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PATENT SPECIFICATION

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(54) DETERGENT COMPOSITIONS

(71) We, SHELL INTERNATIONALE RE-
SEARCH MAATSCHAPPIJ B.V. (formerly N.V.),
a company organised under the laws of The
Netherlands, of 30 Carel van Bylandtlaan,
The Hague, The Netherlands, do hereby de-
clare the invention, for which we pray that a
patent may be granted to us, and the method
by which it is to be performed, to be par-
ticularly described in and by the following
statement:—

The present invention is concerned with
a composition suitable for emulsifying oil
and with a process for dispersing oil, and
relates to an improvement in or modifica-
tion of the invention claimed in U.K. Speci-
fication No. 1,280,259.

U.K. Specification No. 1,280,259 claims a
method for dispersing oil spilled on water or
on shores, comprising applying a composi-
tion comprising a monoester of an aliphatic
carboxylic acid and a polyoxyalkylene
glycol, and a liquid hydrocarbon solvent
containing from 0 to 10% weight, based on
weight of said liquid hydrocarbon, of aro-
matic compounds, to the oil and agitating
the mixture formed thereby to disperse the
oil.

Although such monoesters, for example,
the fatty acid monoesters of polyethylene
glycols have been well-known per se as
surface-active agents for many years — see,
for example, the paper by J.D. Malkemus
and J.D. Swan in *The Journal of the
American Oil Chemists' Society* Vol. 34,
1957, at pages 372-4, the Applicants found
that their use in combination with hydro-
carbon solvents as just specified provided
unexpected advantages in regard to the
treatment of oil spillages, which, of course,
is a problem which has received very con-
siderable attention in recent years. Surpris-
ingly, the Applicants have now found that
if a mixture of two different such monoesters
is used in such compositions, the composi-
tions have particularly advantageous charac-

teristics in terms of oil-emulsifying prop-
erties and level of toxicity to aquatic life,
in particular to marine life.

According to the present invention a
composition suitable for emulsifying oil, 50
comprises (i) a monoester, having an
average molecular weight of at least 530, of
an aliphatic carboxylic acid and a poly-
oxyalkylene glycol, (ii) a monoester, having
an average molecular weight of below 530, 55
of an aliphatic carboxylic acid and a poly-
oxyalkylene glycol, and (iii) a liquid hydro-
carbon solvent containing from 0 to 10% by
weight, based on weight of said liquid
hydrocarbon, of aromatic compounds, the 60
average molecular weight of the mixture of
(i) and (ii) in the composition being from
430 to 680, preferably from 470 to 570.

The average molecular weight of the
mixture of (i) and (ii) is determined by 65
dividing the sum of the number of parts by
weight of (i) and (ii) in the composition by
the sum of the number of parts by weight
of (i) divided by the average molecular
weight of (i) and the number of parts by 70
weight of (ii) divided by the average molecu-
lar weight of (ii).

Preferably, the difference between the
average molecular weights of monoesters (i)
and (ii) is at least 100 and more preferably 75
at least 190.

Preferably, the composition according to
the invention comprises 5 to 50%, more
preferably 10 to 20% by weight, based on
weight of composition, of the mixtures of 80
monoesters (i) and (ii).

Generally, the monoesters should form a
homogenous solution or a stable dispersion
with the liquid hydrocarbon. Suitably, the
monoesters are in the liquid state at ambient 85
temperatures.

The monoesters present in the composi-
tions according to the invention, are mono-
esters of the same or different aliphatic
carboxylic acids, and polyoxyalkylene gly- 90

cols; and their nature is well-known per se. Preferably, monoesters of unsaturated or saturated aliphatic monocarboxylic acids comprising from 10 to 20 carbon atoms, more preferably from 14 to 18 carbon atoms, are used in carrying out the present invention. Generally, in order that the monoesters prepared from such acids are liquids at ambient temperatures, a higher degree of olefinic unsaturation is required in the aliphatic carboxylic acids containing a high number of carbon atoms, e.g. from 17 to 20 carbon atoms, than in the aliphatic carboxylic acids containing a low number of carbon atoms. As suitable aliphatic monocarboxylic acids may be mentioned lauric acid, myristic acid, palmitic acid, oleic acid, linoleic acid and linolenic acid, oleic acid being preferred.

Preferably, the monoesters are monoesters of polyoxyethylene and/or polyoxypropylene glycols, with polyoxyethylene glycols being preferred. The molecular weight of suitable polyoxyalkylene glycols is advantageously from 106 to 1,000, with from 106 to 600 being preferred. Preferably, the monoester having an average molecular weight of at least 530 is a monoester of an aliphatic carboxylic acid and a polyoxyethylene glycol having an average molecular weight of from 300 to 600. Preferably, the monoester having an average molecular weight of below 530 is a monoester of an aliphatic carboxylic acid and diethylene glycol or triethylene glycol. Commercial processes are available for the manufacture of the monoesters referred to herein, such processes, which are well-known per se, comprising esterifying aliphatic carboxylic acids with polyoxyalkylene glycols in the presence of an esterification catalyst or alkoxylating aliphatic carboxylic acids with alkylene oxides in the presence of an alkoxylation catalyst (it being understood that these alkoxylation products may be described as monoesters of aliphatic carboxylic acids and polyoxyalkylene glycols). Monoesters made by such processes are accordingly used in carrying out the present invention.

The composition according to the invention also comprises a liquid hydrocarbon solvent containing from 0 to 10% by weight, preferably less than 5% by weight, more preferably less than 3% by weight based on weight of the liquid hydrocarbon, of aromatic compounds. Suitable liquid hydrocarbons have a viscosity of less than 20cs, more preferably less than 10cs at 20°C. The liquid hydrocarbon preferably comprises from 5 to 20 carbon atoms per molecule and has a boiling point above 50°C. As examples of suitable liquid hydrocarbons may be mentioned pentanes, hexanes, octanes, decanes, dodecanes, cyclopentanes, cyclohexanes, and alkyl substituted deriva-

tives thereof such as di- and trimethylhexanes, butylcyclopentanes and butylcyclohexanes. Mixtures of suitable liquid hydrocarbons may be obtained by the distillation of petroleum.

A preferred liquid hydrocarbon can be prepared by taking the kerosene fraction obtained during the distillation of petroleum and reducing the amount of aromatic compounds therein to 10% or less. Such kerosene fractions may have a boiling point range of from 140° to 325°C e.g. 175° to 325°C and may have a flash point of from 65°C to 75°C. A particularly preferred kerosene fraction are those products frequently referred to "odourless" kerosenes. Such "odourless" kerosenes usually have an aromatic content of 3% or below e.g. 2%, 1% or 0.1%. "Odourless" kerosenes usually mainly comprise a mixture of C₁₀ to C₁₈ paraffins, isoparaffins, naphthenes and alkyl-substituted naphthenes.

The composition according to the invention may comprise components in addition to those disclosed above. Suitable additional components include surface-active agents, such as alkali-metal salts of alkyl aryl sulphonates, and alkali-metal salts of fatty acids.

The compositions according to the invention can be used to disperse oil in any known manner. According to this aspect of the invention a method for dispersing oil comprises applying a composition as described above to the oil and agitating the mixture formed thereby to disperse the oil. This method may be used to disperse oil spillages on water or on shores or to clean out vessels which have been used to store oil. The compositions are particularly suitable for dispersing crude oil spillages e.g. oil-slicks on sea-water. Advantageously the amount of composition applied to the crude oil spillages is from 10% to 100% by volume, based on the volume of crude oil, with from 25% to 50%, by volume, being preferred. Suitably the compositions are sprayed on to the surface of the crude oil to form a mixture. The mixture is then agitated which helps break it into small droplets and disperse the oil. For example, the mixture produced by applying such compositions to an oil slick on the sea surface may be agitated by ship's propellers, hosed sea water or by towing a surface agitator through the mixture. Alternatively, the aforesaid application and agitation can be achieved simultaneously by hosing a mixture of the composition and sea water onto the oil slick.

The invention will now be illustrated by the following examples.

Example 1

Six compositions according to the invention were formulated as described in Table 1.

Table 1

Monoester	Compositions (pbw)					
	1	2	3	4	5	6
PEG ⁶⁰⁰ mono-oleate	7.5		5.63			
PEG 400 mono-oleate		11.25			6.0	
PEG 300 mono-oleate				12		10.0
TEG ³ mono-oleate	7.5		9.37		9.0	
DEG ³ mono-oleate		3.75		3		5.0
Odourless Kerosene	85	85	85	85	85	85
Average molecular weight of monoester mixture	560	554	515	511	552	480

1. Polyoxyethylene glycols (the number following PEG refers to the average molecular weight thereof)

5 2. Triethylene glycol

3. Diethylene glycol

The term odourless kerosene as used above represents a mixture of C₁₀ to C₁₈ paraffins, isoparaffins, naphthenes and 10 alkyl-substituted naphthenes and about 3% wt. based on weight of mixture, of aromatic compounds. The mixture has a flash point of about 72°C (determined by the Persky-Martens Closed Cup Method); a 15 boiling range of 175° to 325°C and a viscosity of about 5cs at 20°C.

Two further compositions (7, 8) were formulated for comparative purposes.

Composition 7 consisted of 15 pbw of 20 PEG200 mono-oleate and 100 pbw of odourless kerosene.

Composition 8 consisted of oleyl/cetyl ethoxylate (containing three molecules of ethylene oxide) in a mixture of hexylene 25 glycol and kerosene.

Example 2

The eight compositions of Example 1 were used to disperse oil on sea water. Mixtures of oil and the composition were 30 poured onto sea-water and the time taken to disperse the oil was noted. Compositions 1 to 6 dispersed the oil more effectively and rapidly than compositions 7 and 8.

35 WHAT WE CLAIM IS:—

1. A composition suitable for emulsifying oil, comprising

40 (i) a monoester, having an average molecular weight of at least 530, of an aliphatic carboxylic acid and a polyoxyalkylene glycol,

(ii) a monoester, having an average molecular weight of below 530, of an aliphatic carboxylic acid and a polyoxyalkylene glycol, and 45 (iii) a liquid hydrocarbon solvent containing from 0 to 10% by weight, based on weight of said liquid hydrocarbon, of aromatic compounds. 50

wherein the average molecular weight of the mixture of (i) and (ii) in the composition is from 430 to 680.

2. A composition as claimed in claim 1, wherein said composition comprises from 5 55 to 50% wt. based on weight of said composition of the mixture of monoesters (i) and (ii).

3. A composition as claimed in claim 1 or 2, wherein said monoesters are both 60 monoesters of the same or different aliphatic monocarboxylic acids comprising from 14 to 18 carbon atoms.

4. A composition as claimed in claim 3, wherein both monoesters are monoesters of 65 oleic acid.

5. A composition as claimed in any one of claims 1 to 4, wherein said monoester, having an average molecular weight of at least 530, is a monoester of an aliphatic 70 carboxylic acid and a polyoxyethylene glycol having an average molecular weight of from 300 to 600.

6. A composition as claimed in any one of claims 1 to 5, wherein said monoester, 75 having an average molecular weight of below 530 is a monoester of an aliphatic carboxylic acid and diethylene glycol or triethylene glycol.

7. A composition as claimed in any one 80 of claims 1 to 5, wherein the difference in

Table 1

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PEG 400 mono-oleate		11.25			6.0	
PEG 300 mono-oleate				12		10.0
TEG ³ mono-oleate	7.5		9.37		9.0	
DEG ³ mono-oleate		3.75		3		5.0
Odourless Kerosene	85	85	85	85	85	85
Average molecular weight of monoester mixture	560	554	515	511	552	480

1. Polyoxyethylene glycols (the number following PEG refers to the average molecular weight thereof)
 - 5 2. Triethylene glycol
 3. Diethylene glycol
- The term odourless kerosene as used above represents a mixture of C₁₀ to C₁₈ paraffins, isoparaffins, naphthenes and alkyl-substituted naphthenes and about 3% wt. based on weight of mixture, of aromatic compounds. The mixture has a flash point of about 72°C (determined by the Persky-Martens Closed Cup Method); a boiling range of 175° to 325°C and a viscosity of about 5cs at 20°C.
- Two further compositions (7, 8) were formulated for comparative purposes.
- Composition 7 consisted of 15 pbw of 20 PEG200 mono-oleate and 100 pbw of odourless kerosene.
- Composition 8 consisted of oleyl/cetyl ethoxylate (containing three molecules of ethylene oxide) in a mixture of hexylene 25 glycol and kerosene.
- Example 2**
- The eight compositions of Example 1 were used to disperse oil on sea water. Mixtures of oil and the composition were 30 poured onto sea-water and the time taken to disperse the oil was noted. Compositions 1 to 6 dispersed the oil more effectively and rapidly than compositions 7 and 8.
- 35 **WHAT WE CLAIM IS:—**
1. A composition suitable for emulsifying oil, comprising
 - (i) a monoester, having an average molecular weight of at least 530, of 40 an aliphatic carboxylic acid and a polyoxyalkylene glycol,
 - (ii) a monoester, having an average molecular weight of below 530, of an aliphatic carboxylic acid and a polyoxyalkylene glycol, and 45
 - (iii) a liquid hydrocarbon solvent containing from 0 to 10% by weight, based on weight of said liquid hydrocarbon, of aromatic compounds, 50
 wherein the average molecular weight of the mixture of (i) and (ii) in the composition is from 430 to 680.
 2. A composition as claimed in claim 1, wherein said composition comprises from 5 55 to 50% wt. based on weight of said composition of the mixture of monoesters (i) and (ii).
 3. A composition as claimed in claim 1 or 2, wherein said monoesters are both 60 monoesters of the same or different aliphatic monocarboxylic acids comprising from 14 to 18 carbon atoms.
 4. A composition as claimed in claim 3, wherein both monoesters are monoesters of 65 oleic acid.
 5. A composition as claimed in any one of claims 1 to 4, wherein said monoester, having an average molecular weight of at least 530, is a monoester of an aliphatic 70 carboxylic acid and a polyoxyethylene glycol having an average molecular weight of from 300 to 600.
 6. A composition as claimed in any one of claims 1 to 5, wherein said monoester, 75 having an average molecular weight of below 530 is a monoester of an aliphatic carboxylic acid and diethylene glycol or triethylene glycol.
 7. A composition as claimed in any one 80 of claims 1 to 5, wherein the difference in



* C L M S *

the molecular weights of monoesters (i) and (ii) is at least 190.

8. A composition as claimed in any one of claims 1 to 7, wherein said liquid hydrocarbon contains less than 5% by weight, based on weight of the liquid hydrocarbon, of aromatic compounds.

9. A composition as claimed in claim 8, wherein said liquid hydrocarbon comprises a mixture of C_{10} to C_{28} paraffins, isoparaffins, naphthenes and alkyl-substituted naphthenes and about 3% by weight based on weight of the liquid hydrocarbon, of aromatic compounds.

10. A composition as claimed in any one of the preceding claims wherein the viscosity of said liquid hydrocarbon is less than 10cs at 20°C.

11. A composition as claimed in any one of the preceding claims wherein the liquid hydrocarbon is "odourless" kerosene.

12. A composition as claimed in claim 1, substantially as hereinbefore described with particular reference to the Examples.

13. A method for dispersing oil comprising applying a composition as claimed in

any one of claims 1 to 12 to the oil and agitating the mixture formed thereby to disperse the oil.

14. A method as claimed in claim 13, 30 wherein said oil is a crude oil slick on sea water.

15. A method as claimed in claim 14, wherein the amount of composition applied to said crude oil slick is from 25% to 50% 35 by volume, based on the volume of said crude oil slick.

16. A method as claimed in claim 14 or 15, comprising applying a mixture of sea water and a composition as claimed in any one of claims 1 to 12 to the oil and agitating the mixture formed thereby to disperse the oil.

17. A method as claimed in claim 13, substantially as hereinbefore described with 45 particular reference to Example 2.

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