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(11) Publication number:

**0 475 620 B1**

(12)

## EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: **08.11.95** (51) Int. Cl.<sup>6</sup>: **C10L 1/32**

(21) Application number: **91307780.6**

(22) Date of filing: **23.08.91**

(54) **Microemulsion diesel fuel compositions and method of use.**

(30) Priority: **07.09.90 US 578482**  
**07.09.90 US 578483**

(43) Date of publication of application:  
**18.03.92 Bulletin 92/12**

(45) Publication of the grant of the patent:  
**08.11.95 Bulletin 95/45**

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

(56) References cited:  
**EP-A- 0 022 110**  
**EP-A- 0 209 758**  
**DE-B- 1 088 759**  
**US-A- 4 477 258**

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**EP 0 475 620 B1**

## Description

There is a wide variety of microemulsion fuel compositions known in the art. A disadvantage of these has been a lack of stability under conditions to which the fuels have been exposed. Prior compositions, for example, have been unstable and have tended to de-emulsify at high and at low temperatures; high temperature de-emulsification has been a special problem. Further, the addition of even very small amounts of salt as by exposure to salt-containing air or water has caused severe de-emulsification problems in prior formulations that did not contain alcohols. Another disadvantage of prior microemulsion fuel compositions has been the high concentrations of surfactants required to form the microemulsions. Prior inventions, generally, employed one or more parts of surfactant per part of solubilized water.

In EP-A-22110 there is disclosed an emulsifier system comprising (i) an alkylphenol ethylene oxide adduct nonionic surface active agent and (ii) a calcium dodecylbenzene sulphonate anionic surface active agent in a specified range of proportions. The system may be employed to manufacture aqueous emulsions of diesel oil. From 1 to 10 wt.% of water and 0.5 to 5 grams per litre of the emulsifier system may be employed.

It is well-known in the art that dispersions of water and/or one or two carbon alkanols in diesel fuel reduce harmful diesel emissions such as smoke, soot, particulates, and  $\text{NO}_x$ . It is also well-known that debits associated with water and alkanols in diesel fuels entail a severe reduction in cetane number and a marked ignition delay often requiring engine and/or operating parameter modification such as advanced ignition timing or the installation of glow plugs.

It is an object of the present invention to provide a diesel fuel microemulsion (a) in which these debits are diminished or eliminated, (b) which still retains the advantage of emissions reduction and (c) which still has good stability.

According to the present invention there is provided a diesel fuel composition which comprises:

- (a) a diesel fuel;
- (b) 1.0 to 30.0 weight percent of water based upon said diesel fuel;
- (c) a cetane number improver additive, present in an amount up to, but less than, 20.0 weight percent based upon said water, said additive being selected from an inorganic oxidizer, a polar organic oxidizer and a nitrogen oxide-containing compound; and
- (d) 0.5 to 15.0 wt.% based on the diesel fuel, of a surfactant system comprising
  - (i) one or more first surfactants selected from surfactants capable of forming a lower phase microemulsion at 20 °C when combined with equal volumes of the fuel and water at a concentration of 2 grams of surfactant per deciliter of fuel plus water, which microemulsion phase has a volume ratio of water to surfactant of at least 2; at least one said first surfactant being an ethoxylated  $\text{C}_{12}$ - $\text{C}_{18}$  alkyl ammonium salt of a  $\text{C}_9$ - $\text{C}_{24}$  alkyl carboxylic or alkylaryl sulfonic acid containing 6 or more ethylene oxide groups; and
  - (ii) one or more second surfactants selected from surfactants capable of forming an upper phase microemulsion at 20 °C when combined with equal volumes of the fuel and water at a concentration of 2 grams of surfactant per deciliter of fuel plus water, which microemulsion phase has a volume ratio of water to surfactant of at least 2; at least one said surfactant being an ethoxylated  $\text{C}_{12}$ - $\text{C}_{18}$  alkyl ammonium salt of a  $\text{C}_9$ - $\text{C}_{24}$  alkyl carboxylic or alkylaryl sulfonic acid containing less than 6 ethylene oxide groups;

the said first and second surfactants being present in a weight ratio which forms with components (a), (b) and (c) a single phase translucent microemulsion.

Preferably the said first and second surfactants are each selected only from said ethoxylated compounds

Preferably the said amount of water present is from 2 to 20 wt.%, more especially from 2 to 15 wt.%

The composition may also contain up to 30 wt.%, based on the weight of water present, of a  $\text{C}_1$  to  $\text{C}_3$  alkanol.

The cetane improver additive is preferably selected from ammonium nitrate, ammonium nitrite, hydrogen peroxide, ammonium hypochlorite, ammonium chlorite, ammonium perchlorate, ammonium chlorate, perchloric acid, chlorous acid, hypochlorous acid, ammonium hypobromite, ammonium bromate, hypobromous acid, bromic acid, ammonium hypoiodite, ammonium periodate, hypoiodous acid, iodic acid, periodic acid, 2,4 dinitrophenyl hydrazine, 2,5 dinitrophenol, 2,6 dinitrophenol, 2,4 dinitroresorcinol, nitroguanidine, 3 nitro-1,2,4-triazole, 2 nitro imidazole, 4 nitro imidazole, picric acid, cumene hydroperoxide, cyanuric acid, nitroglycerin, nitrobenzene, trinitrotoluene, and mixtures thereof.

In the practice of the present invention, at least one defined hydrophilic surfactant ((d)(i)) and at least one defined lipophilic surfactant ((d)(ii)) are selected and their ratio adjusted with respect to their combined

hydrophilic and lipophilic properties such that they form with the fuel and the aqueous composition a single phase, translucent microemulsion. The said hydrophilic surfactant(s) is defined by a set of operations wherein a blend of equal volumes of fuel and aqueous composition with 2 grams of said surfactant per deciliter of liquids forms a lower phase microemulsion at 20 °C such that the volume ratio of fuel (oil) to surfactant (Vo/Vs) in the microemulsion phase is at least 0.5, preferably greater than 1 and more preferably greater than 2. The term "lower phase" microemulsion is descriptive in context since it means that the aforementioned system consisting of the hydrophilic surfactant and equal volumes of fuel and aqueous composition separates into an aqueous lower phase containing most of the surfactant in equilibrium with an excess fuel (oil) phase which is essentially surfactant-free.

Optional hydrophilic surfactants defined by the above properties include the alkyl carboxylic and alkylaryl sulfonic acid salts wherein the alkyl group is a C<sub>9</sub> to C<sub>18</sub> linear, branched or bilinear structure, the aryl group is selected from benzene, toluene, orthoxylene, and naphthalene, and the salt is a salt of an alkali metal, ammonia, or alkanol amine. Essential in the present invention are the ethoxylated C<sub>12</sub>-C<sub>18</sub> alkyl ammonium salts of C<sub>9</sub>-C<sub>24</sub> alkyl carboxylic and alkylaryl sulfonic acids containing 6 or more ethylene oxide (hereinafter EO) groups, wherein the alkyl and aryl groups are suitably as previously defined above.

Representative examples of the optional hydrophilic alkyl carboxylic and alkylaryl sulfonic acid salts include monoethanol ammonium laurate, ammonium palmitate, diethanol ammonium stearate, monoethanol ammonium nonyl o-xylene sulfonate, sodium dodecyl benzene sulfonate, ammonium tetradecyl benzene sulfonate, diethanol ammonium hexadecyl benzene sulfonate, and sodium dodecyl naphthalene sulfonate.

Preferred hydrophilic carboxylic acid salts include monoethanol ammonium oleate, penta-, deca-, and hexadeca-ethoxy octadecyl ammonium oleate. Preferred hydrophilic sulfonic acid salts include penta- and deca-ethoxy octadecyl ammonium benzene sulfonate (designated C<sub>12</sub>BS-E18-5 and C<sub>12</sub>BS-E18-10, respectively), heptaethoxy octadecyl ammonium dodecyl o-xylene sulfonate (designated C<sub>12</sub>XS-E18-7) and decaethoxy octadecyl ammonium dodecyl ortho xylene sulfonate (designated C<sub>12</sub>XS-E18-10). The ethoxylated alkyl amines used in preparing the ethoxylated alkyl ammonium salts of alkyl aryl sulfonic acids can be obtained from Exxon Chemical, Performance Products, Tomah Products.

Representative hydrophilic ethoxylated alkyl phenols include Igepal® DM 710, Igepal® DM 730, and Igepal® DM 880 available from GAF which are chemically dinonyl phenols ethoxylated with 15, 24, and 49 moles of EO, respectively. Preferred is Igepal® DM 530 which is dinonyl phenol ethoxylated with 9 moles of ethylene oxide. Other suitable ethoxylated alkyl phenols include Tritons® X100, X102, and X114 available from Rohm and Haas of Philadelphia, Pa., and Igepals® CO 610, 630, 660, 710, 720, 730, 850, and 880 which are chemically mono-octyl or nonyl phenols ethoxylated with from 8 to 30 EO.

The said lipophilic surfactant for purposes of this invention is a surfactant having the properties of providing at 2 g/dl concentration in equal volumes of fuel and aqueous composition an upper phase microemulsion at 20 °C such that the volume ratio of water to surfactant (Vw/Vs) in the microemulsion phase is at least 0.5, preferably greater than 1 and most preferably greater than 2. The term "upper phase" microemulsion as used in defining the lipophilic surfactant ingredient means that the system consisting of the surfactant in equal volumes of fuel and aqueous composition separates into a surfactant containing oil upper phase in equilibrium with an excess aqueous phase which is essentially surfactant free.

The lipophile having been defined by the above properties includes ethoxylated alkyl phenols and alkyl and alkylaryl sulfonic acid salts wherein the alkyl group is a C<sub>12</sub> to C<sub>24</sub> linear, branched, or bilinear structure, the aryl group is selected from benzene, toluene, orthoxylene, and naphthalene; and the salt is a salt of an alkali metal, ammonia or alkanol amine. Essential in the present invention are the ethoxylated C<sub>12</sub>-C<sub>18</sub> alkyl ammonium salts of C<sub>9</sub>-C<sub>24</sub> alkyl carboxylic and alkylaryl sulfonic acids containing less than six EO groups, wherein the alkyl and aryl groups are suitably as previously defined above.

Representative examples of optional lipophilic alkyl aryl sulfonates include monoethanol ammonium dodecyl o-xylene sulfonate, sodium tetradecyl o-xylene sulfonate, sodium hexadecyl o-xylene sulfonate, diethanol ammonium pentadecyl o-xylene sulfonate, triethanol ammonium octadecyl o-xylene sulfonate (prepared from penta and hexa propylene), sodium octapropylene benzene sulfonate, sodium tetracosyl toluene sulfonate, and various high molecular weight petroleum sulfonates. Preferred are the sodium and monoethanol ammonium salts of dodecyl o-xylene sulfonic acid. Representative of essential lipophilic surfactants are di-ethoxy octadecyl ammonium oleate, di- and penta-ethoxy octadecyl ammonium dodecyl o-xylene sulfonate (designated E18-2 oleate, C<sub>12</sub>XS-E18-2 and C<sub>12</sub>XS-E18-5, respectively).

Representative optional lipophilic ethoxylated alkyl phenols include Igepals CO 210 and CO 430 which are nonyl phenols containing 1.5 and 4 moles of EO, respectively, and Tritons X15 and X35 which are octyl phenols containing 1 and 3 moles of EO, respectively.

Preferred lipophilic/hydrophilic blends of ethoxylated alkyl ammonium salts of alkylaryl sulfonic acids include penta-ethoxy octadecyl ammonium dodecyl benzene sulfonate combined with hepta-ethoxy oc-

tadecyl ammonium dodecyl benzene sulfonate and di-ethoxy cocoa ammonium dodecyl o-xylene sulfonate with deca-ethoxy octadecyl ammonium dodecyl oxylen sulfonate. Most preferred is the blend of penta-ethoxy octadecyl ammonium dodecyl o-xylene sulfonate with hepta or deca-ethoxy octadecyl ammonium dodecyl o-xylene sulfonate, i.e., a blend of C<sub>12</sub>XS-E18-5 with C<sub>12</sub>XS-E18-10.

Under certain circumstances, up to 20, generally 2 to 10, weight percent of a cosurfactant is included in the surfactant blend to improve the solubility of the surfactant in the fuel and reduce the viscosity of the microemulsion diesel fuel composition. The cosurfactants are of the class of alkylene glycol monoalkyl ethers, C<sub>4</sub> to C<sub>6</sub> alkanols and mixtures thereof. Representative cosurfactants include ethers such as ethylene glycol monopropyl ether, methylene glycol monoethyl ether, ethylene glycol monomethyl ether, ethylene glycol monobutyl ether, diethyl glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol n-butyl ether, propylene glycol monomethyl ether, dipropylene glycol monomethyl ether and tripropylene glycol monomethyl ether, and alkanols which include straight and branched chain members such as butanol and pentanol. Of the alkanols, tertiary amyl alcohol (TAA) is preferred. Of the ethers, ethylene glycol monobutyl ether is preferred.

It is understood that when using a cosurfactant, the ratio of the surfactants may have to be readjusted for changes in phase behavior brought about by the addition of cosurfactant. It is also understood that the weight ratio of hydrophilic to lipophilic surfactants may have to be readjusted for changes in phase behavior brought about by different aqueous reagents and variations in their concentration. For example, an increase in the concentration of the aqueous reagent ammonium nitrate, requires an increase in the ratio of hydrophilic to lipophilic surfactants. Likewise changes in the composition of the fuel necessitate readjustment of the surfactant ratio. For example, a higher concentration of aromatics in the fuel requires an increase in the ratio of hydrophilic to lipophilic surfactants. It is also understood that when a change in surfactant ratio is inadequate to compensate for a given change in the fuel or aqueous composition, choice of a more (or less) hydrophilic surfactant pair. These points will become clear from the following Examples.

In the following Examples, Nos. I to IV are not examples of the invention, but are included as background material.

#### Example I

#### Preparation of Anionic-Ethoxy Cationic Complexes

One hundred grams of the alkyl carboxylic or alkyl aryl sulfonic acid is weighed into a wide mouth jar. An appropriate weight of the ethoxylated alkyl amine, as listed in Table I, is added and stirred vigorously while warm from the heat of neutralization. Properties, neutralization weights, and chemical suppliers are listed in Table I.

TABLE I  
Preparation of Anionic-Ethoxy Cationic Complexes

|    | <u>Component</u>                                                | Average         | wt. %          |                    |
|----|-----------------------------------------------------------------|-----------------|----------------|--------------------|
|    |                                                                 | <u>Mol. wt.</u> | <u>Actives</u> | <u>Equ/100g</u>    |
|    | Oleic acid                                                      | 282             | 100            | 0.354              |
| 10 | C <sub>12</sub> BSH (Vista SA 597)                              | 326             | -98            | 0.336 <sup>1</sup> |
|    | C <sub>12</sub> XSH (ESSAF SA 149)                              | 354             | -81            | 0.226 <sup>1</sup> |
|    | C <sub>18</sub> N(EO) <sub>2</sub> (Tomah E18-2) <sup>a</sup>   | 357             | -98            | 0.275              |
| 15 | C <sub>18</sub> N(EO) <sub>5</sub> (Tomah E18-5) <sup>b</sup>   | 489             | -98            | 0.200              |
|    | C <sub>18</sub> N(EO) <sub>10</sub> (Tomah E18-10) <sup>c</sup> | 709             | -98            | 0.138              |
|    | C <sub>18</sub> N(EO) <sub>15</sub> (Tomah E18-15) <sup>d</sup> | 929             | -98            | 0.105              |
| 20 | MEA (mono ethanol amine)                                        | 61              | 100            | 1.639              |

| <u>Weight(g) of Amine/100 g Acid</u> |              |                          |                          |                   |
|--------------------------------------|--------------|--------------------------|--------------------------|-------------------|
|                                      | <u>Amine</u> |                          |                          |                   |
|                                      |              | <u>C<sub>12</sub>XSH</u> | <u>C<sub>12</sub>BSH</u> | <u>Oleic Acid</u> |
| 25                                   | MEA          | 13.8                     | 20.5                     | 21.6              |
|                                      | E18-2        | 82.3                     | 122.4                    | 128.0             |
| 30                                   | E18-5        | 112.8                    | 167.7                    | 176.6             |
|                                      | E18-10       | 163.5                    | 243.1                    | 256.1             |
|                                      | E18-15       | 214.2                    | 318.5                    | 335.6             |

<sup>1</sup> By titration

<sup>2</sup> Direct replacements: a) Akzo Ethomeen 18/12

40 b) Ethomeen 18/15

c) Ethomeen 18/20

d) Ethomeen 18/25

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## Example II

### Microemulsion Preparation

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Microemulsions were prepared as follows. The surfactants were weighed into a 16 x 125 mm flat bottom tube fitted with a teflon-lined cap. A total of 15 ml of diesel fuel and water were added. The tubes were shaken and heated -30 minutes to 1 hour at 60-70 °C. They were then tumbled overnight to 2 days on an automated tumbler. Most systems, particularly those made with the alkyl benzene sulfonates, did not clear at room temperature after 2 days of tumbling. They could be made to clear in most cases by temperature cycling 2 or 3 times from 70 °C to 0 °C. On storage at room temperature, clarity improved with age for the systems containing the MEA soaps. Systems based solely on the C<sub>12</sub>XS E18-n surfactants were found to be extremely temperature sensitive and to deteriorate with age. Often systems which were initially

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single phase and clear, phase separated on storage at room temperature. The assumed cause was laboratory temperature fluctuations coupled with the extreme temperature sensitivity of these systems. Because of poor storage stability, blends of only C<sub>12</sub>XS E18-n surfactants were eliminated early on from further study. However, work with these surfactants did demonstrate that clear microemulsions could be prepared with 3 vol.% water and as little as 1 g/dl (~1%) surfactant. Clear single phase systems containing 5% water stabilized by 2 g/dl of the C<sub>12</sub>XS E18-n surfactants were also prepared. Blends of these C<sub>12</sub>XS E18-n surfactants with surfactants based on MEA (e.g. C<sub>12</sub>BS-MEA or C<sub>12</sub>XS-MEA) gave good stability and are described below.

### 10 Example III

#### Selecting and Balancing the Hydrophilic and Lipophilic Surfactant Blend

A 2 gm/dl mixture of monoethanol ammonium dodecyl benzene sulfonate (hereafter C<sub>12</sub>BS-MEA) with equal volumes of Maraven diesel fuel (oil) and water forms a lower phase microemulsion at 20 °C. The volume of oil solubilized per gm of surfactant (oil uptake) is greater than the most preferred design criterion for a hydrophilic surfactant of 2 ml oil/gm surfactant. A 2 gm/dl mixture of di-ethoxy octadecyl ammonium dodecyl benzene sulfonate (hereafter C<sub>12</sub>BS E18-2) with equal volumes of Maraven diesel fuel and water forms an upper phase microemulsion at 20 °C. The volume of water solubilized per gm of surfactant (water uptake) is greater than the most preferred design criterion for a lipophilic surfactant of 2 ml water/gm surfactant.

The combination C<sub>12</sub>BS-MEA/C<sub>12</sub>BS E18-2 represents a hydrophile-lipophile surfactant couple and their combined hydrophilic and lipophilic properties are varied by adjusting the weight ratio of C<sub>12</sub>BS-MEA/C<sub>12</sub>BS E18-2. Table II presents phase data for the C<sub>12</sub>BS-MEA/C<sub>12</sub>BS E18-2 surfactant couple at various water to Maraven oil ratios and total surfactant concentrations. The data were generated as follows. The surfactant concentration was fixed at, for example, 2 g per deciliter of oil and water at a water/oil ratio of 5/95. The weight fraction of C<sub>12</sub>BS-MEA, the hydrophile in the surfactant couple was then varied in the range between 0.45 and 0.60. The type of microemulsion at each weight fraction of C<sub>12</sub>BS-MEA was noted after equilibrium was reached. A change in microemulsion type indicated the approximate phase transition boundary between upper and single or single and lower phase microemulsions. These transition boundaries are noted in Table II. The procedure was repeated at 1.5 and 1.0 g/dl surfactant concentration and the approximate transition boundaries determined. Note that the data was developed on a series of individual equilibrated tubes, each containing the specific ratio of surfactants at the listed total surfactant concentration in water and oil at a 5/95 volume ratio. The single phase region lies between the upper and lower phase transition boundaries. The point where these phase boundaries coincide indicates the minimum surfactant concentration which will solubilize 5% water in Maraven diesel fuel; in this case, it takes somewhat more than 1 g/dl of surfactant to form a stable microemulsion. However, the proximity to the phase transition boundaries indicates that this will not be a clear system. In general, the clearest systems are found farthest from the transition boundaries, that is, in the center of the single phase region. The closer the transition boundaries, the hazier the systems located between them. Thus, maximum clarity at a given water concentration is attained at higher surfactant concentrations.

Table II presents similar phase data for the C<sub>12</sub>BS-MEA/C<sub>12</sub>BS E18-2 surfactants holding the water/oil volume ratio fixed at 4/96. The single phase region has broadened and at 2 g/dl surfactant extends between 0.47 and 0.59 wt. fraction of C<sub>12</sub>BS-MEA compared with a range of 0.48 to 0.56 for the 5/95 water/oil system. Again the clearest systems are found in the center of the single phase region and since the 4/96 systems are farther from the phase transition boundaries than are the 5/95 systems, they are also clearer in comparison. The 4/96 water/oil systems form single phase microemulsions at surfactant concentrations somewhat below 1 g/dl. Again, these microemulsions are turbid because of their proximity to the phase transition boundaries.

The data in Table II reinforce the conclusion that higher surfactant/water ratios provide clearer microemulsions. The single phase region at a surfactant concentration of 2 g/dl for the 3/97 water/oil system extends between 0.46 and 0.60 wt. fraction C<sub>12</sub>BS-MEA. Thus microemulsions in the center of this range are even farther from the transition boundaries and, therefore, clearer than those found with 5/95 or 4/96 water/oil systems. The 3/97 system forms single phase microemulsions at surfactant concentrations above 0.75 g/dl. Comparison with the 5/95 and 4/96 water/oil systems shows that for all these water/oil ratios, the minimum surfactant concentration for single phase microemulsions corresponds to a water/surfactant ratio of -4/1.

The data in Table II illustrate the critical nature of selecting and balancing the hydrophile/lipophile surfactant blend for a given amount of water and surfactant. The data indicate that stable microemulsions can be prepared with up to 5% water with less than 1.5% surfactant. An increase in surfactant concentration permits a proportionate increase in the amount of water solubilized. These surfactants are more efficient than those found in the previous art.

TABLE II  
C<sub>12</sub>BS-MEA/C<sub>12</sub>BS E18-2 Compositions for Single Phase

| W/O Vol.<br>Ratio | Surfactant<br>Concn g/dl | <u>Wt Fraction C<sub>12</sub>BS-MEA<sup>1</sup> at the</u><br><u>Upper Phase TB<sup>2</sup> Lower Phase TB<sup>3</sup></u> |      |
|-------------------|--------------------------|----------------------------------------------------------------------------------------------------------------------------|------|
| 5/95              | 1.0                      | 0.52                                                                                                                       | 0.52 |
|                   | 1.5                      | 0.50                                                                                                                       | 0.54 |
|                   | 2.0                      | 0.48                                                                                                                       | 0.56 |
| 4/96              | 1.0                      | 0.53                                                                                                                       | 0.53 |
|                   | 1.5                      | 0.50                                                                                                                       | 0.56 |
|                   | 2.0                      | 0.47                                                                                                                       | 0.59 |
| 3/97              | 0.75                     | 0.52                                                                                                                       | 0.52 |
|                   | 1.0                      | 0.50                                                                                                                       | 0.54 |
|                   | 1.5                      | 0.48                                                                                                                       | 0.57 |
|                   | 2.0                      | 0.46                                                                                                                       | 0.60 |

1) At the indicated total surfactant concentration

2) Upper phase transition boundary U S

3) Lower phase transition boundary S L

The C<sub>12</sub>XS-MEA/C<sub>12</sub>XS E18-5 system, though not as extensively investigated as the C<sub>12</sub>BS-MEA/C<sub>12</sub>BS E18-2 system described above, provides a similar phase behavior pattern. In this case, the C<sub>12</sub>XS-MEA is the hydrophile; its increasing weight fraction leads to lower phase microemulsions. Phase data obtained for three water/oil ratios at a surfactant concentration fixed at 1.5 g/dl are given in the following table.

C<sub>12</sub>XS-MEA/C<sub>12</sub>XS E18-5 Compositions for Single Phase

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| <u>W/O Vol. Ratio</u> | <u>Wt. Fraction C<sub>12</sub>XS-MEA<sup>1</sup></u> |                        |
|-----------------------|------------------------------------------------------|------------------------|
|                       | <u>UTB<sup>2</sup></u>                               | <u>LTB<sup>3</sup></u> |
| 10 5.0/95.0           | 0.49                                                 | 0.55                   |
| 4.5/95.5              | 0.47 (estim.)                                        | 0.57                   |
| 15 4.0/96.0           | 0.44 (estim.)                                        | 0.60                   |

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1 At a total surfactant concentration of 1.5 g/dl.

2 Upper phase transition boundary: u s

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3 Lower phase transition boundary: s l

As discussed previously, the single phase region, which lies between the upper phase transition (UTB) and the lower phase transition boundary (LTB), broadens and clarity improves with decreased water/oil ratio.

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The clarity of microemulsions in the center of the single phase region is somewhat better than observed with the C<sub>12</sub>BS-MEA/C<sub>12</sub>BS E18-2 system. In addition, the rate of equilibration is faster with the C<sub>12</sub>XS-MEA/C<sub>12</sub>XS E18-5 system; less temperature cycling is required and clarity is obtained sooner on ambient storage after temperature cycling.

30 Example IV

Microemulsion Preparation From Concentrates

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In order to check whether other compositional paths to the final microemulsion might speed equilibration, we explored the use of concentrates as intermediate compositions. These concentrates were prepared by backing out oil and in some cases part of the water from the final composition. For example, the following concentrate was prepared:

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Concentrate NB 14483-75A

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|                        |            |
|------------------------|------------|
| C <sub>12</sub> XS-MEA | 3.0        |
| C <sub>12</sub> E18-5  | 12.0 wt. % |
| Ck #90537 D.O.         | 25.0       |
| Water                  | 50.0       |

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The surfactants were dissolved in diesel oil at room temperature and the water mixed in last. The system forms a thin, clear gel at room temperature which melts into a clear fluid on gentle warming. If 1.2 g of this concentrate is added to 14.1 ml of diesel fuel, the resulting mixture is turbid and clears slowly over a period of several hours to form a bright microemulsion. If the diesel fuel is mixed in stages with the concentrate over a period of several minutes, the final system is a clear microemulsion. This shows that equilibration rate depends on composition path as well as temperature path. It also suggests that it would be advantageous to predilute the above concentrate with some added diesel oil. With this in mind we prepared the following concentrate:

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Concentrate NB 14483-76A

|    |                          |           |
|----|--------------------------|-----------|
| 5  | C <sub>12</sub> XS-MEA   | 10.4      |
|    | C <sub>12</sub> XS E18-5 | 9.6 wt. % |
|    | Ck #90537 D.O.           | 40.0      |
| 10 | Water                    | 40.0      |

The surfactants were dissolved in the diesel oil at room temperature and the water added last. The mixture was turbid initially but slowly cleared with mild warming (-40 °C) and stirring over a period of several hours to finally form a clear amber "solution." This fluid concentrate when diluted by a factor of 10 instantly forms with little mixing a bright microemulsion containing 2 wt.% surfactant and 4% water. This microemulsion remains clear over the temperature range of -10 °C (lower cloud point) to >70 °C (upper cloud point) and is indefinitely stable at room temperature. It is not known at this time whether the turbidity below -10 °C is due to phase separation in the microemulsion or wax precipitation from the diesel fuel.

The above concentrates have a water/surfactant volume ratio of 2/1. In an attempt to raise the water/surfactant ratio, the following concentrate was prepared:

Concentrate NB 14483-78B

|    |                          |            |
|----|--------------------------|------------|
| 25 | C <sub>12</sub> XS-MEA   | 5.78 wt. % |
|    | C <sub>12</sub> XS E18-5 | 5.33       |
| 30 | Ck #90537 D.O.           | 55.56      |
|    | Water                    | 33.33      |

The water/surfactant ratio in this package is 3/1. No attempt was made to optimize the surfactant H/L ratio for the added water. Clarity was achieved by adjusting the oil/water ratio in the package. A quantity, 1.89 g of this concentrate when diluted with 8.2 g of diesel oil instantly forms a clear microemulsion containing 2% surfactant and 6% water. This microemulsion is not quite as bright as the microemulsion prepared with concentrate NB 1448376A due to the higher water content. Brightness may be improved with optimization of surfactant H/L ratio. This essay holds promise of achieving even higher water/surfactant ratios.

## Example V

Ammonium Nitrate Diesel Fuel Microemulsions

In order to determine whether the loss in cetane number due to microemulsified water could be eliminated by the addition of potential cetane improvers, we initiated experiments designed to incorporate NH<sub>4</sub>NO<sub>3</sub> into the microemulsified aqueous phase. Table III describes the results of our studies to incorporate up to 10 wt.% NH<sub>4</sub>NO<sub>3</sub> based on water. Since the microemulsions contain 10% aqueous phase, 10% NH<sub>4</sub>NO<sub>3</sub> based on water translates into a 1% NH<sub>4</sub>NO<sub>3</sub> concentration overall. Based on previous results with oil-soluble cetane improvers such as octyl nitrate, 0.1% or 1000 ppm NH<sub>4</sub>NO<sub>3</sub> was thought to be an effective level for cetane improvement.

Table III describes microemulsion phase behavior with varying surfactant hydrophile/lipophile (H/L) ratio and salinity. H/L ratio depends on the average degree of ethoxylation in the surfactant mixture and is varied by changing the weight ratio of ethoxylated surfactants. Listed under the column heading microemulsion (ME) type is the phase separation characteristic of a given composition. An upper phase microemulsion (U) forms at low H/L ratio and high salinity as a phase-separated system where an oil-continuous microemulsion is in equilibrium with excess settled water. A lower phase microemulsion (L) forms at high H/L ratio and low

salinity as a system where water-continuous microemulsion is in equilibrium with excess floating oil. A single phase microemulsion (S) forms over a relatively narrow range of H/L ratios and salinity and is a relatively clear, thermodynamically stable dispersion containing all the components. The last column lists the nephelometer turbidity units (NTU), which are a measure of single phase microemulsion clarity. Below  
5 -50 NTU the system looks quite bright. From ~50 to 100 NTU the system is clear but with very slight haze developing. From 100 to 200 NTU haze visibly increases but the microemulsion remains transparent. Above 200 NTU the system becomes more and more cloudy though it remains translucent. Readings below 150 NTU are considered satisfactory.

Table III shows that in order to prepare single phase microemulsions at higher salinity, the proportion of  
10 more highly ethoxylated surfactant must be increased. Thus the ratio of C<sub>12</sub>XS E18-10/C<sub>12</sub>XS E18-5 increases from 1/1 to 2.3/1 as we go from 5% to 10% NH<sub>4</sub>NO<sub>3</sub>. This ratio lies in the middle of the single phase region and has the lowest haze. The haziest systems occur near the U → S and S → L phase transition boundaries.

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TABLE III  
NH<sub>4</sub>NO<sub>3</sub> Microemulsions in DF2

| Surfactant, g/dl       |                          | NH <sub>4</sub> NO <sub>3</sub> 1) | ME Type | NTU |
|------------------------|--------------------------|------------------------------------|---------|-----|
| C <sub>12</sub> BS-MEA | C <sub>12</sub> XS E18-2 |                                    |         |     |
| 1.67                   | 2.33                     | 0                                  | U       | -   |
| 1.87                   | 2.13                     | 0                                  | S       | 97  |
| 2.00                   | 2.00                     | 0                                  | S       | 95  |
| 2.00                   | 1.67                     | 0.5                                | S       | 100 |
| 2.00                   | 1.00                     | 0.5                                | L       | -   |
| 2.00                   | 0.00                     | 0.5                                | L       | -   |
| 2.00                   | 1.33                     | 0.75                               | S       | 125 |
| 2.00                   | 1.00                     | 1.0                                | S       | 97  |
| 2.00                   | -                        | 1.0                                | L       | -   |
| 2.00                   | -                        | 2.0                                | S       | 170 |
| 2.00                   | 1.33                     | 3.0                                | S       | 170 |
| 2.00                   | 1.00                     | 5.0                                | S       | 170 |
| 2.00                   | 0.33                     | 7.0                                | L       | -   |
| 2.00                   | 0.80                     | 10.0                               | U       | -   |
| 2.00                   | 0.67                     | 10.0                               | S       | 150 |
| 2.00                   | 0.60                     | 10.0                               | S       | 125 |
| 2.00                   | 0.47                     | 10.0                               | S       | 180 |
| 2.00                   | 0.33                     | 10.0                               | L       | -   |

All systems contain 10 Vol. % aqueous + 90 Vol. % DF2.

1) Based on water content.

#### Example VI

#### Hydrogen Peroxide Diesel Fuel Microemulsions

Another approach to raising the cetane number of microemulsified fuels is the incorporation of aqueous hydrogen peroxide. The following table shows that direct replacement of water with 3% H<sub>2</sub>O<sub>2</sub> in the salt-free microemulsion results in a clear, stable microemulsion without rebalancing.

Microemulsions in DF2 Containing Cetane Improvers

| 5  | Surfactant, g/dl            |                            | Aqueous<br>Phase                 | ME<br>Type | NTU |
|----|-----------------------------|----------------------------|----------------------------------|------------|-----|
|    | <u>C<sub>12</sub>XS-MEA</u> | <u>C<sub>12</sub>XS-E5</u> |                                  |            |     |
| 10 | 2.00                        | 2.00                       | Water                            | S          | 68  |
|    | 2.00                        | 2.00                       | 3% H <sub>2</sub> O <sub>2</sub> | S          | 55  |

All Systems Contain 10 Vol. % aqueous + 90 Vol. % DF2.

## Example VII

20 Oleate Surfactants for Diesel Fuel Microemulsions

The advantage for carboxylate surfactants is that they do not add sulfur to the diesel fuel microemulsion composition. Sulfur-containing compounds in diesel fuel are environmentally undesirable since they may lead to sulfur oxides in the diesel exhaust. Some localities have established maximum sulfur levels in diesel fuels; California, for example, specifies no more than 500 ppm. The examples in Table IV show that oleate surfactants are effective in preparing single phase microemulsions of water and aqueous NH<sub>4</sub>NO<sub>3</sub> in diesel fuel. The aqueous phase to surfactant ratio is 2.5:1 indicating that the instant ethoxylated alkyl ammonium oleate surfactants are efficient microemulsifiers when properly balanced. As in the case with the ethoxylated alkyl ammonium alkyl aryl sulfonates, increasing ethoxylation is required to balance the surfactants when using higher NH<sub>4</sub>NO<sub>3</sub> concentrations. This shows the criticality of surfactant balancing which depends strongly on aqueous phase composition. Temperature sensitivity is again minimized by blending two or more surfactants with opposing temperature dependencies; MEA-oleate becomes more hydrophilic while the ethoxylated alkyl ammonium oleate become more lipophilic with increasing temperature. Blends of these surfactants give temperature insensitive microemulsions.

TABLE IV  
Oleate Surfactant Stabilized Microemulsions<sup>1)</sup>

| MEA Oleate | Surfactant, g/dl |              |               | El8-10 Oleate | El8-15 Oleate | $\chi$ NH <sub>4</sub> NO <sub>3</sub> <sup>2)</sup> | ME Type |
|------------|------------------|--------------|---------------|---------------|---------------|------------------------------------------------------|---------|
|            | El8-2 Oleate     | El8-5 Oleate | El8-10 Oleate |               |               |                                                      |         |
| 1.67       | 1.67             | 0.66         | -             | -             | -             | -                                                    | U       |
| 1.67       | 1.50             | 0.83         | -             | -             | -             | -                                                    | S       |
| 1.67       | 1.33             | 1.00         | -             | -             | -             | -                                                    | L       |
| 2.00       | -                | 2.00         | -             | -             | -             | 1                                                    | U       |
| 2.00       | -                | 1.83         | 0.17          | -             | -             | 1                                                    | S       |
| 2.00       | -                | 0.67         | 0.33          | -             | -             | 1                                                    | L       |
| 2.00       | -                | 0.17         | 1.83          | -             | -             | 5                                                    | U       |
| 2.00       | -                | -            | 2.00          | -             | -             | 5                                                    | S       |
| 2.00       | -                | -            | 1.83          | 0.17          | -             | 5                                                    | L       |
| 2.00       | -                | -            | 1.67          | 0.33          | -             | 10                                                   | U       |
| 2.00       | -                | -            | 1.33          | 0.67          | -             | 10                                                   | S       |
| 2.00       | -                | -            | 1.00          | 1.00          | -             | 10                                                   | L       |

1) All systems contain 10 Vol. % aqueous and 90 Vol. % DF6.

2) Based on water content.

## Claims

1. A diesel fuel composition which comprises:
  - (a) a diesel fuel;
  - (b) 1.0 to 30.0 weight percent of water based upon said diesel fuel;

(c) a cetane number improver additive, present in an amount up to, but less than, 20.0 weight percent based upon said water, said additive being selected from an inorganic oxidizer, a polar organic oxidizer and a nitrogen oxide-containing compound; and

(d) 0.5 to 15.0 wt% based on the diesel fuel, of a surfactant system comprising

(i) one or more first surfactants selected from surfactants capable of forming a lower phase microemulsion at 20 °C when combined with equal volumes of the fuel and water at a concentration of 2 grams of surfactant per deciliter of fuel plus water, which microemulsion phase has a volume ratio of water to surfactant of at least 2; at least one said first surfactant being an ethoxylated C<sub>12</sub>-C<sub>18</sub> alkyl ammonium salt of a C<sub>9</sub>-C<sub>24</sub> alkyl carboxylic or alkylaryl sulfonic acid containing 6 or more ethylene oxide groups; and

(ii) one or more second surfactants selected from surfactants capable of forming an upper phase microemulsion at 20 °C when combined with equal volumes of the fuel and water at a concentration of 2 grams of surfactant per deciliter of fuel plus water, which microemulsion phase has a volume ratio of water to surfactant of at least 2; at least one said surfactant being an ethoxylated C<sub>12</sub>-C<sub>18</sub> alkyl ammonium salt of a C<sub>9</sub>-C<sub>24</sub> alkyl carboxylic or alkylaryl sulfonic acid containing less the 6 ethylene oxide groups;

the said first and second surfactants being present in a weight ratio which forms with components (a), (b) and (c) a single phase translucent microemulsion.

2. A fuel composition as claimed in claim 1, wherein the said first and second surfactants are each selected only from said ethoxylated compounds.

3. A diesel fuel composition according to either preceding claim, further including up to 20, preferably 2 to 10, weight percent based upon said diesel fuel, of a cosurfactant selected from alkylene glycol monoalkylethers and C<sub>4</sub> to C<sub>6</sub> alkanols and mixtures thereof.

4. A diesel fuel composition according to any preceding claim, wherein said additive (c) is an ammonium compound selected from nitrate, nitrite, hypochlorite, chlorite, chlorate, perchlorate, hypobromite, bromate, hypoiodite and periodate.

5. A diesel fuel composition according to any of claims 1 to 3, wherein said additive (c) is hydrogen peroxide or an acid selected from perchloric, chlorous, hypochlorous, cyanuric, hypobromous, bromic, hypoiodous, iodic and periodic.

6. A diesel fuel composition according to any preceding claim, further containing an amount of up to 30 weight percent, based on the weight of water, of a C<sub>1</sub> to C<sub>3</sub> alkanol.

## Patentansprüche

1. Dieselkraftstoffzusammensetzung, die

(a) Dieselkraftstoff,

(b) 1,0 bis 30,0 Gew.% Wasser, bezogen auf den Dieselkraftstoff,

(c) ein Cetanzahlverbesserungsadditiv, das in einer Menge bis zu, aber weniger als 20 Gew.%, bezogen auf das Wasser, vorhanden ist, wobei das Additiv ausgewählt ist aus einem anorganischen Oxidationsmittel, einem polaren organischen Oxidationsmittel und einer Stickstoffoxid enthaltenden Verbindung, und

(d) 0,5 bis 15,0 Gew.%, bezogen auf den Dieselkraftstoff, eines Tensidsystems umfaßt, das

(i) ein oder mehrere erste Tenside ausgewählt aus Tensiden, die in der Lage sind, bei 20 °C eine Mikroemulsion als untere Phase zu bilden, wenn sie mit gleichen Volumina des Kraftstoffs und Wasser bei einer Konzentration von 2 Gramm Tensid pro Deziliter Kraftstoff plus Wasser kombiniert werden, wobei die Mikroemulsionsphase ein Volumenverhältnis von Wasser zu Tensid von mindestens 2 hat und mindestens ein erstes Tensid ein ethoxyliertes C<sub>12</sub>-bis C<sub>18</sub>-Alkylammoniumsalz einer C<sub>9</sub>- bis C<sub>24</sub>-Alkylcarbonsäure oder Alkylarylsulfonsäure mit 6 oder mehr Ethylenoxidgruppen ist, und

(ii) ein oder mehrere zweite Tenside ausgewählt aus Tensiden umfaßt, die in der Lage sind, bei 20 °C eine Mikroemulsion als obere Phase zu bilden, wenn sie mit gleichen Volumina des Kraftstoffs und Wasser bei einer Konzentration von 2 Gramm Tensid pro Deziliter Kraftstoff plus Wasser kombiniert werden, wobei die Mikroemulsionsphase ein Volumenverhältnis von Wasser

zu Tensid von mindestens 2 hat und mindestens ein Tensid ein ethoxyliertes C<sub>12</sub>- bis C<sub>18</sub>- Alkylammoniumsalz einer C<sub>9</sub>- bis C<sub>24</sub>-Alkylcarbonsäure oder Alkylarylsulfonsäure mit weniger als 6 Ethylenoxidgruppen ist,  
wobei die ersten und zweiten Tenside in einem Gewichtsverhältnis vorhanden sind, das mit den  
5 Komponenten (a), (b) und (c) durchsichtige Einphasenmikroemulsionen bildet.

2. Kraftstoffzusammensetzung nach Anspruch 1, in der die ersten und zweiten Tenside jeweils nur aus den ethoxylierten Verbindungen ausgewählt sind.
- 10 3. Dieselkraftstoffzusammensetzung nach einem der vorhergehenden Ansprüche, die außerdem bezogen auf den Dieselkraftstoff bis zu 20, vorzugsweise 2 bis 10 Gew.% eines Cotensids ausgewählt aus Alkylenglykolmonoalkylethern und C<sub>4</sub>- bis C<sub>6</sub>-Alkanolen und Mischungen daraus einschließt.
- 15 4. Dieselkraftstoffzusammensetzung nach einem der vorhergehenden Ansprüche, in der das Additiv (c) eine Ammoniumverbindung ausgewählt aus Nitrat, Nitrit, Hypochlorit, Chlorit, Chlorat, Perchlorat, Hypobromit, Bromat, Hypiodit und Periodat ist.
- 20 5. Dieselkraftstoffzusammensetzung nach einem der Ansprüche 1 bis 3, in der das Additiv (c) Wasserstoffperoxid oder eine Säure ausgewählt aus Perchlorsäure, chloriger Säure, hypochloriger Säure, Cyanursäure, hypobromiger Säure, Bromsäure, hypoiodiger Säure, Iodsäure und Periodsäure ist.
6. Dieselkraftstoffzusammensetzung nach einem der vorhergehenden Ansprüche, die außerdem eine Menge von bis zu 30 Gew.%, bezogen auf das Gewicht des Wassers, von einem C<sub>1</sub>- bis C<sub>3</sub>-Alkanol enthält.

## Revendications

1. Composition de carburant diesel comprenant :
  - (a) un carburant diesel,
  - 30 (b) 1,0 à 30,0 % en poids d'eau par rapport audit carburant diesel,
  - (c) un additif améliorant l'indice de cétane, présent en quantité allant jusqu'à 20,0 % en poids, mais inférieure à ce chiffre, par rapport à ladite eau, ledit additif étant sélectionné parmi un oxydant minéral, un oxydant organique polaire et un composé contenant de l'oxyde d'azote, et
  - 35 (d) 0,5 à 15,0 % en poids, par rapport au carburant diesel, d'un système tensioactif comprenant :
    - (i) un ou plusieurs premiers agents tensioactifs sélectionnés parmi les agents tensioactifs susceptibles de former une phase inférieure de microémulsion à 20 °C lorsqu'ils sont combinés avec des volumes égaux du carburant et d'eau en concentration de 2 grammes d'agent tensioactif par décilitre de carburant plus l'eau, ladite phase de microémulsion ayant un rapport volumique de l'eau à l'agent tensioactif d'au moins 2, au moins un desdits premiers agents tensioactifs étant un sel d'alkylammonium en C<sub>12</sub>-C<sub>18</sub> éthoxylé d'un acide alkyl carboxylique ou alkylaryl sulfonique en C<sub>9</sub>-C<sub>24</sub> contenant 6 groupes d'oxyde d'éthylène ou davantage, et
    - 40 (ii) un ou plusieurs deuxièmes agents tensioactifs sélectionnés parmi les agents tensioactifs susceptibles de former une phase supérieure de microémulsion à 20 °C lorsqu'ils sont combinés avec des volumes égaux du carburant et d'eau en concentration de 2 grammes d'agent tensioactif par décilitre de carburant plus l'eau, ladite phase de microémulsion ayant un rapport volumique de l'eau à l'agent tensioactif d'au moins 2, au moins un desdits agents tensioactifs étant un sel d'alkylammonium en C<sub>12</sub>-C<sub>18</sub> éthoxylé d'un acide alkyl carboxylique ou alkylaryl sulfonique en C<sub>9</sub>-C<sub>24</sub> contenant moins de 6 groupes d'oxyde d'éthylène,
    - 45 le(s)dit(s) premier(s) et deuxième(s) agents tensioactifs étant présents selon un rapport pondéral tel qu'il se forme avec les composants (a), (b) et (c) une microémulsion translucide à phase unique.
    - 50
2. Composition de carburant selon la revendication 1, dans laquelle le(s)dit(s) premier(s) et deuxième(s) agents tensioactifs sont sélectionnés individuellement uniquement parmi lesdits composés éthoxylés.
- 55 3. Composition de carburant diesel selon l'une quelconque des revendications précédentes, comprenant jusqu'à 20, de préférence 2 à 10 % en poids, par rapport audit carburant diesel, d'un agent co-tensioactif sélectionné parmi les monoalkyléthers d'alkylène glycols et les alcanols en C<sub>4</sub> à C<sub>6</sub>, et leurs mélanges.

4. Composition de carburant diesel selon l'une quelconque des revendications précédentes, dans laquelle ledit additif (c) est un composé d'ammonium sélectionné parmi les nitrates, les nitrites, les hypochlorites, les chlorites, les chlorates, les perchlorates, les hypobromites, les bromates, les hypoiodites et les periodates.

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5. Composition de carburant diesel selon l'une quelconque des revendications 1 à 3, dans laquelle ledit additif (c) est du peroxyde d'hydrogène ou un acide sélectionné parmi les acides perchlorique, chloreux, hypochloreux, cyanurique, hypobromeux, bromique, hypoiodeux, iodique et periodique.

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6. Composition de carburant diesel selon l'une quelconque des revendications précédentes, contenant par ailleurs une quantité jusqu'à 30 % en poids, par rapport au poids d'eau, d'un alcanol en C<sub>1</sub> à C<sub>3</sub>.

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