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(72) Inventor: **Marelli, Ernesto**
23887 Olgiate Molgora (Lecco) (IT)

(74) Representative: **Modiano, Guido et al**
Modiano & Associati,
Via Meravigli, 16
20123 Milano (IT)

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(71) Applicant: **Marelli, Ernesto**
23887 Olgiate Molgora (Lecco) (IT)

(54) **Fuel for diesel engines in microemulsion form and method for preparing the same**

(57) A fuel in microemulsion form, particularly for Diesel engines, comprising a primary fuel constituted by mineral oils and/or vegetable oils, water, a lipophilic emulsifying agent (W/O) and a hydrophilic emulsifying/

detergent agent (O/W), wherein the hydrophilic emulsifying/detergent agent (O/W) is a mixture of two or more polyol esters having different molecular weights.

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Description

[0001] The present invention relates to a fuel in microemulsion form, particularly for Diesel engines, and to a method for preparing said fuel.

[0002] Emulsions and microemulsions of petroleum products and water, in which particular surfactants or mixtures of surfactants are used, are known in the art.

[0003] Generally, the use of surfactants or other additives in emulsions or microemulsions of petroleum products and water can entail problems, such as corrosion of the systems with which they make contact and generation of toxic byproducts during composition.

[0004] Moreover, emulsions and microemulsions of liquid fuels and water prepared according to known methods by adding suitable surfactants may have stability problems even in optimum storage conditions, with consequent partial separation of the phases after a certain storage period. This phase separation leads during the combustion process to many drawbacks caused by lack of homogeneity of the fuel.

[0005] A stabilized emulsion of a fuel, particularly a fuel for Diesel engines and water with the addition of a product acting as a lubricant and antifreeze, for example sorbitol monooleate, is disclosed in EP 372 353 by the same Applicant. The emulsions described therein are stabilized emulsions of fuel prepared with the use of a turbotransducer such as the one disclosed in EP 124 061 by the same Applicant.

[0006] Applicant has noticed that in some cases the preparation of fuels as described in the above cited patents entails a relatively high energy expenditure and a reduction in the productivity of the system when high productivity and emulsion stability are to be achieved.

[0007] The aim of the present invention is to provide a fuel, particularly for Diesel engines, in the form of a stable microemulsion, which leads to a reduction, in exhaust gases, of 97% in smokiness, of over 50% in carbon monoxide content, of more than 1% in carbon dioxide, and of more than 35-40% in nitrogen oxides with respect to the conventional basic fuel.

[0008] An object of the present invention is to provide a fuel in the form of a microemulsion that is simple to prepare for example also by mixing the components with a minimum agitation time and without requiring a preferential order in the addition of the components.

[0009] Another object of the present invention is to provide a fuel in microemulsion form that causes no problems for engine management and can be kept in storage tanks in the same conditions as Diesel fuel.

[0010] Another object of the present invention is to provide a fuel for use in the supply of Diesel engines such as large marine engines, engines for medium-heavy road vehicle propulsion, engines for heavy road vehicle propulsion, electric power generators and turbines, and can also be used in civil heating applied to gas oil burners.

[0011] This aim and these and other objects that will become better apparent from the following description are achieved by a fuel, particularly for Diesel engines, in microemulsion form, comprising a primary fuel constituted by mineral oils and/or vegetable oils, water, a lipophilic emulsifying agent (W/O), and a hydrophilic emulsifying/detergent agent (O/W).

[0012] Preferably, the lipophilic emulsifying agent (W/O) has a HLB value between 4 and 6 and the hydrophilic emulsifying/detergent agent (O/W) has a HLB value higher than 12.

[0013] The fuel according to the present invention is in the form of a microemulsion with microcells having a diameter of less than 0.15 μm .

[0014] The water used is preferably demineralized water, but it is also possible to use mains water, preferably filtered and at a maximum temperature, acquired during the microemulsion generation process, of 40-45 °C. The amount of water can be 10 to 15 parts by weight, for reasons of applicability to Diesel engines, without introducing modifications.

[0015] Preferably, 100 parts by weight of fuel containing primary fuel, constituted by mineral oils and/or vegetable oils, comprise 2 to 5 parts by weight of activator, understood as the total content of lipophilic emulsifying agent and hydrophilic emulsifying/detergent agent; in particular, the lipophilic emulsifying agent constitutes 50 to 95 parts by weight and the hydrophilic emulsifying/detergent agent constitutes 50 to 5 parts by weight of the total activator, in addition to 10-15 parts by weight of water. The remainder to 100 parts by weight is the primary fuel.

[0016] The lipophilic emulsifying agent (W/O) used in the present invention is preferably a fatty ester of sorbitol, the fatty fraction of which must be pure, even if derived from mixed seeds.

[0017] Examples, provided by way of illustration, of lipophilic emulsifying agents (W/O) to be used in the combustible microemulsion according to the present invention are sorbitan monooleate and other compounds that belong to the same chemical class, for example sorbitan monooleate ethoxylate (20), sorbitan dioleate, sorbitan trioleate, sorbitan hexaoleate, sorbitan monolaurate, sorbitan monolaurate ethoxylate (20), sorbitan monopalmitate, sorbitan monostearate, sorbitan monostearate ethoxylate (20), sorbitan monostearate-palmitate and sorbitan tristearate. In all these cases, the choice of the "fatty" part is the one that provides an individual suitable imprint, i.e., particular characteristics that have proved decisive for forming the stable microemulsion.

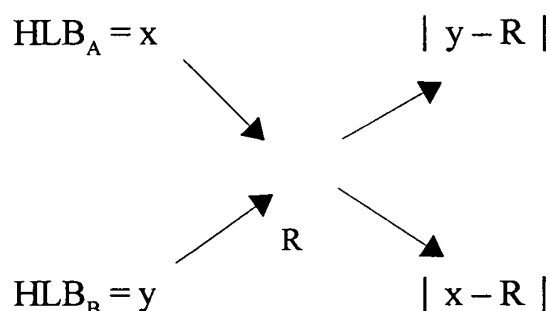
[0018] The hydrophilic emulsifying/detergent agent (O/W) used in the present invention is a mixture of two or more

esters that belong to other combined chemical groups, so long as the "mixing rules" are observed, such as for example complex esters, compound esters, glycerin esters, monoalcohol esters, sorbitol esters, polyalcohol esters, glycol esters, trimethylpropane esters, and more specifically monococoates, cocoates, monooleates, monolaurates, stearates and distearates with various polyethyleneglycols PEGs and/or polyol esters POEs, including mixtures of non-ionic emulsifiers, but with specific combinations and ratios having different molecular weights, preferably one having a low molecular weight and one having a high molecular weight.

[0019] The molecular weight of the supplied product is preferably comprised between 600 and 1000, more preferably between 840 and 880.

[0020] Inclusion in combined chemical groups is considered in order to obtain the sought final HLB, as indeed the "mixing rule" proposes, as exemplified hereafter in theoretical terms.

[0021] Considering, for example, a PEG 200 (200 is the molecular weight and is "low") and a PEG 6000 (6000 is the molecular weight and is "high") and using the expression "component A" to reference the PEG 200, the expression "component B" to reference the PEG 6000, and "R" to reference the sought final HLB value, one can write:



[0022] From which:

$$K = |y - R| + |x - R|$$

$$|y - R| / K \times 100 = \text{percentage parts of component A}$$

$$|x - R| / K \times 100 = \text{percentage parts of component B}$$

[0023] The inventor of the present invention has found that such a hydrophilic emulsifying/detergent agent gives greater, and therefore better, stability to the resulting final microemulsion.

[0024] A preferred emulsifying/detergent agent comprises glycol esters.

[0025] Among these, particular preference is given to: diethylene glycol monococoate, PEG 200 cocoate, PEG 400 cocoate, diethylene glycol monooleate, PEG 200 monooleate, PEG 300 monooleate, PEG 400 monooleate, PEG 600 monooleate, PEG 1000 monooleate, PEG 40000 monooleate, PEG 6000 monooleate, PEG 400 oleate, dipropylene glycol monooleate, PEG dioleate, PEG 400 dioleate, PEG 600 dioleate, diethylene glycol monolaurate, PEG 300 monolaurate, PEG 400 monolaurate, PEG 400 dilaurate, diethylene glycol monostearate, PEG 200 monostearate, PEG 300 monostearate, PEG 400 monostearate, PEG 15000 monostearate, PEG 40000 monostearate, PEG POE 40 stearate, PEG 400 distearate, PEG 600 distearate, PEG 2000 distearate, and PEG 6000 distearate.

[0026] In all these cases, the imprint that leads to improvement of the characteristics of the final combustible microemulsion related to the stability and preservation of the fuel is defined by the choice, combination and ratio of the components that constitute the hydrophilic emulsifying/detergent agent as expressed with the example cited earlier.

[0027] The hydrophilic emulsifying/detergent agent can also comprise, in addition to the mixture of polyethylene glycol esters, one or more fatty acid esters.

[0028] The fuel in microemulsion form according to the present invention can be prepared by using a known emulsification method, for example also by mixing the components with a minimum agitation time.

[0029] The two emulsifying agents, i.e., the lipophilic emulsifying agent (W/O) and the hydrophilic emulsifying/deter-

gent agent (O/W), can be introduced in an emulsifier that contains the primary fuel either separately or premixed as a single premixed emulsifying agent (activator).

[0030] The resulting microemulsion, moreover, has intrinsic antifreeze and antiseptic properties. A series of tests conducted in very low temperature conditions, even below -30 °C for at least three months, on emulsions constituted by means of various combinations of emulsifying agents according to the present invention and compared with emulsions containing activators constituted by emulsifying agents as such, have yielded positive results, while the latter underwent phase separation even after just 24 hours, so much as to block operation of the Diesel engine and also stop or block starting of the burner.

[0031] The same results have also been obtained with microemulsions subjected to ultrasound treatment, which is considered one of the most energetic physical methods for emulsion degradation, at a frequency comprised between 28 and 34 kHz and with a specific power (watt/liter) of even more than 80 for periods of even more than 20 minutes and a temperature comprised between +30 °C and +40 °C. The most evident manifestation that a "destroyed" microemulsion exhibits is the distinct separation (stratification) of the phases it contains and the "demixing" of the water, in addition to immediate degradability if subjected to centrifugation (as required for example by the CUNA NC 637-01 (2001) and UNICHIM 1547 and 1548 (2001) standards).

[0032] The microemulsion obtained according to the present invention has proved to be stable even after centrifugation at no less than 5750 rpm for at least 15 minutes.

[0033] Positive results have also been achieved following microbiological attack tests: the microemulsion according to the present invention has demonstrated good protection against bacteria, fungi and molds (-10^2 CFU/ml).

[0034] The composition according to the present invention, while having inherent antifermentation properties, can also contain biocidal substances, mostly as an additional assurance of stability against external bacterial contaminations in particularly hot environmental conditions and due to the natural bacterial presence in Diesel fuel containment tanks that is generated especially in a warm climate, particularly above 27 °C and in compliance with a future standard that will regulate labeling of certain substances that regrettably are still currently in use despite having a proven toxicity.

[0035] In particular, these are biocidal substances such as paraoxybenzoates, isothiazoles and derivatives thereof, idantoin, parabens and the like, which are not subjected to restrictive labeling and are in any case free from teratogenic and/or carcinogenic risks, as can instead occur for agents used in traditional compositions such as nonylphenol, nonylphenol ethoxylate, formaldehyde and derivatives thereof, or even alkyl nitrates.

[0036] Moreover, the composition according to the present invention (despite not containing products based on alkyl nitrates, as tested for example by the "Stazione Sperimentale per i Combustibili" [Fuel Experimental Station] in Milan Italy, as regards the ignition quality index (cetane number), despite being a microemulsion and not whole Diesel fuel, has the same characteristics as a whole Diesel fuel (which usually has a cetane number of 50 to 52), can contain (in response to any need to improve the cetane number) products based on polyisobutylene succinic anhydride, preferably 400 to 800 ppm.

[0037] Moreover, the composition according to the present invention does not contain nonylphenol, nonylphenol ethoxylate, formaldehyde and derivatives thereof, alkyl nitrates or ammonium nitrates, and therefore is neither carcinogenic nor teratogenic.

[0038] The composition according to the present invention can be obtained with increased efficiency by using a method for forming the fuel microemulsion disclosed in US patent no. 6,538,041 B1 by the same Applicant, herein enclosed by reference. This method requires the use of an apparatus that has a particular geometry, which forms the microemulsion practically instantaneously, as shown by an instantaneous change of color of the mixture of components, which becomes bright white. The instantaneous occurrence of the bright white color is also a visual parameter that is essential for ascertaining the perfect result.

[0039] Emulsions and/or microemulsions not formed with homogeneity and stability characteristics retain a scarcely milky coloring (milk-and-coffee color), with a substantially immediate tendency toward component stratification.

[0040] The disclosures in Italian Patent Application no. MI2004A000296, from which this application claims priority, are incorporated herein by reference.

Claims

1. A fuel in microemulsion form, particularly for Diesel engines, comprising a primary fuel constituted by mineral oils and/or vegetable oils, water, a lipophilic emulsifying agent (W/O) and a hydrophilic emulsifying/detergent agent (O/W), wherein the hydrophilic emulsifying/detergent agent (O/W) is a mixture of two or more polyol esters having different molecular weights.
2. The fuel according to claim 1, **characterized in that** said lipophilic emulsifying agent (W/O) has a HLB value between 4 and 6.

3. The fuel according to claim 1 or 2, **characterized in that** said hydrophilic emulsifying/detergent agent (O/W) has a HLB value higher than 12.
- 5 4. The fuel according to any one of the preceding claims, **characterized in that** it has an average microcell diameter of less than 0.15 μm .
5. The fuel according to any one of the preceding claims, **characterized in that** it comprises 10 to 15% by weight of water relative to said primary fuel.
- 10 6. The fuel according to any one of the preceding claims, **characterized in that** it comprises 50 to 95, preferably 55 to 75, parts by weight of lipophilic emulsifying agent relative to the total weight of the hydrophilic emulsifying/detergent agent and of the lipophilic emulsifying agent.
- 15 7. The fuel according to any one of the preceding claims, **characterized in that** it comprises 50 to 5, preferably 45 to 25, parts by weight of hydrophilic emulsifying/detergent agent relative to the total weight of the hydrophilic emulsifying/detergent agent and of the lipophilic emulsifying agent.
- 20 8. The fuel according to any one of the preceding claims, **characterized in that** said lipophilic emulsifying agent is a fatty ester of sorbitol.
- 25 9. The fuel according to claim 8, **characterized in that** said lipophilic emulsifying agent is selected from the group consisting of sorbitan monooleate ethoxylate (20), sorbitan dioleate, sorbitan trioleate, sorbitan hexaoleate, sorbitan monolaurate, sorbitan monolaurate ethoxylate (20), sorbitan monopalmitate, sorbitan monostearate, sorbitan monostearate ethoxylate (20), sorbitan monostearate-palmitate and sorbitan tristearate.
- 30 10. The fuel according to any one of the preceding claims, **characterized in that** said hydrophilic emulsifying/detergent agent (O/W) is a mixture of glycol esters, particularly a mixture of glycol esters containing polyglycol oleate.
- 35 11. The fuel according to any one of the preceding claims, **characterized in that** said hydrophilic emulsifying/detergent agent (O/W) is a mixture of esters selected from the group consisting of PEG esters other than polyglycol oleate, such as for example complex esters and compound esters, glycerin esters, glycol esters, monoalcohol esters, sorbitol POE esters, polyalcohol esters, and trimethylpropane esters.
- 40 12. The fuel according to claim 11, **characterized in that** said hydrophilic emulsifying/detergent agent (O/W) is a mixture of esters selected from the group consisting of diethylene glycol monococoate, PEG 200 cocoate, PEG 400 cocoate, diethylene glycol monooleate, PEG 200 monooleate, PEG 300 monooleate, PEG 400 monooleate, PEG 600 monooleate, PEG 1000 monooleate, PEG 40000 monooleate, PEG 6000 monooleate, PEG 400 oleate, dipropylene glycol monooleate, PEG dioleate, PEG 400 dioleate, PEG 600 dioleate, diethylene glycol monolaurate, PEG 300 monolaurate, PEG 400 monolaurate, PEG 400 dilaurate, diethylene glycol monostearate, PEG 200 monostearate, PEG 300 monostearate, PEG 400 monostearate, PEG 15000 monostearate, PEG 40000 monostearate, PEG POE 40 stearate, PEG 400 distearate, PEG 600 distearate, PEG 2000 distearate, and PEG 6000 distearate.
- 45 13. The fuel according to one of the preceding claims, **characterized in that** said hydrophilic emulsifying/detergent agent is a mixture of esters of PEG 200 and PEG 6000.
- 50 14. A method for preparing a fuel according to any one of claims 1 to 12, comprising the steps of preparing a hydrophilic emulsifying/detergent agent (O/W) by mixing two or more esters of polyols, providing a lipophilic emulsifying agent (W/O), and introducing said hydrophilic emulsifying/detergent agent (O/W) and said lipophilic emulsifying agent (W/O) separately or premixed into a primary fuel constituted by mineral oils and/or vegetable oils and/or mixtures thereof.



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EUROPEAN SEARCH REPORT

Application Number
EP 05 00 3206

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X	US 6 068 670 A (HAUPAIS ET AL) 30 May 2000 (2000-05-30) * column 3, lines 25-56 * * example F; tables 2,3 * * column 3, line 66 - column 5, line 7 * * column 6, lines 18-32 * * column 6, line 39 - column 7, line 9 * * column 8, lines 47-52 * -----	1-12,14	C10L1/32
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A	US 2004/020105 A1 (BURREINGTON JAMES D ET AL) 5 February 2004 (2004-02-05) * paragraphs [0006], [0020], [0054] * -----	4	
A	US 3 876 391 A (MCCOY ET AL) 8 April 1975 (1975-04-08) * column 6, lines 26-58 * -----	1-14	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C10L
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 9 June 2005	Examiner Bertin-van Bommel, S
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 P : intermediate document 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			

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EPO FORM 1503 03/82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 05 00 3206

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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09-06-2005

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