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(54) **Clear liquid fuel mixture for combustion engines.**

(57) The invention relates to a clear liquid fuel mixture for combustion engines which consist of:

a. a liquid hydrocarbon mixture;
b. 1-10 % by weight of water;
c. 0.1-25 % by weight of methanol as alcohol fully soluble in water;
d. 0.1-15 % by weight of surface-active substances; and
e. 0.01-20 % by weight of alcohols with 4 to 12 C atoms not or sparingly soluble in water.

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CLEAR LIQUID FUEL MIXTURE FOR COMBUSTION ENGINES

The invention relates to a clear, liquid fuel mixture for combustion engines, which mixture comprises:

a. a liquid hydrocarbon mixture;

b. water;

c. an alcohol fully soluble in water and

d. surface-active substances.

Such a clear, liquid fuel mixture is know from United States patent 4,002,435.

The fuel mixuture described in this patent specification consists of:

a. petrol or diesel oil;

b. 0.1-10 % of water;

c. 0.1-20 % of an alcohol fully soluble in water and

d. a combination of surface-active agents, consisting of:

1. a salt of saturated or unsaturated higher fatty acid;

2. an unsaturated organic acid; and

3. an ethylene oxide condensation product.

According to this patent specification, a special combination of surface-active agents is required for the dispersion of alcohol and water in petrol or oil in order to obtain a stable water-containing fuel mixture with a water-soluble alcohol, such as methanol. As alcohol fully soluble in water, methanol, ethanol, propanol or a mixture of these alcohols is applied.

The disadvantage of this fuel mixture is that it is relatively expensive, because special surface-active agents are necessary for dispering the alcohols fully soluble in water in petrol to a mixture which is stable over a wide temperature range.

The Dutch patent application 7416290 relates to the operation of Otto and rotary reciprocating engines, using petrol as fuel simultaneously with water-containing crude methanol. It is true that the alcohol used is cheap, but this is amply offset by the disadvantage that for each motor vehicle separate tanks and separate injection systems for the petrol and for the water-containing crude methanol are required.

When combined in advance, such a mixture will show phase separation, which makes application impossible. In order to be able to use this fuel each motor vehicle, will require the necessary investments.

The European patent application 12345 relates to engine and turbine fuels containing water and alcohol and using a special and expensive nonionogenic emulsifier to obtain good stability, even in coldness. Relatively much stirring energy is required in order to prepare a milky emulsion of the various components. Another disadvantage is that, if this fuel mixture has been left to stand for some time, or if unfortunately water has found its way into it, further stirring energy will be required again in order to obtain an emulsion. This is rather problematical if this fuel mixture is contained in the tank of a motor vehicle. Furthermore, it is difficult to determine if phase separation has already taken place. The stability in coldness, too, is not quite satisfactory.

The purpose of the invention is to remove the said disadvantages and to provide a clear liquid fuel mixture for combustion engines, as stated in the preamble, which fuel mixture is cheap, does not separate out even after it has been left to stand for a long time, which is stable at -20 °C and which allows the various components to be mixed with each other virtually without use of stirring energy to form a clear liquid mixture.

A further purpose of the invention is to provide a fuel mixture containing relatively few petroleum-recovered hydrocarbons and relatively many liquid raw materials which can be prepared form natural gas and/or coal. Furthermore, the fuel mixture must be applicable in the existing engines.

It has been found that higher alcohols not or sparingly soluble in water have a positive effect on the increase of the stability range of clear fuel mixtures containing hydrocarbons, methanol and water, even if these higher alcohols are present in very small quantities. Very small quantities are understood to mean quantities in the order of 0.02 % by volume.

It is very important for the stability range, i.e. the range in which a clear mixture is obtained and/or kept, to be as wide as possible, particularly at -20 °C. This will strongly reduce the risk of phase separation at fluctuations in the composition of the mixture.

Furthermore, it will also give greater freedom in the composition of the fuel mixture.

According to the invention the clear fuel mixture consists of:

a. a liquid hydrocarbon mixture;

b. 1-10 % by weight of water;

c. 0.1-25 % by weight of methanol as alcohol fully soluble in water;

d. 0.1-15 % by weight of surface-active substances and

e. 0.01-20 % by weight of alcohols with 4-12 C atoms not or sparingly soluble in water.

The alchols with 4-12 C atoms not or sparingly solubility in water may also be divalent alcohols, such as diols. Preference, however, is given to monovalent alcohols.

The mixture can be converted very simply into a clear whole. This can be done by shaking, filling of the storage tank or simply by transport.

It is supposed that a so-called micro-emulsion is formed, which is understood to mean a transparant, stable, liquid system consisting of a least two liquids which cannot or hardly be mixed, in which system one liquid is dispersed by means of one or more surface-active substances in the other. The drop size is substantially smaller than that of an ordinary emulsion and,in consequence, a micro-emulsion, unlike an ordinary emulsion, is transparent. Apart form the limited amount of energy required for mixing the components, the formation of micro-emulsions requires no special measures. They are formed spontaneously as soon as the various components are brought together.

Sparingly soluble in water is understood here to mean tha only very subordinate quantities will dissolve in water, i.e. smaller than 25 % by weight, preferably smaller than 10 % weight.

The fuel mixture according to the invention has the following advantages:

a. it is clear;

b. requires little of no stirring energy during its preparation;

c. is stable to at least -20 °C;

d. gives lower emission of harmful components in the exhaust gases than petrol;

e. gives good knock resistance so that the addition of tetra-alkyl lead

to raise the octane number is not necessary.

It has specifically been found that, in addition to small quantities of these higher alcohols not or sparingly soluble in water, a larger quantity of alcohols with 2-4 C atoms fully soluble in water has the effect that a substantially smaller quantity of surface-active agents is required.

Another major advantage of the invention is that, without adversely affecting the clearness and stability of the fuel mixture, the quantities of water-soluble alcohols and alcohols not or sparingly soluble in water can be varied in respect of each other.

Thus the liquid mixture according to the invention may contain, for instance:

a. 5-20 % by weight of alcohols with 2-4 C atoms fully soluble in water and

b. 0.01-5 % by weight of alcohols with 4-12 C atoms not or sparingly soluble in water.

The alcohol with 2-4 C atoms fully soluble in water is preferably tertiary butanol, together with the small quantities of alcohols not or sparingbly soluble in water.

Most preference is given to the addition or use of larger quantities of alcohols with 4-12 C atoms not or sparingly soluble in water. Thus the quantity of surface-active substances can be reduced, while a simultaneous widening of the stability range will be found. Thus the mixture preferred most contains 5-20 % by weight of alcohols with 4-12 C atoms not or sparingly soluble in water.

Preferably the alcohol with 4-12 C atoms not or sparingly soluble in water is n-butanol or n-pentanol. The quantity of alcohols with 4-12 C atoms not or sparingly soluble in water and contained in the said liquid mixture preferably amounts to 5-15 % by weight.

The mixture may in addition yet contain 0.01-5 % by weight of alcohols with 2-4 C atoms fully soluble in water.

As stated earlier, the quantities of water and methanol in the liquid mixture can be varied in respect of each other. The liquid mixture preferably contains 1-5 % by weight of water and 2-15 % by weight of methanol.

For dispersing the water and the alcohols in the petrol, in which process, in the conviction of the applicant, a micro-

emulsion is obtained, surface-active substances are required. Preferably anionogenic or nonionogenic surface-active substances and specifically combinations thereof are applied. A mixture of surface-active acid and salts of these acids as surface-active substances have the greatest preference, because these have been found very suitable and are, moreover, cheap. The liquid mixture preferably contains 0.1-10 % by weight of surface-active substances. Th quantity can easily be determined by one skilled in the art. If a nonclear emulsion is formed, the quantity must be increased.

As anionogenic surface-active substances the following are eligible:

- salst of surface-active carboxylic acids, specifically fatty acids with 10 to 20 C atoms;
- sulphuric acid esters, specifically alkyl esters with an alkyl group of 10 to 20 C atoms;
- alkyl and alkylaryl sulphonates, in which the alkyl group has 10 to 20 C atoms and the alkylaryl group 10 to 26 C atoms;
- paraffin sulphonates, lignin sulphonates;
- phosphoric acid esters, specifically alkyl esters with an alkyl group of 10 to 20 C atoms;
- salts of surface-active phophorous and phosphoric acids.

As nonionogenic surface-active substances the following are eligible:

- ethylene oxide condensation products with, for instance, alcohols with 6 to 18 C atoms, alkyl phenols, polyols or propylene oxide;
- polyhydroxy compounds, such as esters of polyols and fatty acids;
- fatty acids, both saturated and unsaturated, with 10 to 20 C atoms.

It is a great advantage of the present invention that a mixture can directly be applied as obtained in the preparation of methanol, starting form methane, without water and higher alcohols having to be removed.

A mixture of methanol, water and alcohols not or sparingly soluble in water can be obtained directly by catalytic steam reforming of methane an successive catalytic synthesis of the gas mixture obtained, without sccessive purification, such as removal of water and higher alcohols. The mixture formed is extremely suitable for dispersion in petrol by means of surface-active substances and optionally a higher alcohol, in which process a mixture is obtained which remains clear and

stable within a wide temperature range (-20 °C to +30 °C). The mixture obtained contains, in respect of methanol, 10-25 % by volume of water and 0.05-0.5 % by volume or more of higher alcohols.

According to the invention it is possible to incorporate the mixture of methanol, water and higher alcohols in hydrocarbons just by means of surface-active substances, although it is an advantage to add an extra quantity of alcohol with 2 to 12 C atoms, because the quantity of surface-active substances required may then be smaller. Preferably, 5-20 % by weight of these alcohols is added.

In order to even further improve the stability of the clear liquid mixture obtained even further, the mixture may additionally contain an ether with 2-8 C atoms, specifically methyl-tertiary butyl-ether. The alcohol not soluble in water can then be partly replaced by the said ether. Preferably 0.01 to 15 % by weight, specifically 0.05-10 % by weight, of ether is added.

Example I

Clear liquid mixtures were formed by bringing together in a test tube:

Premium petrol (RON = 99; MON = 88; boiling range 35 to 200 °C); methanol in the form of crude methanol with 21.5 % by volume of water and 0.02 % by volume of alcohols not or sparingly soluble in water, such as butanol, pentanol and higher alcohols, and 0.08 % by volume of alcohols completely soluble in water, such as ethanol and propanol; or pure methanol with 21.5 % by volume of water; a mixture of Na-oleate and oleic acid in the ratio of 80 : 20 and n-butanol.

The mixture of surface-active substances was dissolved in the alcohol mixture and as such added to the petrol.

The quantities of the various components are mentioned in the following table, which also states if the mixture is stable after 1 day's storage at -20 °C.

Mixtures at -20 °C

Premium petrol	Na-oleate oleic acid (80 : 20)	n-butanol	Pure MeOH* 21.5 % by volume H_2O	Crude MeOH*	Stability at -20 °C
ml	g	g	g	g	
10(= 7.4 g)	1.00	0.50	1.20	-	phase separation
10	1.00	0.50	-	1.20	clear
10	0.75	0.75	1.20	-	phase separation
10	0.75	0.75	-	1.20	clear

*MeOH = methanol.

With 1.00 g methanol (pure and crude) the same results are obtained.

It is, furthermore, found that, if 0.75 to 1.75 g crude methanol is added, a clear mixture is obtained at both surfactant butanol ratios. It has, furhtermore, been found that the stability range is twice as large as that when pure methanol with 21.5 % by volume of water is used.

Example II

In order to show the effects of different types of alcohol on the stability of the clear liquid mixture according to the invention, the quantities in grammes of each type of alcohol at +20 °C respectively -20 °C to be added in order to obtain a clear stable liquid mixture were determined.

The mixture contains 10 ml regular petrol (RON 88; MON 82), 0.8 g ammonium oleate-oleic acid mixture in the proportion of 60 : 40; 1.8 g crude methanol of the composition as in example I.

	+20 °C	-20 °C	solubility in water
iso-propanol	1.51 g	inactive	fully soluble
n-propanol	1.35 g	2.25 g	fully soluble
tert. butanol	1.23 g	1.79 g	fully soluble
iso-butanol	1.10 g	1.60 g	not soluble
n-butanol	0.98 g	1.30 g	not soluble
n-pentanol	0.90 g	1.12 g	not soluble

These results show that the non-soluble alcohols, particularly n-butanol and n-pentanol, clearly produce the greatest effects.

Example III

In this example the effect of the addition of methyl-tertiary-butylether (MTBE) on the stability of the liquid mixtures according to the invention is shown.

The results are given in the following table. A mixture of regular petrol, surfactants and crude methanol was started from as in example II.

Petrol (regular)	NH_4-oleate-oleic acid (60 : 40)	n-butanol	MTBE	crude MeOH	stability
g	g	g	g	g	
7.27*	-	-	0.5**	1.81	unstable
7.27	0.80	1.20	-	1.81	stable to +10 °C
7.27	0.80	1.20	0.5	1.81	stable to -20 °C

* = 10 ml

** = 0.625 ml.

CLAIMS

1. Clear liquid mixture for application as fuel in combustion engines, comprising:
   a. a liquid hydrocarbon mixture;
   b. water;
   c. an alcohol fully soluble in water;
   d. surface-active substances;
   characterized in that the fuel mixture consists of:
   a. a liquid hydrocarbon mixture;
   b. 1-10 % by weight of water;
   c. 0.1-25 % by weight of methanol as alcohol fully solble in water;
   d. 0.1-15 % by weight of surface-active substances; and
   e. 0.01-20 % by weight of alcohols with 4 to 12 C atoms not or sparingly soluble in water.

2. Clear liquid mixture according to claim 1, characterized in that the liquid mixture contains:
   0.01-5 % by weight of alcohols with 4-12 C atoms not or sparingly soluble in water and additionally 5-10 % by weight of alcohols with 2-4 C atoms fully soluble in water.

3. Clear liquid mixture according to claim 2, characterized in that the alcohol with 2-4 C atoms fully soluble in water is tertiary butanol.

4. Clear liquid mixture according to claim 1, characterized in that the mixture contains 5-20 % by weight of alcohols with 4-12 C atoms not or sparingly soluble in water.

5. Clear liquid mixture according to claim 4, characterized in that the mixture contains additionally 0.01-5 % by weight of alcohols with 2-4 C atoms fully soluble in water.

6. Clear liquid mixture according to claim 4, characterized in that the alcohol with 4-12 C atoms not or sparingly soluble in water is n-butanol or n-pentanol.

7. Clear liquid mixture according to claims 4 and 6, characterized in that the liquid mixture contains 5-15 % by weight of alcohols with 4-12 C atoms not or sparingly soluble in water.

8. Clear liquid mixture according to claim 1, characterized in that the mixture contains 1-5 % by weight of water.

9. Clear liquid mixture according to claim 1, characterized in that the

the mixture contains 2-15 % by weight of methanol.

10. Clear liquid mixture according to claim 1, characterized in that the mixture contains a combination of anionogenic or noniongenic surface-active substances.

11. Clear liquid mixture according to claim 10, characterized in that the mixture contains surface-active acids and salts of these acids as surface-active substances.

12. Clear liquid mixture according to claim 1, characterized in that the mixture contains 0.1-10 % by weight of surface-active substances.

13. Clear liquid mixture according to claim 1, characterized in that the mixture of methanol, water and alcohols not soluble in water has been obtained by steam reforming of methane and subsequent catalytic synthesis of the gas mixture obtained.

14. Clear liquid mixture according to claim 13, characterized in that the mixture contains in addition 5-20 % by weight of an alcohol with 2-12 C atoms.

15. Clear liquid mixture according to any one or more of the above claims, characterized in that the mixture contains in addition 0.01-15 % by weight of ether.

MHP/TS/MH

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EUROPEAN SEARCH REPORT

Application number EP 81 20 1092

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
X	FR - A - 2 114 465 (THE GOODYEAR TIRE & RUBBER) * Claims 1-4; page 8, line 18 - page 10,line 31 * & US - A - 3 822 119 & DE - A - 2 150 362 & NL - A - 71 15922	1-12
	US - A - 4 154 580 (P.S. LANDIS) * Claims 1-4,6-11; column 7, line 29 - columns 9,10; examples 11-61 *	1-7,9
X	US - A - 4 093 029 (P.B. WEISZ) * Claim 1; column 1, lines 12-14 *	13
AD	US - A - 4 002 435 (E.C. WENZEL) * Claims 1-6 *	1,10, 11,12
AD	EP - A - 0 012 345 (BAYER) * Claim 1; page 7, lines 11-28 * & DE - A - 2 854 540 & US - A - 4 297 107	1-10, 12

CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)

C 10 L 1/32
1/02
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TECHNICAL FIELDS SEARCHED (Int.Cl. ³)

C 10 L 1/10
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CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same category
A: technological background
O: non-written disclosure
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T: theory or principle underlying the invention
E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	07-01-1982	ROTSAERT