

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
17 April 2003 (17.04.2003)

PCT

(10) International Publication Number  
**WO 03/031540 A1**

- (51) International Patent Classification<sup>7</sup>: **C10L 1/32**
- (21) International Application Number: PCT/GB02/04254
- (22) International Filing Date:  
19 September 2002 (19.09.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
0124117.3 8 October 2001 (08.10.2001) GB
- (71) Applicant (for all designated States except US): **IMPERIAL CHEMICAL INDUSTRIES PLC** [GB/GB]; 20 Manchester Square, London W1U 3AN (GB).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **OLDFIELD, Andrew, Simon** [GB/GB]; 3 Zetland Mews, Saltburn by Sea, Cleveland TS12 1DF (GB). **THOMPSON, Lee** [GB/GB]; 12 Harwood Court, Trimdon Grange, County Durham TS29 6HU (GB).

(74) Agents: **GRAHAM, John, George** et al.; Uniqema Intellectual Property Department, Wilton Centre, Wilton, Redcar TS10 4RF (GB).

**Published:**

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: DIESEL FUEL EMULSION

(57) Abstract: A fuel emulsion consists of diesel, water and an emulsifier composition having a hydrophile/lipophile balance value at least 4. The emulsifier composition comprises a polymeric non-ionic surfactant having hydrophilic and hydrophobic repeating units together with at least one component selected from fatty acid esters or partial esters of polyhydric alcohols; alkoxyfated fatty acid esters or partial esters of polyhydric alcohols; and alkoxyfated primary alcohols. Preferred emulsifier compositions according to the invention include mixtures of the polymeric non-ionic surfactant with at least two of the components. Especially preferred compositions comprise mixtures of the polymeric non-ionic surfactant with the fatty acid (partial) esters or alkoxyfated fatty acid (partial) esters. The emulsifier composition may include an emulsion coupler such as a primary alcohol, e.g. octanol.



**WO 03/031540 A1**

## DIESEL FUEL EMULSION

The invention relates to fuel emulsions and to emulsifier compositions for use therein.

5 Diesel engines are used in a wide variety of applications including automotive, marine, electricity generation and compressors. Such engines are often relatively inefficient and emit significant quantities of pollutant gases and particles. This is of particular concern when the engines are in public service vehicles such as buses and the resultant pollution affects significant numbers of people in town centres.

10 To increase the efficiency with which the diesel fuel is burnt in such engines and to reduce the generation of pollutants, water is added to the diesel to form an emulsion therewith. Typically, such emulsions contain at least 80% by weight diesel and up to 15% by weight of water (the weight percentages being based on the total weight of the composition). As water and oils such as diesel do not naturally mix, it is necessary to use emulsifiers in the water/diesel mixture to aid the formation and retention of emulsions. The emulsifiers are typically present in amounts up to 6% by weight based on the total weight of the composition.

20 Diesel fuels also typically include additives for various purposes. For example, such fuels may contain cetane number improvers, eg nitrates, nitro and nitroso compounds and peroxides, at levels of up to 0.3% by weight. Dispersants and detergents, for example low molecular weight amines, are used to improve engine cleanliness. To improve the low temperature properties of the fuel, cold flow blending agents, eg kerosene, may be added in quantities up to several percent to dilute the formation of wax crystals. Additionally, cold flow additives, eg ethylene-vinyl ester copolymers, chlorinated hydrocarbons and polyolefins, may be used at ppm levels to alter the formation of wax crystals.

30 Other additives may include oxygenates, eg rapeseed oil methyl ester, to improve fuel combustion characteristics; antioxidants, eg amines and other nitrogen-containing compounds, to improve the long term stability of the fuel with respect to colour and sediment formation; lubricity aids and metal deactivators.

35 Owing to the shelf life requirement for such water/diesel fuel emulsions (from blending to use in an engine), a primary requirement for the emulsions is that they are stable for a minimum period, ie 10,000 minutes (1 week). Another primary requirement for the fuel emulsions is that they are competitively priced in the relevant markets; consequently, any additives such as emulsifiers need to be used in minimum amounts and/or be as inexpensive as possible.

40 Current water/diesel fuel formulations use simple, low-cost emulsifiers such as partial esters of polyhydric alcohols at relatively high levels, eg 4% to 6% by weight. However, such emulsifiers at those levels may result in deposits being formed within engines leading to greater inefficiency of operation.

45 Known water/diesel fuel formulations are disclosed in WO 85/04183 A1, WO 00/63322 A1, WO 01/02516 A1, US-A-3876391, GB-A-2066288, GB-A-2352246, EP-B1-0012292, EP-B1-0242832, EP-B1-0372353, EP-B1-0888421, EP-A1-0893488, EP-A2-1101815, DE-A-3229918, CN 1079499 and JP-B2-2793190.

It is an object of the present invention to provide a stable, cost-effective fuel emulsion and emulsifier compositions for use in fuel emulsions.

According to the present invention, a fuel emulsion comprises a water-in-diesel emulsion containing an emulsifier composition in an amount effective to form a stable emulsion, the emulsifier composition comprising a polymeric non-ionic surfactant having hydrophilic and hydrophobic repeating units together with at least one component selected from:-

- a) fatty acid esters or partial esters of polyhydric alcohols;
- b) alkoxyated fatty acid esters or partial esters of polyhydric alcohols; and
- c) alkoxyated primary alcohols;

the polymeric non-ionic surfactant and said at least one component being selected such that the emulsifier composition has an hydrophile/lipophile balance value of at least 4 and, more preferably at least 5.

The hydrophile/lipophile balance (HLB) of surfactants is described in Preservation of Surfactant Formulations, Ed F F Morpeth, Published by Blackie Academic & Professional, 1995, Ch 4, Section 4.5, p77 *et al*

The invention also includes an emulsifier composition for use in fuel emulsions, which composition comprises a polymeric non-ionic surfactant having hydrophilic and hydrophobic repeating units together with at least one component selected from:-

- a) fatty acid esters or partial esters of polyhydric alcohols;
- b) alkoxyated fatty acid esters or partial esters of polyhydric alcohols; and
- c) alkoxyated primary alcohols;

the polymeric non-ionic surfactant and said at least one component being selected such that the emulsifier composition has an hydrophile/lipophile balance value of at least 4 and, more preferably at least 5.

Preferred emulsifier compositions according to the invention have an hydrophile/lipophile balance value of not more than 8 and, more preferably not more than 7 and more especially not more than 6.

Preferably, the fuel emulsion according to the invention contains at least 70% by weight diesel and up to 25%, more particularly around 10% to 20%, by weight of water, the weight percentages being based on the total weight of the emulsion.

The fuel emulsion may also contain conventional additives as previously discussed.

Preferably, the fuel emulsion comprises an amount of emulsifier composition in the range 0.1% to 4% by weight of the total weight of the composition; more preferably, an amount of emulsifier composition in the range 1% to 3% by weight; and especially an amount in the range 1% to 2.5% by weight.

Preferably, the polymeric non-ionic surfactant has an HLB of between 4 and 13, more preferably between 4 and 8. The polymeric non-ionic surfactant is preferably a polyester. Preferably, the hydrophilic units are polyoxyalkylene units, especially polyoxyethylene units; and the hydrophobic units are long chain hydrocarbon residues. Suitable polymeric non-ionic surfactants of this type are available from

Uniqema under the trade mark Hypermer (Hypermer is a trade mark owned by the ICI group of companies).

5 Preferably, component a) is the reaction product of one or more polyhydric alcohols and one or more fatty acids. The ester reaction products may be monoesters or di-, tri- or higher esters or partial esters or mixtures thereof.

10 More particularly, the polyhydric alcohols comprise glycols, ie dihydric alcohols, and higher alcohols such as glycerol, sorbitol and neopentyl alcohols such as trimethylol propane, pentaerythritol, neopentyl glycol and oligomers thereof such as di-trimethylol propane, tri-trimethylol propane, di-pentaerythritol and tri-pentaerythritol and mixtures of two or more thereof. More especially, the polyhydric alcohols comprise alcohols having at least three hydroxyl groups such as glycerol and sorbitol and preferably are sorbitol.

15 The fatty acid comprises a  $C_{12}$  to  $C_{24}$ , straight or branched chain, saturated or unsaturated acid such as myristic, palmitic, isopalmitic, stearic, isostearic, oleic and linoleic acids or mixtures thereof. More especially, the fatty acid comprises a  $C_{16}$  to  $C_{20}$  straight chain acid such as stearic or oleic acid and preferably it is oleic acid.

20 Examples of component a) are sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate, sorbitan tristearate, sorbitan sesquioleate, sorbitan monooleate and sorbitan trioleate. Suitable esters of this type are available from Uniqema under the trade mark Span (Span is a trade mark owned by the ICI group of companies).

25 Preferably, component b) is the reaction product of at least one component a) ester with an alkylene oxide.

30 Component a) esters are preferably alkoxyated using ethylene oxide or propylene oxide; especially ethylene oxide. In particular, the esters are alkoxyated with not more than 50 moles of alkylene oxide, preferably not more than 30 moles of alkylene oxide

35 Examples of component b) are polyoxyethylene versions of sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate, sorbitan tristearate, sorbitan sesquioleate, sorbitan monooleate, and sorbitan trioleate. Suitable alkoxyated esters of this type are available from Uniqema under the trade mark Tween (Tween is a trade mark owned by the ICI group of companies).

40 Preferred component c) alkoxyated primary alcohols are derived from  $C_7$ - $C_{20}$ , more especially from  $C_9$  to  $C_{15}$ , primary alcohols or mixtures thereof. The primary alcohols are preferably alkoxyated using ethylene oxide or propylene oxide; especially ethylene oxide. In particular, the alcohols are alkoxyated with not more than 50 moles of alkylene oxide, preferably not more than 30 moles of alkylene oxide.

45 Examples of component c) are polyoxyethylene versions of  $C_9/C_{11}$  and  $C_{13}/C_{15}$  mixtures of primary alcohols. Suitable alkoxyated primary alcohols are available from Uniqema under the trade mark Synperonic (Synperonic is a trade mark owned by the ICI group of companies).

50 Other components that function as emulsion couplers may also be used in the emulsifier compositions of the invention. For example, a primary alcohol may be added to the composition. The primary alcohol may be added in amounts up to 5% by weight, more preferably up to 3% by weight of the emulsifier composition. The

primary alcohol is preferably selected from C<sub>5</sub> to C<sub>15</sub>, more especially C<sub>6</sub> to C<sub>12</sub>, primary alcohols and is typically octanol.

5 Preferred emulsifier compositions according to the invention include mixtures of the polymeric non-ionic surfactant with at least two components selected from components a), b) and c). Mixtures of components a) and b) comprise especially preferred compositions of the invention.

10 Preferred emulsifier compositions according to the invention comprise not more than 50% by weight, based on the total weight of the emulsifier composition, more preferably between 1% and 30%, and more especially between 2.5% and 20% of the polymeric non-ionic surfactant in combination with at least one of components a), b) and c). More especially, emulsifier compositions comprise the polymeric non-ionic surfactant in combination with at least two of components a), b) and c). The most preferred emulsifier compositions comprise the polymeric non-ionic surfactant in combination with components a) and b). Preferably, the emulsifier compositions are formulated to have an HLB in the range 5 to 6.

20 The present invention includes a method of making a fuel emulsion which comprises a water-in-diesel emulsion containing an emulsifier composition in an amount effective to form a stable emulsion, the emulsifier composition comprising a polymeric non-ionic surfactant having hydrophilic and hydrophobic repeating units together with at least one component selected from:-

- 25 a) fatty acid esters or partial esters of polyhydric alcohols;  
b) alkoxyated fatty acid esters or partial esters of polyhydric alcohols; and  
30 c) alkoxyated primary alcohols;

the polymeric non-ionic surfactant and said at least one component being selected such that the emulsifier composition has an hydrophobe/ lipophobe balance value of at least 4 and, more preferably at least 5, which method comprises, in a single mixing operation introducing diesel and the emulsifier composition and then water into a mixing vessel whilst subjecting the mixture to high shear mixing at a speed and for a period sufficient to create the emulsion.

40 The invention will now be described further by way of example only with reference to the following Examples.

#### Example 1

45 Samples of emulsifier compositions were prepared by mixing, in a beaker, specific amounts of a polymeric non-ionic surfactant and components a) and b) as defined above. The components used in the emulsifier compositions are identified in Table 1 below and the compositions themselves are identified in Table 2 below.

50 Samples of fuel emulsions were prepared by adding the emulsifier composition samples identified in Table 2 together with a diesel fuel, available from Petroplus, into a Turrax mixer operating on setting 1 (11,000 rpm). Demineralised water was then added slowly. The samples were mixed for a further 20 minutes after completion of water addition. A proportion of each sample was transferred to a 100ml crow measuring cylinder, which was filled to the 100ml mark, to stand under observation to determine the stability of the samples.

55

The samples of fuel emulsions are identified in Table 3 below and the results of the observations are detailed in Table 4 below.

Table 1 – Emulsifier Composition Components

5

	HLB	Description
Polymeric Surfactant		
Hypermer A60*	6.0	Polyester non-ionic surfactant available from Uniqema
Hypermer A70*	6.0	Polyester non-ionic surfactant available from Uniqema. This product is a direct replacement for Hypermer A60 surfactant.
Component a)		
Span 80*	4.3	Sorbitan monooleate available from Uniqema
Span 85*	1.8	Sorbitan trioleate available from Uniqema
Component b)		
Tween 85*	11.0	POE (20) sorbitan trioleate available from Uniqema

\* Trade marks owned by the ICI group of companies.

10

15 Table 2 – Emulsifier Compositions

Sample	Span 80 % wt	Span 85 % wt	Tween 85 % wt	Hypermer A60 % wt	HLB
EC1	95			5	4.4
EC2	90			10	4.5
EC3	80			20	4.6
EC4	60			40	5.0
EC4a	58.8			41.2	5.0
EC5			10	90	6.5
EC6			20	80	7.0
EC7			30	70	7.5
EC8			40	60	8.0
EC9	76.5		13.5	10	5.4
EC10		54	36	10	5.5
EC11		65.2	34.8		5.0
EC12		54.3	45.7		6.0
EC13		4.3.5	56.5		7.0

Table 3 – Fuel Emulsions

Sample	Emulsifier Composition % wt	Diesel % wt	Water % wt
FE1	EC1 – 2.0%	88.0	10.0
FE2	EC2 - 1.6%	88.4	10.0
FE3	EC3 - 1.2%	88.8	10.0
FE4	EC4 - 0.7%	89.3	10.0
FE4a	EC4a - 0.7%	89.3	10.0
FE5	EC5 – 2.0%	88.0	10.0
FE6	EC6 – 2.0%	88.0	10.0
FE7	EC7 – 2.0%	88.0	10.0
FE8	EC8 – 2.0%	88.0	10.0
FE9	EC9 – 1.0%	89.0	10.0
FE9a	EC9 – 2.0%	88.0	10.0
FE10	EC10 – 1.0%	89.0	10.0
FE10a	EC10 – 2.0%	88.0	10.0
FE11	EC11 – 1.0%	89.0	10.0
FE11a	EC11 – 2.0%	88.0	10.0
FE12	EC12 – 1.0%	89.0	10.0
FE12a	EC12 – 2.0%	88.0	10.0
FE13	EC13 – 1.0%	89.0	10.0
FE13a	EC13 – 2.0%	88.0	10.0

In Table 4, the observations are as follows:

5

- a) “cloudy” = emulsion;
- b) “cream” = water rich layer at bottom of cylinder;
- c) “oil” = separated diesel layer at top of cylinder; and
- d) “water” = separated water layer at bottom of cylinder.

10

As fuel is drawn from the bottom of tanks supplying engines, the presence of “water” at the bottom of the fuel emulsion is the most detrimental observation. It will be readily apparent that too high a proportion of water drawn into the engine will result in stoppage of the engine. Although the presence of “cream”, ie the water-rich layer, is not particularly desired for the same reason, “cream” is still an emulsion containing diesel.

15

The observations in Table 4 were taken at regular intervals. The observations for Samples FE1 to FE4 were taken at 5, 7, 11, 13 and 15 days; the observations of the Samples FE4a to FE13a were taken variously at 6, 9 and 13 days, 3, 7 and 11 days, 3, 7, 11 and 18 days and 3 and 11 days. The columns for 7 and 11 days observations are the same throughout the table for ease of reference.

20

Samples FE1 to FE4 and FE4a were prepared on an equal cost basis, ie the cost of the amount of emulsifier composition in each sample is substantially the same. It is to be noted opposite Samples FE4 and FE4a that they maintained the water in the fuel emulsion even though they were present at a relatively low level. However, a significant amount of oil separated from the emulsion.

25

Comparative Samples FE11 to FE13a show significant water separation even after only 3 days.

30

Table 4 – Fuel Emulsion Stability Observations

Sample	HLB	5 days	7 days	11 days	13 days	15 days
FE1	4.4	1ml oil Cloudy to bottom	1ml oil Cloudy to bottom	1ml oil Cloudy to bottom	1ml oil Cloudy to bottom	2ml oil Cloudy to bottom
FE2	4.5	<0.5ml oil Cloudy to bottom	0.5ml oil Cloudy to bottom	0.5ml oil Cloudy to bottom	0.5ml oil Cloudy to bottom	2ml oil Cloudy to bottom
FE3	4.6	<0.5ml oil Cloudy to bottom	<0.5ml oil Cloudy to bottom	<0.5ml oil Cloudy to bottom	<0.5ml oil Cloudy to bottom	<0.5ml oil Cloudy to bottom
FE4	5.0	2ml oil Cloudy to bottom	3ml oil Cloudy to bottom	5ml oil Cloudy to bottom	5ml oil Cloudy to bottom	7.5ml oil Cloudy to bottom
		6 days	9 days		13 days	
FE4a	5.0	1ml oil 1ml cream	1.5ml oil 1ml cream		1ml oil 2ml cream	
		3 days	7 days	11 days		
FE5	6.5	Trace oil Cloudy to bottom	Trace oil Cloudy to bottom	1ml oil Cloudy to bottom		
FE6	7.0	Trace oil Cloudy to bottom	Trace oil Cloudy to bottom	1ml oil Cloudy to bottom		
FE7	7.5	Trace oil Cloudy to bottom	Trace oil Cloudy to bottom	1ml oil Cloudy to bottom		
FE8	8.0	Trace oil Cloudy to bottom	Trace oil Cloudy to bottom	1ml oil Cloudy to bottom		
		3 days	7 days	11 days		18 days
FE9	5.4	<0.5ml oil <0.5ml cream	1.0 oil <0.5ml cream	Trace oil 4ml cream		2ml oil 7.5ml cream
FE9a	5.4	<0.5ml oil <0.5ml cream	1.0 oil <0.5ml cream	1ml oil 1.5ml cream		1ml oil 2ml cream
FE10	5.5	<0.5ml oil <0.5ml cream	1.0 oil <0.5ml cream	1.5 oil <0.5ml cream		2ml oil 1ml water
FE10a	5.5	<0.5ml oil <0.5ml cream	0.5 oil <0.5ml cream	1.0 oil <0.5ml cream		1ml oil No water
FE11*	5.0	1ml oil 5ml water		1ml oil 5ml water		

Table 4 (continued)

FE11a*	5.0	No clear oil 1ml cream		No clear oil 1ml cream		
FE12*	6.0	1ml oil 7ml water		1ml oil 8ml water		
FE12a*	6.0	1ml oil 2ml water		Trace oil 4ml water		
FE13*	7.0	1ml oil 8ml water		3ml oil 9ml water		
FE13a*	7.0	1ml oil 6ml water		2.5ml oil 8ml water		

\* Comparative examples.

5

#### Example 2 – Comparative Method

Samples EC1 to EC4 were each mixed in a beaker with diesel in the proportions shown in Table 5. To each fuel/emulsifier composition sample CFE1 to CFE4 was added 0.25g of demineralised water, mixing being effected by low shear stirring. The water was not dispersed in the diesel but remained as separate globules in the bottom of the beaker.

10

#### Table 5 – Comparative Fuel/Emulsifier Compositions

15

Sample	Emulsifier Composition % wt	Diesel % wt
CFE1	EC1 – 2.0%	98.0
CFE2	EC2 - 1.6%	98.4
CFE3	EC3 - 1.2%	98.8
CFE4	EC4 - 0.7%	99.3

This Example demonstrates that, even with very small quantities of water, low shear mixing is ineffective.

#### Example 3 – Comparative Method

Samples CFE5 to CFE8 were prepared using quantities of EC1 to EC4 as shown in Table 6. To each of those samples was added drop wise 100g of demineralised water, mixing being effected by high shear stirring using a Turrax stirrer on setting 1 (11,000rpm). 20g of each of diesel/emulsifier composition/water sample (Samples CFE5a to CFE8a) was added to 80g of diesel; transferred to a 100ml stoppered measuring cylinder; and the cylinder was inverted four times to mix the contents thereof.

25

This resulted in a final percentage by weight concentration of emulsifier composition as shown in Table 7. The observations on the samples are shown in Table 7.

30

There was no water layer present in any of the samples although there were significant levels of cream, ie a water rich layer, in the samples. This Example demonstrates that preparing a separate "master batch" of fuel emulsion was not as

35

effective as mixing the ingredients in a single mixing operation as set out in Example 1.

Table 6 – Comparative Fuel/Emulsifier Compositions

5

Sample	Emulsifier Composition % wt	Diesel % wt
CFE5	EC1 – 20.0%	80.0
CFE6	EC2 – 16.0%	84.0
CFE7	EC3 – 12.0%	88.0
CFE8	EC4 – 7.00%	93.0

Table 7 – Comparative Fuel Emulsion Compositions

Sample	HLB	%age concentration of emulsifier composition	2 days	4 days	7 days	21 days
CFE5a	4.39	2.0	2ml oil 1.5ml cream	2ml oil 2.5ml cream	Tracel oil* 7ml cream	Tracel oil* 13ml cream
CFE6a	4.47	1.6	2ml oil 1.5ml cream	2ml oil 1.5ml cream	Tracel oil* 5ml cream	Tracel oil* 13ml cream
CFE7a	4.64	1.2	2ml oil 1ml cream	2ml oil 1ml cream	Tracel oil* 3ml cream	Tracel oil* 12ml cream
CFE8a	5.0	.07	1ml oil <0.5ml cream	2ml oil <0.03ml cream	2.5ml oil 1.5ml cream	7ml oil 8ml cream

10 \* Very difficult to estimate as progressively cloudy with no clear interface.

Claims

1. A fuel emulsion comprises a water-in-diesel emulsion containing an emulsifier composition in an amount effective to form a stable emulsion, the emulsifier composition comprising a polymeric non-ionic surfactant having hydrophilic and hydrophobic repeating units together with at least one component selected from:-
- 5
- 10
- 15
- 20
- 25
- 30
- 35
- 40
- 45
- 50
- 55
- a) fatty acid esters or partial esters of polyhydric alcohols;
  - b) alkoxyated fatty acid esters or partial esters of polyhydric alcohols; and
  - c) alkoxyated primary alcohols;
- the polymeric non-ionic surfactant and said at least one component being selected such that the emulsifier composition has an hydrophile/lipophile balance value of at least 4.
2. A fuel emulsion according to claim 1 which contains at least 70% by weight diesel and up to 25% by weight of water, the weight percentages being based on the total weight of the emulsion.
3. A fuel emulsion according to claim 1 or claim 2 comprising an amount of emulsifier composition in the range 0.1% to 4% by weight of the total weight of the composition; more preferably, an amount of emulsifier composition in the range 1% to 3% by weight; and especially an amount in the range 1% to 2.5% by weight.
4. A fuel emulsion according to any one of the preceding claims in which the emulsifier composition has an hydrophile/lipophile balance value of at least 5.
5. A fuel emulsion according to any one of the preceding claims in which the emulsifier composition has an hydrophile/lipophile balance value of not more than 8 and, more preferably not more than 7 and more especially not more than 6.
6. A fuel emulsion according to any one of the preceding claims which comprises not more than 50% by weight, based on the total weight of the emulsifier composition, more preferably between 1% and 30%, and more especially between 2.5% and 20% of the polymeric non-ionic surfactant in combination with at least one of components a), b) and c).
7. A fuel emulsion any one of the preceding claims which comprises the polymeric non-ionic surfactant in combination with at least two of components a), b) and c).
8. A fuel emulsion according to any one of the preceding claims which comprises the polymeric non-ionic surfactant in combination with components a) and b).
9. A fuel emulsion according to any one of the preceding claims in which the polymeric non-ionic surfactant is a polyester in which the hydrophilic units are polyoxyalkylene units and the hydrophobic units are long chain hydrocarbon residues.

- 5
10. A fuel emulsion according to any one of the preceding claims in which component a) is a reaction product of one or more polyhydric alcohols and one or more fatty acids.
11. A fuel emulsion according to claim 10 in which the polyhydric alcohol comprises alcohols having at least three hydroxyl groups.
- 10 12. A fuel emulsion according to claim 10 or claim 11 in which the polyhydric alcohol is selected from glycerol and sorbitol.
13. A fuel emulsion according to any one of claims 10 to 12 in which the fatty acid comprises a C<sub>12</sub> to C<sub>24</sub>, straight or branched chain, saturated or unsaturated acid.
- 15 14. A fuel emulsion according to any one of claims 10 to 13 in which the fatty acid comprises a C<sub>16</sub> to C<sub>20</sub> straight chain acid.
- 20 15. A fuel emulsion according to any one of claims 10 to 13 in which the fatty acid is selected from stearic acid or oleic acid.
- 25 16. A fuel emulsion according to any one of the preceding claims in which component b) is a reaction product of at least one component a) with an alkylene oxide.
17. A fuel emulsion according to any one of the preceding claims in which component b) is a reaction product of at least one component a) with not more than 50 moles, and preferably not more than 30 moles, of an alkylene oxide.
- 30 18. A fuel emulsion according to any one of the preceding claims in which component c) is a reaction product of C<sub>7</sub>-C<sub>20</sub>, more especially from C<sub>9</sub> to C<sub>15</sub>, primary alcohols or mixtures thereof with an alkylene oxide.
- 35 19. A fuel emulsion according to any one of the preceding claims in which component c) is a reaction product of C<sub>7</sub>-C<sub>20</sub>, more especially from C<sub>9</sub> to C<sub>15</sub>, primary alcohols or mixtures thereof with not more than 50 moles, and preferably not more than 30 moles, of an alkylene oxide.
- 40 20. A fuel emulsion according to any one of the preceding claims comprising a primary alcohol.
21. A fuel emulsion according to claim 20 comprising a primary alcohol selected from C<sub>5</sub> to C<sub>15</sub>, more especially C<sub>6</sub> to C<sub>12</sub>, primary alcohols.
- 45 22. A fuel emulsion according to claim 20 or claim 21 in which the primary alcohol comprises up to 5% by weight, more preferably up to 3% by weight of the emulsifier composition.
- 50 23. An emulsifier composition for use in fuel emulsions, which composition comprises a polymeric non-ionic surfactant having hydrophilic and hydrophobic repeating units together with at least one component selected from:-
- 55 a) fatty acid esters or partial esters of polyhydric alcohols;

b) alkoxyated fatty acid esters or partial esters of polyhydric alcohols;  
and

5 c) alkoxyated primary alcohols;

the polymeric non-ionic surfactant and said at least one component being  
selected such that the emulsifier composition has an hydrophile/lipophile  
balance value at least 4.

10

24. An emulsifier composition according to claim 23 having an hydrophile/  
lipophile balance value of at least 5.

15 25. An emulsifier composition according to claim 23 or claim 24 having an  
hydrophile/lipophile balance value of not more than 8 and, more preferably  
not more than 7 and more especially not more than 6.

20 26. An emulsifier composition according to any one of claims 23 to 25 which  
comprises not more than 50% by weight, based on the total weight of the  
emulsifier composition, more preferably between 1% and 30%, and more  
especially between 2.5% and 20% of the polymeric non-ionic surfactant in  
combination with at least one of components a), b) and c).

25 27. An emulsifier composition according to any one of claims 23 to 26 which  
comprises the polymeric non-ionic surfactant in combination with at least two  
of components a), b) and c).

30 28. An emulsifier composition according to any one of claims 23 to 27 which  
comprises the polymeric non-ionic surfactant in combination with components  
a) and b).

35 29. An emulsifier composition according to any one of claims 23 to 28 in which  
the polymeric non-ionic surfactant is a polyester in which the hydrophilic units  
are polyoxyalkylene units and the hydrophobic units are long chain  
hydrocarbon residues.

40 30. An emulsifier composition according to any one of claims 23 to 29 in which  
component a) is a reaction product of one or more polyhydric alcohols and  
one or more fatty acids.

31. An emulsifier composition according to claim 30 in which the polyhydric  
alcohol comprises alcohols having at least three hydroxyl groups.

45 32. An emulsifier composition according to claim 30 or claim 31 in which the  
polyhydric alcohol is selected from glycerol and sorbitol.

50 33. An emulsifier composition according to any one of claims 30 to 32 in which  
the fatty acid comprises a C<sub>12</sub> to C<sub>24</sub>, straight or branched chain, saturated or  
unsaturated acid.

34. An emulsifier composition according to any one of claims 30 to 33 in which  
the fatty acid comprises a C<sub>16</sub> to C<sub>20</sub> straight chain acid.

35. An emulsifier composition according to any one of claims 30 to 34 in which the fatty acid is selected from stearic acid or oleic acid.
- 5 36. An emulsifier composition according to any one of claims 23 to 35 in which component b) is a reaction product of at least one component a) with an alkylene oxide.
- 10 37. An emulsifier composition according to claim 36 in which component b) is a reaction product of at least one component a) with not more than 50 moles, and preferably not more than 30 moles, of an alkylene oxide.
- 15 38. An emulsifier composition according to any one of claims 23 to 37 in which component c) is a reaction product of C<sub>7</sub>-C<sub>20</sub>, more especially from C<sub>9</sub> to C<sub>15</sub>, primary alcohols or mixtures thereof with an alkylene oxide.
- 20 39. An emulsifier composition according to claim 38 in which component c) is a reaction product of C<sub>7</sub>-C<sub>20</sub>, more especially from C<sub>9</sub> to C<sub>15</sub>, primary alcohols or mixtures thereof with not more than 50 moles, and preferably not more than 30 moles, of an alkylene oxide.
- 25 40. An emulsifier composition according to any one of claims 23 to 39 comprising a primary alcohol.
- 30 41. An emulsifier composition according to claim 40 comprising a primary alcohol selected from C<sub>5</sub> to C<sub>15</sub>, more especially C<sub>6</sub> to C<sub>12</sub> primary alcohols.
- 35 42. An emulsifier composition according to claim 40 or claim 41 in which the primary alcohol comprises up to 5% by weight, more preferably up to 3% by weight of the emulsifier composition.
- 40 43. A method of making a fuel emulsion which comprises a water-in-diesel emulsion containing an emulsifier composition in an amount effective to form a stable emulsion, the emulsifier composition comprising a polymeric non-ionic surfactant having hydrophilic and hydrophobic repeating units together with at least one component selected from:-
- a) fatty acid esters or partial esters of polyhydric alcohols;
  - b) alkoxyated fatty acid esters or partial esters of polyhydric alcohols; and
  - c) alkoxyated primary alcohols;
- 45 the polymeric non-ionic surfactant and said at least one component being selected such that the emulsifier composition has an hydrophobe/lipophobe balance value of at least 4 and, more preferably at least 5., wherein said method comprises, in a single mixing operation introducing diesel and the emulsifier composition and then water into a mixing vessel whilst
- 50 subjecting the mixture to high shear mixing at a speed and for a period sufficient to create the emulsion.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCI/GB 02/04254

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C10L1/32

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 002 400 A (ICI LTD) 21 February 1979 (1979-02-21)  page 4, line 14 - line 51; claim 1; examples 6,7	1-6, 18-21, 23-26, 38-41
X	--- WO 01 55282 A (BASF AG ;STANG MICHAEL (DE); HUEFFER STEPHAN (DE); EISENBEIS ANSGA) 2 August 2001 (2001-08-02)  page 5, line 23 -page 6, line 5; claims; examples  --- -/--	1-7, 9-15, 18-20, 22-27, 29-35, 38-40, 42,43

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

6 March 2003

18/03/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax: (+31-70) 340-3016

Authorized officer

Keipert, 0

## INTERNATIONAL SEARCH REPORT

International Application No

PC 1/GB 02/04254

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 01 51593 A (AMBROSINI TIZIANO ;RIVOLTA GUIDO (IT); CAMFIN S P A (IT); ALBIZZAT) 19 July 2001 (2001-07-19) page 9, line 32 -page 10, line 3 page 11, line 30 -page 12, line 9; examples 1,2,4 ---	1-20, 23-40,43
Y	GB 2 066 288 A (LABOFINA SA) 8 July 1981 (1981-07-08) cited in the application page 2, line 5-38; example 1 ---	1-20, 23-40,43
A	GB 2 117 398 A (ICI PLC) 12 October 1983 (1983-10-12) claim 1; examples 5,8 ---	1-43
A	WO 99 63024 A (CATERPILLAR INC) 9 December 1999 (1999-12-09) example 1 -----	1-43

## INTERNATIONAL SEARCH REPORT

International Application No

PC 1/GB 02/04254

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 2002400	A	21-02-1979	AU 523572 B2	05-08-1982
			AU 3777378 A	10-01-1980
			CA 1126288 A1	22-06-1982
			DE 2862369 D1	08-03-1984
			DK 311278 A	13-01-1979
			EP 0000424 A1	24-01-1979
			ES 471652 A1	01-10-1979
			IT 1097231 B	26-08-1985
			JP 1070525 A	16-03-1989
			JP 1655772 C	13-04-1992
			JP 3017534 B	08-03-1991
			JP 1034532 B	19-07-1989
			JP 1557280 C	16-05-1990
			JP 54018898 A	13-02-1979
			JP 1724315 C	24-12-1992
			JP 3174240 A	29-07-1991
			JP 4011251 B	27-02-1992
			NZ 187767 A	24-10-1980
			US 4203877 A	20-05-1980
			ZA 7803802 A	25-07-1979
WO 0155282	A	02-08-2001	DE 10003105 A1	26-07-2001
			WO 0155282 A1	02-08-2001
			EP 1252272 A1	30-10-2002
			NO 20023524 A	25-09-2002
			US 2003024852 A1	06-02-2003
WO 0151593	A	19-07-2001	AU 2513901 A	24-07-2001
			BR 0107632 A	08-10-2002
			WO 0151593 A1	19-07-2001
			EP 1252271 A1	30-10-2002
GB 2066288	A	08-07-1981	LU 81921 A1	04-06-1981
			LU 82566 A1	20-01-1982
			AT 370764 B	10-05-1983
			AT 552780 A	15-09-1982
			BE 886081 A1	07-05-1981
			CH 644889 A5	31-08-1984
			DE 3042124 A1	11-06-1981
			DK 468980 A	23-05-1981
			ES 8200716 A1	01-02-1982
			FR 2470153 A1	29-05-1981
			IT 1134401 B	13-08-1986
			NL 8006041 A	16-06-1981
			NO 803499 A ,B,	25-05-1981
			PT 72085 A ,B	01-12-1980
			SE 8008173 A	23-05-1981
			AU 532252 B2	22-09-1983
			AU 6452280 A	25-06-1981
			CA 1142871 A1	15-03-1983
			DE 3047502 A1	24-09-1981
			FR 2472011 A1	26-06-1981
			IT 1146246 B	12-11-1986
			JP 1256741 C	29-03-1985
			JP 56093793 A	29-07-1981
			JP 59032511 B	09-08-1984
			MX 156837 A	07-10-1988
			NL 8006703 A	16-07-1981

## INTERNATIONAL SEARCH REPORT

International Application No

PCI/GB 02/04254

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 2066288	A		US 4411768 A	25-10-1983
			US RE32265 E	14-10-1986
			ZA 8007238 A	28-07-1982
-----				
GB 2117398	A	12-10-1983	BR 8300970 A	16-11-1983
-----				
WO 9963024	A	09-12-1999	AU 4228099 A	20-12-1999
			WO 9963024 A1	09-12-1999
-----				