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EUROPEAN PATENT APPLICATION

21 Application number : **91307780.6**

51 Int. Cl.⁵ : **C10L 1/32**

22 Date of filing : **23.08.91**

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

43 Date of publication of application :
18.03.92 Bulletin 92/12

84 Designated Contracting States :
BE DE FR GB IT NL

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

57 The present invention relates to translucent and thermodynamically stable fuel compositions having improved combustion efficiency and reduced smoke, particulate, CO, and NO_x emissions. The fuel compositions comprise, for example, a diesel fuel, water, or an aqueous solution of a low molecular weight alcohol and/or a water-soluble reagent, and a surfactant system which comprises a balanced blend of one or more hydrophilic surfactants and one or more lipophilic surfactants, wherein the diesel fuel composition can contain as high as 30 weight percent of aqueous phase with an aqueous phase/surfactant ratio at least 2/1. The surfactant system may contain, in addition to the hydrophilic and lipophilic surfactants, cosurfactants and polar organic solvents. The reagent solution comprises aqueous solutions of an additive selected from the group consisting of inorganic oxidizing agents, low molecular weight polar organic oxidizing agents, and nitrogen oxide-containing compounds which act as cetane improvers and/or combustion modifiers. These additives offset the well-known loss in cetane number and/or the ignition delay caused by dispersed or microemulsified water and eliminate the need to change engine operating parameters.

The present invention relates to novel microemulsion compositions which are transparent and thermodynamically stable fluids useful in reducing diesel exhaust emissions.

There is a wide variety of micro emulsion 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, 5 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 10 parts of surfactant per part of solubilized water.

The microemulsions of the instant invention seek to overcome the foregoing deficiencies by providing improved temperature and salt stability and employing lower concentrations of surfactants.

The present invention provides a translucent and thermodynamically stable fuel compositions having improved combustion efficiency and reduced smoke, particulate, CO, and NO_x emissions. The fuel compositions 15 comprise for example, diesel fuel, water or an aqueous solution of a low molecular weight alcohol and/or a water-soluble reagent, and a surfactant system which comprises a balanced blend of one or more hydrophilic surfactants and one or more lipophilic surfactants, wherein the diesel fuel composition can contain as high as 30 weight percent of aqueous phase with an aqueous phase/surfactant ratio at least 2/1.

The present translucent and thermodynamically stable microemulsion compositions of this invention comprise a hydrocarbon fuel such as gasoline, jet fuel, or preferably diesel fuel; about 1 to about 30 weight percent, 20 more preferably about 2 to about 20 weight percent, and most preferably about 2 to about 15 weight percent of an aqueous composition comprising water, from 0 to 30 weight percent based on the amount of water of a 1 to 3 carbon alkanol and less than 20 weight percent based on the amount of water of one or more additives selected from the group consisting of ashless inorganic oxidizing agents, low molecular weight polar organic 25 oxidizing agents, and nitrogen oxide-containing compounds wherein the additive is preferably selected from the group consisting of: 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, 30 pricric acid, cumene hydroperoxide, cyanuric acid, nitroglycerin, nitrobenzene, trinitrotoluene, and mixtures thereof; and, about 0.5 to about 15 weight percent, more preferably about 1 to about 10 weight percent and most preferably about 1 to about 5 weight percent of a surfactant system which comprises a balanced blend of one or more hydrophilic surfactants and one or more lipophilic surfactants wherein the ratio of aqueous 35 composition/surfactant system is preferably at least 2/1.

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 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 40 ignition delay often requiring engine and/or operating parameter modification such as advanced ignition timing or the installation of glow plugs. The novel compositions of the instant invention, by the incorporation into the aqueous composition of an oxidizing and/or nitrogenous reagent, offset these debits while still retaining the advantages in emissions reduction.

In the practice of the present invention, at least one hydrophilic surfactant and at least one lipophilic surfactant are selected and their ratio adjusted with respect to their combined hydrophilic and lipophilic properties 45 such that they form with the fuel and the aqueous composition a single phase, translucent microemulsion. The 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 50 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.

The hydrophilic surfactant which is defined by the above properties includes, but is not limited to, the alkyl carboxylic and alkylaryl sulfonic acid salts wherein the alkyl group is a C₉ to C₁₈ linear, branched or bilinear 55 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. Also included, and preferred are the ethoxylated alkylphenols. Most preferred are the ethoxylated C₁₂-C₁₈ alkyl ammonium salts of C₉-C₂₄ alkyl carboxylic and alkylaryl sulfonic acids containing 6 or more ethylene oxide (hereinafter EO) groups, wherein the alkyl and aryl

groups are as previously defined above.

Representative examples of 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 C₁₂BS-E18-5 and C₁₂BS-E18-10, respectively), heptaethoxy octadecyl ammonium dodecyl o-xylene sulfonate (designated C₁₂XS-E18-7) and decaethoxy octadecyl ammonium dodecyl ortho xylene sulfonate (designated C₁₂XS-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.

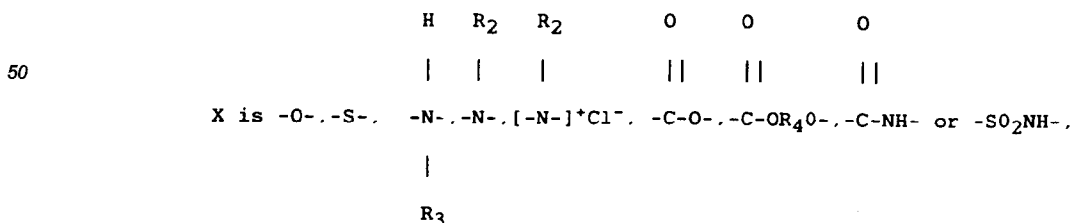
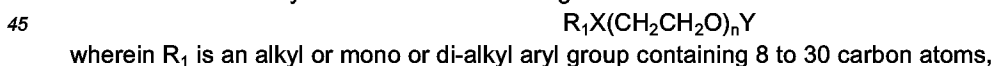
The lipophilic surfactant for purposes of this invention is a surfactant having the properties of providing at 2 g/dl concentration in equal volumes of fuel and aqueous composition an upper phase microemulsion at 20°C such that the volume ratio of water to surfactant (Vw/Vs) in the microemulsion phase 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, but is not limited to, the ethoxylated alkyl phenols. Also included and preferred are the alkyl and alkylaryl sulfonic acid salts wherein the alkyl group is a C₁₂ to C₂₄ 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. More preferred are the ethoxylated C₁₂-C₁₈ alkyl ammonium salts of C₉-C₂₄ alkyl carboxylic and alkylaryl sulfonic acids containing less than six EO groups, wherein the alkyl and aryl groups are as previously defined above.

Representative examples of 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. Most preferred are di-ethoxy octadecyl ammonium oleate, di- and penta-ethoxy octadecyl ammonium dodecyl o-xylene sulfonate (designated E18-2 oleate, C₁₂XS-E18-2 and C₁₂XS-E18-5, respectively).

Representative 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.

The present invention is not confined to the use of the aforementioned ethoxylated alkyl phenols but includes other ethoxylated surfactants of the generic formula:



and Y is -H-, -SO₃-M⁺ or -(PO₃H)-M⁺ wherein M⁺ is an inorganic or ammonium cation including alkyl substituted ammonium cations; R₂ is an alkyl group containing 1 to 20 carbon atoms or a polyethoxy ether group containing

from 1 to 30 (CH₂CH₂O) groups; R₃ is H or an alkyl group containing 1 to 3 carbon atoms; R₄ is a polyhydroxy group derived from glycerol, glycols, sorbitol, or various sugars; and n is an integer of from 1 to 30.

The above ethoxylated alkyl phenols may be blended with an alkali metal, ammonium, alkyl ammonium, alkanol ammonium, or ethoxylated alkyl ammonium salt of an alkyl or alkyl aryl sulfonic acid of the generic formula:



wherein R is an alkyl or alkyl benzene group containing 8 to 30 carbon atoms in the alkyl chain and the benzene ring may be additionally substituted with one or two alkyl groups containing 1 to 3 carbon atoms each to provide the balanced blend of surfactants. Preferred blends of ethoxylated alkyl phenols with alkyl aryl sulfonates include combinations of Igepal CM 530 or Igepal DM 710 with the sodium or monoethanol amine salt of C₁₂ o-xylene sulfonic acid.

Alternatively, ethoxylated alkyl ammonium salts of the above alkylaryl sulfonic acids containing varying degrees of ethoxylated are blended to provide the balanced blend of surfactants. Preferred blends of ethoxylated alkyl ammonium salts of alkylaryl sulfonic acids include penta-ethoxy octadecyl ammonium dodecyl benzene sulfonate combined with hepta-ethoxy octadecyl ammonium dodecyl benzene sulfonate and di-ethoxy cocoa ammonium dodecyl o-xylene sulfonate with deca-ethoxy octadecyl ammonium dodecyl oxylyene 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 C₁₂XS-E18-5 with C₁₂XS-E18-10.

Alternatively, alkali metal, ammonium, alkyl ammonium, alkanol ammonium or ethoxylated alkyl ammonium salts of alkyl carboxylic acids of the generic formula:



wherein R' is an alkyl group of 12 to 20 carbon atoms may be substituted for the sulfonic acid salts described above. These salts may be blended with ethoxylated alkyl phenols. Alternatively, ethoxylated alkyl ammonium salts of the above alkyl carboxylic acids containing varying degrees of ethoxylation are blended together to provide the balanced blend of surfactants. Most preferred is a blend of penta-ethoxy octadecyl ammonium oleate with deca-ethoxy octadecyl ammonium oleate, i.e. a blend of E18-5 oleate with E18-10 oleate.

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 micro-emulsion diesel fuel composition. The cosurfactants are of the class of alkylene glycol monoalkyl ethers, C₄ to C₆ 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 (e.g. more (or less) ethoxylation) may be required. These points will be made clear by the examples cited below. The preferred surfactant blends of the instant invention provide a marked improvement over the art by solubilizing much more aqueous phase per unit of surfactant than disclosed in the art. The art discloses diesel fuel microemulsions containing less than 2 volumes of water per volume of surfactant. The examples cited below disclose compositions with greater than 2 up to 4 volumes of aqueous phase per volume of surfactant.

The most preferred surfactants for the instant invention are selected from Group 1, having the generic formula:

TABLE I
Preparation of Anionic-Ethoxy Cationic Complexes

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

		<u>Weight (g) of Amine/100 g Acid</u>		
25	<u>Amine</u>	<u>C₁₂XSH</u>	<u>C₁₂BSH</u>	<u>Oleic Acid</u>
	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

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¹ By titration

² Direct replacements: a) Akzo Ethomeen 18/12

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b) Ethomeen 18/15

c) Ethomeen 18/20

d) Ethomeen 18/25

45 Example II

Microemulsion Preparation

50 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 C₁₂XS E18-n surfactants were found to be extremely temperature sensitive and to deteriorate with age. Often systems which were initially 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

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C₁₂XS 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 C₁₂XS E18-n surfactants were also prepared. Blends of these C₁₂XS E18-n surfactants with surfactants based on MEA (e.g. C₁₂BS-MEA or C₁₂XS-MEA) gave good stability and are described below.

Example III

Selecting and Balancing the Hydrophilic and Lipophilic Surfactant Blend

A 2 gm/dl mixture of monoethanol ammonium dodecyl benzene sulfonate (hereafter C₁₂BS-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 C₁₂BS 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 C₁₂BS-MEA/C₁₂BS E18-2 represents a hydrophile-lipophile surfactant couple and their combined hydrophilic and lipophilic properties are varied by adjusting the weight ratio of C₁₂BS-MEA/C₁₂BS E18-2. Table II presents phase data for the C₁₂BS-MEA/C₁₂BS 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 C₁₂BS-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 C₁₂BS-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 C₁₂BS-MEA/C₁₂BS 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 C₁₂BS-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 C₁₂BS-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

C₁₂BS-MEA/C₁₂BS E18-2 Compositions for Single Phase

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W/O Vol. Ratio	Surfactant Concn g/dl	<u>Wt Fraction C₁₂BS-MEA¹ at the</u>	
		<u>Upper Phase TB²</u>	<u>Lower Phase TB³</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 C₁₂XS-MEA/C₁₂XS E18-5 system, though not as extensively investigated as the C₁₂BS-MEA/C₁₂BS E18-2 system described above, provides a similar phase behavior pattern. In this case, the C₁₂XS-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.

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C₁₂XS-MEA/C₁₂XS E18-5 Compositions for Single Phase

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<u>W/O Vol. Ratio</u>	<u>Wt. Fraction C₁₂XS-MEA¹</u>	
	<u>UTB²</u>	<u>LTB³</u>
5.0/95.0	0.49	0.55
4.5/95.5	0.47 (estim.)	0.57
4.0/96.0	0.44 (estim.)	0.60

10

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- 1 At a total surfactant concentration of 1.5 g/dl.
- 2 Upper phase transition boundary: u s
- 3 Lower phase transition boundary: s l

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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. The clarity of microemulsions in the center of the single phase region is somewhat better than observed with the C₁₂BS-MEA/C₁₂BS E18-2 system. In addition, the rate of equilibration is faster with the C₁₂XS-MEA/C₁₂XS E18-5 system; less temperature cycling is required and clarity is obtained sooner on ambient storage after temperature cycling.

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Example IV

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Microemulsion Preparation From Concentrates

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 ₁₂ XS-MEA	3.0
C ₁₂ 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 ₁₂ XS-MEA	10.4
	C ₁₂ XS E18-5	9.6 wt. %
	Ck #90537 D.O.	40.0
	Water	40.0

10 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
15 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 ₁₂ XS-MEA	5.78 wt. %
	C ₁₂ XS E18-5	5.33
	Ck #90537 D.O.	55.56
	Water	33.33

30 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
35 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

40 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 NH₄NO₃ into the microemulsified aqueous phase. Table III describes the results of our studies to incorporate up to 10 wt.%
45 NH₄NO₃ based on water. Since the microemulsions contain 10% aqueous phase, 10% NH₄NO₃ based on water translates into a 1% NH₄NO₃ concentration overall. Based on previous results with oil-soluble cetane improvers such as octyl nitrate, 0.1% or 1000 ppm NH₄NO₃ 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
50 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
55 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 -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.

5 Table III shows that in order to prepare single phase microemulsions at higher salinity, the proportion of more highly ethoxylated surfactant must be increased. Thus the ratio of C₁₂XS E18-10/C₁₂XS E18-5 increases from 1/1 to 2.3/1 as we go from 5% to 10% NH₄NO₃. 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
 NH₄NO₃ Microemulsions in DF2

C12BS-MEA	Surfactant, g/dl		C12XS E18-5	C12XS E18-10	% NH ₄ NO ₃ ¹⁾	ME Type	NTU
	C12XS E18-2	C12XS E18-5					
1.67	2.33	-	-	-	0	U	-
1.87	2.13	-	-	-	0	S	97
2.00	2.00	-	-	-	0	S	95
2.00	1.67	0.33	-	-	0.5	S	100
2.00	1.00	1.00	-	-	0.5	L	-
2.00	0.00	2.00	-	-	0.5	L	-
2.00	1.33	0.67	-	-	0.75	S	125
2.00	1.00	1.00	-	-	1.0	S	97
2.00	-	2.00	-	-	1.0	L	-
2.00	-	2.00	-	-	2.0	S	170
2.00	-	1.33	0.67	0.67	3.0	S	170
2.00	-	1.00	1.00	1.00	5.0	S	170
2.00	-	0.33	1.67	1.67	7.0	L	-
2.00	-	0.80	1.20	1.20	10.0	U	-
2.00	-	0.67	1.33	1.33	10.0	S	150
2.00	-	0.60	1.40	1.40	10.0	S	125
2.00	-	0.47	1.53	1.53	10.0	S	180
2.00	-	0.33	1.67	1.67	10.0	L	-

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

1) Based on water content.

Example VI

Hydrogen Peroxide Diesel Fuel Microemulsions

5 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% H₂O₂ in the salt-free microemulsion results in a clear, stable microemulsion without rebalancing.

10 Microemulsions in DF2 Containing Cetane Improvers

Surfactant, g/dl		Aqueous	ME	
<u>C₁₂XS-MEA</u>	<u>C₁₂XS-E5</u>	<u>Phase</u>	<u>Type</u>	<u>NTU</u>
2.00	2.00	Water	S	68
2.00	2.00	3% H ₂ O ₂	S	55

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

Example VII

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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 NH₄NO₃ 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 NH₄NO₃ 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.

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TABLE IV
Oleate Surfactant Stabilized Microemulsions¹⁾

MEA Oleate	Surfactant, g/dl			E18-15 Oleate	% NH ₄ NO ₃ ²⁾	ME Type
	E18-2 Oleate	E18-5 Oleate	E18-10 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

- 5 1. A fuel composition which comprises:
 (a) a fuel;
 (b) about 1.0 to about 30.0 weight percent of water based upon said diesel fuel;
 (c) about 0 to about 30 weight percent of an alkanol based upon said water, said alkanol having about
 10 1 to about 3 carbon atoms;
 (d) less than about 20.0 weight percent of an additive based upon said water, said additive being selected from the group consisting of an inorganic oxidizer, a polar organic oxidizer and a nitrogen oxide-containing compound; and
 (e) about 0.5 to about 15.0 weight percent of a surfactant system based on said diesel fuel, said surfactant system comprising a blend of a hydrophilic surfactant and a lipophilic surfactant in a ratio sufficient to form a single phase translucent microemulsion, wherein said diesel fuel exhibits improved cetane and combustion properties, reduced smoke, soot emissions, particulate emissions and NOx emissions in the combustion of said diesel fuel in a diesel engine.

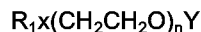
- 20 2. A fuel composition according to claim 1, wherein the fuel is diesel, gasoline or jet fuel, preferably diesel fuel.

3. A fuel composition according to claim 1 or 2, wherein the hydrophilic and lipophilic blend of surfactants is comprised of two or more surfactants selected from one or more of:
 (a) an alkali metal, ammonium, alkyl ammonium, alkanol ammonium, or ethoxylated alkyl or alkanol ammonium salt of an alkyl or alkylaryl sulfonic acid of the generic formula:

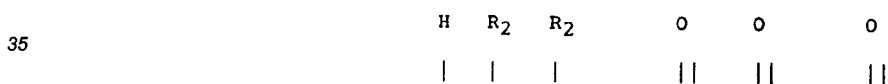


wherein R is an alkyl or alkyl benzene group containing 8 to 30 carbon atoms in the alkyl chain and the benzene ring may be additionally substituted with one or two alkyl groups containing 1-3 carbon atoms each;

- 30 (b) an ethoxylated surfactant of the generic formula:



wherein R₁ is an alkyl or mono- or di-alkyl aryl group containing 8 to 30 carbon atoms,



X is -O-, -S-, -N-, -N-, [-N-]⁺Cl⁻, -C-O-, -C-OR₄O-, -C-NH- or -SO₂NH-



and Y is -H-, -SO₃-M⁺ or -(PO₃H)-M⁺ wherein M⁺ is an inorganic or ammonium cation including alkyl substituted ammonium cations; R₂ is an alkyl group containing 1 to 20 carbon atoms or a polyethoxy ether group containing from 1 to 30 (CH₂CH₂O) groups; R₃ is H or an alkyl group containing 1 to 3 carbon atoms; R₄ is a polyhydroxy group derived from glycerol, glycols, sorbitol, or various sugars; and n is an integer of from 1 to 30; and

- (c) an alkali metal, ammonium, alkyl ammonium, alkanol ammonium, or ethoxylated alkyl ammonium salt of an alkyl carboxylic acid of the generic formula



wherein R' is an alkyl group of 8 to 24 carbon atoms.

4. The composition of claim 3 wherein at least one of the lipophilic surfactants is an ethoxylated C₁₂-C₁₈ alkyl ammonium salt of a C₉-C₂₄ alkyl carboxylic or alkylaryl sulfonic acid containing less than 6 ethylene oxide groups.

5. The composition of claim 3 or 4 wherein at least one of the hydrophilic surfactants is an ethoxylated C₁₂-C₁₈ alkyl ammonium salt of a C₉-C₂₄ alkyl carboxylic or alkylaryl sulfonic acid containing 6 or more ethylene

oxide groups.

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6. A process for reducing smoke, soot emissions, particulate emissions, and NO_x emissions in the combustion of a diesel fuel in a diesel engine which comprises the step of adding to said diesel fuel about 1.0 to about 30.0 weight percent of water and about 0.5 to about 15.0 weight percent of a surfactant system, based on said diesel fuel, said surfactant system comprising a blend of a hydrophilic surfactant and a lipophilic surfactant in a ratio sufficient to form a single phase translucent microemulsion, whereby smoke, soot, particulate and NO_x emissions are reduced.
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7. A process according to claim 6, wherein said hydrophilic surfactant is selected from the group consisting of alkali metal, ammonium, 1 to 3 carbon alkyl ammonium, 2 to 6 carbon alkanol ammonium containing 1 to 3 hydroxy groups, and 6 or more ethoxy C₁₂-C₁₈ alkyl ammonium salts of alkyl carboxylic acids and alkyl aryl sulfonic acids and 6 or more ethoxy alkyl phenols.
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8. A process according to claim 6 or 7, wherein said lipophilic surfactant is selected from the group consisting of less than 6 ethoxy alkyl phenols and less than 6 ethoxy C₁₂-C₁₈ alkyl ammonium salts of alkyl carboxylic acids and alkyl aryl sulfonic acids.

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