. 2 to 5% by volume.

5 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.

10 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 about 390.

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

15 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.

20 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.

25 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

30 Three ignition improvers comprising mixtures of compounds of Formula (I) and having average molecular weights of 292, 390 and 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

35 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.
40 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.

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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.

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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).

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TABLE III

Composition	Ignition Improver		Lubricant Quantity	Corrosion Inhibitor Quantity	Alcohol	
	Design- nation	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.

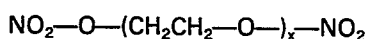
TABLE IV

Fuel Desig- nation	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.

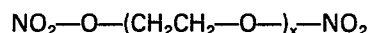
Claims

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



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wherein x = an integer greater than 3, and wherein the average molecular weight of the compound(s) of formula



is between 260 and about 390, with the proviso that no other compounds of formula



are present.

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 component (B) has an average molecular weight of about 292.

4. 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.

5. A composition of matter as claimed in claim 4 wherein component (B) is present in an amount of 2 to 5% by volume of the composition.

6. 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.

7. A liquid composition of matter as claimed in claim 6 wherein the alcohol is methanol and/or ethanol.

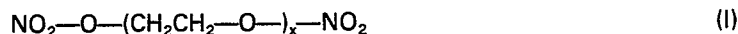
8. A fuel for a compression-ignition engine, said fuel comprising a composition as claimed in any one of the preceding claims, said composition being liquid at ambient temperatures.

9. A fuel as claimed in claim 8 wherein the fuel contains at least one further combustible organic material compatible therewith.

10. A method of operating a compression-ignition engine which comprises supplying the engine a liquid fuel as claimed in claim 8 or 9.

Patentansprüche

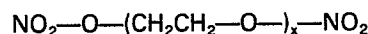
1. Substanzmischung, bestehend aus einer Mischung aus (A) wenigstens einem Alkohol mit einem weniger als 160 betragenden Durchschnittsmolekulargewicht und (B) wenigstens einer organischen Verbindung der Formel



worin x eine ganze Zahl ist, die größer als 3 ist, und worin das Durchschnittsmolekulargewicht der Verbindung(en) der Formel



zwischen 260 und etwa 390 liegt, unter der Bedingung, daß keine anderen Verbindungen der Formel



vorhanden sind.

2. Substanzmischung nach Anspruch 1, bei der die Komponente (B) eine Mischung aus Verbindungen der Formel (I) mit einem Durchschnittsmolekulargewicht zwischen 280 und 350 ist.

3. Substanzmischung nach Anspruch 2, bei der die Komponente (B) ein Durchschnittsmolekulargewicht von etwa 292 hat.

4. Substanzmischung nach einem der vorhergehenden Ansprüche, bei der die Komponente (B) in einer auf die Mischung bezogenen Menge zwischen 0,01 und 10 Volumen% vorhanden ist.

5. Substanzmischung nach Anspruch 4, bei der die Komponente (B) in einer auf die Mischung bezogenen Menge von 2 bis 5 Volumen% vorhanden ist.

6. Substanzmischung nach einem der vorhergehenden Ansprüche, bei der die Alkoholkomponente (A) ein weniger als 90 betragendes Molekulargewicht hat.

7. Flüssige Substanzmischung nach Anspruch 6, bei der der Alkohol Methanol und/oder Ethanol ist.

8. Brennstoff für einen Motor mit Verdichtungszündung, wobei der Brennstoff eine Mischung nach einem der vorhergehenden Ansprüche enthält, wobei die Mischung bei Umgebungstemperaturen flüssig ist.

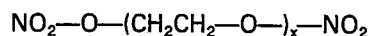
9. Brennstoff nach Anspruch 8, wobei der Brennstoff wenigstens eine weitere brennbare organische Substanz enthält, die damit verträglich ist.

10. Verfahren zum Betreiben eines Motors mit Verdichtungszündung, bei dem dem Motor ein flüssiger Brennstoff nach Anspruch 8 oder 9 zugeführt wird.

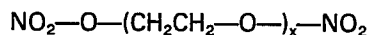
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Revendications

1. Composition de matière comprenant un mélange (A) d'au moins un alcool ayant un poids moléculaire moyen de moins de 160 et (B) d'au moins un composé organique de formule



où x est un entier supérieur à 3, et où le poids moléculaire moyen du ou des composés de formule



se situe entre 260 et environ 390, avec la restriction que d'autres composés de formule



ne sont pas présents.

2. Composition de matière suivant la revendication 1, dans laquelle le composant (B) est un mélange de composés de formule (I) d'un poids moléculaire moyen entre 280 et 350.

3. Composition de matière suivant la revendication 2, dans laquelle le composant (B) est un poids moléculaire moyen d'environ 292.

4. Composition de matière suivant l'une quelconque des revendications précédentes, dans laquelle le composant (B) est présent en une quantité entre 0,01% et 10% en volume de la composition.

5. Composition de matière suivant la revendication 4, dans laquelle le composant (B) est présent en une quantité de 2 à 5% en volume de la composition.

6. Composition de matière suivant l'une quelconque des revendications précédentes, dans laquelle le composant alcool (A) a un poids moléculaire de moins de 90.

7. Composition de matière liquide suivant la revendication 6, dans laquelle l'alcool est le méthanol et/ou l'éthanol.

8. Carburant pour un moteur à allumage par compression, lequel carburant comprend une composition suivant l'une quelconque des revendications précédentes, cette composition étant liquide aux températures ambiantes.

9. Carburant suivant la revendication 8, dans lequel le carburant contient au moins une autre matière organique combustible compatible.

10. Procédé pour faire fonctionner un moteur à allumage par compression, qui comprend l'alimentation du moteur à l'aide d'un carburant liquide suivant la revendication 8 ou 9.