

AMENDED SPECIFICATION

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PATENT SPECIFICATION

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(54) DETERGENT COMPOSITIONS

(71) We, SHELL INTERNATIONAL-
ALE RESEARCH MAATSCHAPPIJ 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 particu-
larly described in and by the following state-
ment:—

The invention is concerned with a method
for dispersing oil.

It is known that oil spilled on water or on
shores can be dispersed by firstly applying
to it a composition containing a surface-active
agent which emulsifies the oil and secondly
agitating the resulting mixture to disperse the
oil. However, one disadvantage of known com-
positions is that they can have a high toxicity
to aquatic life.

It is one object of this invention to provide
a method for dispersing oil which shows ad-
vantages from the point of view of toxicity to
aquatic life.

According to the invention a method for
dispersing oil spilled on water or on shores
comprises applying a composition compris-
ing a monoester of an aliphatic carboxylic
acid and a polyoxyalkylene glycol, and a liquid
hydrocarbon solvent containing from 0 to 10%,
by weight, based on weight of said liquid hy-
drocarbon, of aromatic compounds, to the oil
and agitating the mixture formed thereby to
disperse the oil.

Preferably, the composition used in the in-
vention comprises 5 to 50% by weight, based
on weight of composition, of said monoester.

Generally, the monoester should form a
homogeneous solution or a stable dispersion
with the liquid hydrocarbon. Suitable, the
monoester is in the liquid state at ambient tem-
peratures.

The monoester, present in the composition
used in the invention, is a monoester of an
aliphatic carboxylic acid and a polyoxyalkylene
glycol. Preferably such monoesters are mono-
esters of unsaturated or saturated aliphatic car-
boxylic acids comprising from 10 to 20 carbon
atoms, preferably from 14 to 18 carbon atoms.
Generally, in order that the monoesters pre-
pared from such acids are liquids at ambient
temperatures, a higher degree of olefinic un-
saturation is required in the aliphatic car-
boxylic acids containing a high number of
carbon atoms, e.g. from 17 to 20 carbon
atoms, than in the aliphatic carboxylic acids
containing a lower number of carbon atoms.
As suitable aliphatic carboxylic acids may be
mentioned lauric acid, myristic acid, palmitic
acid, oleic acid, linoleic acid and linolenic acid,
oleic acid being preferred.

Preferably, the monoester is a monoester of
a polyoxyethylene and/or polyoxypropylene
glycol. The molecular weight of suitable poly-
oxyalkylene glycols is advantageously from
100 to 500, from 150 to 300 being preferred.
Such polyalkoxyglycols can be prepared by any
known process.

The aforesaid monoester can be prepared
by known techniques, such as by esterifying an
aliphatic carboxylic acid with a polyoxyalky-
lene glycol preferably in the presence of an
esterification catalyst. Alternatively, the mono-
ester can be prepared by reacting an aliphatic
carboxylic acid with an alkylene oxide in the
presence of an alkoxylation catalyst.

The composition used in the invention also
comprises a liquid hydrocarbon solvent con-
taining from 0 to 10% by weight, preferably
from 0 to 5% by weight, based on weight of
the liquid hydrocarbon, of aromatic com-
pounds. Suitable liquid hydrocarbons include
paraffins and isoparaffins, naphthenes and
alkyl naphthenes and mixtures thereof. The

liquid hydrocarbon preferably comprises from 5 to 20 carbon atoms per molecule and has a boiling point above about 50° C. As examples of suitable liquid hydrocarbons may be mentioned pentanes, hexanes, octanes, decanes, dodecanes, cyclopentanes, cyclohexanes, and alkyl substituted derivatives 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 comprises a mixture of C₁₀ to C₁₈ paraffins, isoparaffins, naphthenes and alkyl-substituted naphthenes and about 3% by weight, based on weight of the liquid hydrocarbons, of aromatic compounds. Such a mixture may have a boiling range of 175° to 325° C and a flash point of about 66° C. Such a mixture can be obtained by taking the kerosene fraction obtained during the distillation of petroleum and then reducing the amount of aromatic compounds in the kerosene to about 3% by weight. The resulting mixture is frequently referred to as "odourless" kerosene.

The composition used in 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 composition may suitably comprise from 25 to 200% by weight, based on weight of the monoester, of an alkali-metal salt of an alkyl aryl sulphonate.

The compositions used in the invention can be applied to the oil to be emulsified in any known manner. The amount of composition required to emulsify the oil depends on the nature of the oil and the conditions under which it is applied. Advantageously, the amount of composition applied is from 10% to 100% by volume, based on volume of oil, with from 25% to 50%, by volume, being preferred. Suitably the compositions are sprayed on to the surface of the oil to form a mixture. The mixture is then agitated which helps break it into small droplets and disperse the oil. For example, the oil mixture produced by applying such compositions to an oil slick on the sea surface can be agitated by ships' 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 on to the oil slick.

The invention will now be illustrated by the following Examples.

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Example 1.

In this Example, and in the following Examples, the compositions A to F have the following formulations. (The percentages by weight (%wt.) being based on the total weight

of the composition). Compositions A to C are compositions according to the invention. Compositions D to F have been included for comparative purposes.

Composition A

Polyoxyethylene glycol mono-oleate	— 30% wt.	70
(average molecular weight 480)		
Odourless kerosene	— 70% wt.	

Composition B

Polyoxyethylene glycol mono-oleate	— 15% wt.	75
(average molecular weight 480)		
Odourless kerosene	— 85% wt.	

Composition C

Polyoxyethylene glycol mono-oleate	— 15% wt.	80
(average molecular weight 480)		
Sodium salt of an alkylated (C ₁₀ to C ₁₃) benzene sulphonate	— 15% wt.	85
Sodium oleate	— 3% wt.	
Water	— 2% wt.	
Odourless kerosene	— 65% wt.	

Composition D

Glycerol/Sorbitol oleates	— 30% wt.	90
Highly branched aliphatic hydrocarbons (B.Pt.200° to 250° C)	— 70% wt.	

Composition E

Oleyl/cetyl alcohol ethoxylates (approximately 3 molecules of ethylene oxide per molecule of ethoxylate)	— 12% wt.	95
Isopropanol	— 2% wt.	
Odourless Kerosene	— 86% wt.	100

Composition F

Nonyl phenol ethoxylate (approximately 9 molecules of ethylene oxide per molecule of ethoxylate)	— 20% wt.	
Hydrocarbon mixture comprising 60% wt of aromatic compounds	— 80% wt.	105

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 66° C (determined by the Persky-Martens Closed Cup Method) and a boiling range of 175° to 325° C.

The following experiment was performed to demonstrate the ability of certain of the above compositions to disperse oil.

One millilitre of a mixture of oil and long residue comprising the fractions of Ku-

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wait crude oil boiling above 245° C was placed on to the middle of the surface of the water of several beakers. Each beaker contained 2 litres of synthetic sea water prepared by dissolving British Drug House Sea Water Corrosion Test Tablets in distilled water.

Various volumes (0.25ml, 0.5ml and 1.0ml) of compositions A, B, C and D and a standard composition comprising 30% wt. of sodium dioctyl sulphosuccinate in petroleum ether (B.Pt.100 to 120° C) were pipetted on to the oil surfaces of different beakers. The beakers were allowed to stand for 10 minutes and then they were rotated on a table revolving 100 times per minute. The table was stopped momentarily after 5, 12 and 30 minutes and the beakers' contents examined immediately and rated according to the procedure set out below. The above procedure was then repeated using other rotating speeds (115 and 130 revolutions per minute) of the revolving table.

The compositions performances were rated as follows:

Rating 0:— Negligible dispersion of the oil. The sea water is uncoloured and clear.

Rating $\frac{1}{2}$:— Very slight dispersion. The sea water is slightly coloured brown. Practically all the oil is floating on the surface or fixed to the wall of the beaker.

Rating 1:— Some dispersion of the oil. Some oil is floating on the surface or present in the depth of the water as droplets clearly visible to the naked eye. The water is definitely coloured brown.

Rating $1\frac{1}{2}$:— Almost complete dispersion of oil. Droplets of oil are present which are distinctly larger than those in the beaker containing the standard composition. No oil is floating on the surface of the water.

Rating 2:— Complete dispersion of the oil. A negligible amount of oil may be floating on the surface but no droplets of oil are clearly visible to the naked eye. The standard composition gave Rating 2 at 100% volume (1 millilitre of standard composition), based on volume of oil, at all the rotating speeds and times. In case of doubt, Rating 2 was defined as the rating given by the standard composition, and the composition tested were then compared directly with the performance of the standard composition (at 100% vol.).

Thus for each composition 27 ratings were obtained. Each rating is multiplied by a factor to give a modified rating. Each factor depends on the amount of the composition applied to the oil, the rotating speed of the table and the revolving time. (The factors are given in Table I.) The modified ratings for each composition are then totalled and expressed as a percentage of the maximum total (686) possible, which gives the overall rating for that composition. The ratings of composition A are given in Table II with the modified ratings indicated in parentheses. The total of the modified ratings for composition A is 524 and thus its overall rating is 76%. The overall ratings obtained for the compositions A to D are given in Table III.

TABLE I

Amount of Composition	Rotating Speed (revolution per minute)								
	100			115			130		
	Rotating Time (minutes)			Rotating Time (minutes)			Rotating Time (minutes)		
	5	12	30	5	12	30	5	12	30
0.25ml (25% vol.) ¹	(X64)	(X32)	(X16)	(X32)	(X16)	(X8)	(X16)	(X8)	(X4)
0.5ml (50% vol.)	(X32)	(X16)	(X8)	(X16)	(X8)	(X4)	(X8)	(X4)	(X2)
1.0ml (100% vol.)	(X16)	(X8)	(X4)	(X8)	(X4)	(X2)	(X4)	(X2)	(X1)

1. The percentages by volume are based on the volume of oil added to each beaker.

TABLE II

Amount of Composition A	Rotating Speed (revolution per minute)								
	100			115			130		
	Rotating Time (minutes)			Rotating Time (minutes)			Rotating Time (minutes)		
	5	12	30	5	12	30	5	12	30
0.23ml (25% vol)	1½ (96)	1½ (48)	2 (32)	1 (32)	1½ (24)	2 (16)	1½ (24)	2 (16)	2 (8)
0.5ml (50% vol)	1 (32)	1½ (24)	2 (15)	1½ (24)	2 (16)	2 (8)	2 (16)	2 (8)	2 (4)
1.0ml (100% vol)	1 (16)	2 (16)	2 (8)	2 (16)	2 (8)	2 (4)	1½ (6)	2 (4)	2 (2)

TABLE III

Composition	Overall Rating
A	76%
B	70%
C	72%
D	40%

Example II.

5 Several small oil slicks were formed by pouring a mixture of gas oils and long residue comprising the fractions of Es Sider crude boiling above 227° C on to the surface of the sea. Various amounts (12.5% to 50% vol

based on volume of oil slick) of compositions A, B and C were sprayed on to the slicks and the resulting mixture agitated for several minutes. In all cases the oil was dispersed completely.

Example III.

The toxicities of compositions A to F to marine life were evaluated.

Tanks containing sea water were maintained at 20° C for several days. Various sea animals were placed in different tanks and various amounts of the compositions added to the tanks. The animals were exposed to each concentration of each composition for a number of hours. The sea water containing the compositions was then replaced by fresh sea water and the dead animals counted after a further period of 5 days. The results are expressed in Table IV as the lowest concentration of the composition which kills 50% of the animals after the further period of 5 days (LC₅₀).

From the results it can be seen that the compositions used in the present invention are less toxic to certain forms of marine life than known dispersing compositions.

TABLE IV

Composition	Animal	Exposure Time (hours)	LC ₅₀ (ppm)
A	Hermit Crab	48	>10,000
D	Hermit Crab	48	> 6,000
E	Hermit Crab	48	200
F	Hermit Crab	48	16
A	Gunnel	6	>10,000
C	Gunnel	6	8,000
A	Sole	48	>10,000
B	Sole	48	>10,000
E	Sole	48	1,000
A	Limpet	10	100,000
E	Limpet	10	5,000
F	Limpet	10	20

WHAT WE CLAIM IS:—

1. A method for dispersing oil spilled on water or on shores, comprising applying a composition comprising a monoester of an aliphatic carboxylic acid and a polyoxyalkylene glycol, and a liquid hydrocarbon solvent containing from 0 to 10% by weight, based on weight of said liquid hydrocarbon, of aromatic compounds, to the oil and agitating the mixture formed thereby to disperse the oil.

2. A method as claimed in claim 1, wherein said composition comprises from 5 to 50% wt. based on weight of said composition of said monoester.

3. A method as claimed in claim 1 or 2, wherein said monoester is a monoester of an aliphatic acid comprising from 14 to 18 carbon atoms.

4. A method as claimed in claim 3 wherein said monoester is a monoester of oleic acid.

5. A method as claimed in any one of claims 1 to 4, wherein said monoester is an ester of a polyalkoxy glycol having a molecular weight of from 150 to 300.

6. A method as claimed in claim 5, wherein said monoester is an ester of a polyoxyethylene and/or polyoxypropylene glycol.

7. A method as claimed in any one of claims 1 to 6, wherein said liquid hydrocarbon solvent contains from 0 to 5% by weight, based on weight of the liquid hydrocarbon, of aromatic compounds.

8. A method as claimed in claim 7, wherein said liquid hydrocarbon solvent comprises a mixture of C₁₀ to C₁₈ paraffins, isoparaffins, naphthenes and alkyl-substituted naphthenes

TABLE IV

Composition	Animal	Exposure Time (hours)	LC ₅₀ (ppm)
A	Hermit Crab	48	>10,000
D	Hermit Crab	48	> 6,000
E	Hermit Crab	48	200
F	Hermit Crab	48	16
A	Gunnel	6	>10,000
C	Gunnel	6	8,000
A	Sole	48	>10,000
B	Sole	48	>10,000
E	Sole	48	1,000
A	Limpet	10	100,000
E	Limpet	10	5,000
F	Limpet	10	20

WHAT WE CLAIM IS:—

1. A method for dispersing oil spilled on water or on shores, comprising applying a composition comprising a monoester of an aliphatic carboxylic acid and a polyoxyalkylene glycol, and a liquid hydrocarbon solvent containing from 0 to 10% by weight, based on weight of said liquid hydrocarbon, of aromatic compounds, to the oil and agitating the mixture formed thereby to disperse the oil.

2. A method as claimed in claim 1, wherein said composition comprises from 5 to 50% wt. based on weight of said composition of said monoester.

3. A method as claimed in claim 1 or 2, wherein said monoester is a monoester of an aliphatic acid comprising from 14 to 18 carbon atoms.

4. A method as claimed in claim 3 wherein said monoester is a monoester of oleic acid.

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6. A method as claimed in claim 5, wherein said monoester is an ester of a polyoxyethylene and/or polyoxypropylene glycol.

7. A method as claimed in any one of claims 1 to 6, wherein said liquid hydrocarbon solvent contains from 0 to 5% by weight, based on weight of the liquid hydrocarbon, of aromatic compounds.

8. A method as claimed in claim 7, wherein said liquid hydrocarbon solvent comprises a mixture of C₁₁ to C₁₈ paraffins, isoparaffins, naphthenes and alkyl-substituted naphthenes



and about 3% by weight, based on weight of the liquid hydrocarbon, of aromatic compounds.

5 9. A method as claimed in any one of claims 1 to 8, comprising 25% to 200% by weight, based on weight of said monoester, of an alkali-metal salt of an alkyl aryl sulphonate.

10 10. A method as claimed in any one of the preceding claims, comprising applying a mixture of sea water and said composition to

the oil and agitating the mixture formed thereby to disperse the oil.

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

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