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(54) Cleaning of petroleum or its derivatives on soil

(57) A liquid mixture consisting essentially of (i) one or more fatty esters and (ii) one or more non-ionic surface-active agents is used in the cleaning of oil-covered soils.

Oil is removed from soils essentially by:

(i) applying an effective amount of the composition to the oil-covered surfaces of the soil to form a mixture of oil with said composition;
(ii) washing said mixture with a liquid selected from the group consisting of water and mixtures of water with one or more surface-active agents.

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Description

[0001] The present invention relates to the cleaning of soil contaminated as a result of a hydrocarbon oil spill. More particularly, it relates to the cleaning of river banks, beaches, rocky shores and/or rocky coastlines.

[0002] Petroleum or its derivatives such as bitumen may have to be removed from soil (including river banks, beaches, rocky shores and rocky coastlines) in case of accidental spilling. The removal of this petroleum or derivative may be particularly difficult when pollutant penetrates in the interstices of the soil. Cleanup workers traditionally have had to manually scrape away the oil coating.

[0003] The task is even more difficult with viscous oil, particularly crude oil and viscous fractions thereof such as heavy oils, refined heavy oil and bituminous residues.

[0004] There is thus a need for a more efficient method for removing oil from soil.

[0005] In addition, the products used for the cleaning operation may not be harmful for the aquatic animals and must be environmental friendly (i.e. biodegradable).

[0006] The present invention provides a composition for use in the cleaning of soil, and particularly of rocky shores and rocky coastlines. It also provides for the use of said composition in the cleaning of soil covered by oil.

[0007] The composition of the invention essentially consists of a mixture of (i) one or more fatty esters and (ii) one or more surface-active agents.

[0008] As fatty ester, there may be used the ester of a monofunctional alcohol and a monocarboxylic fatty acid.

[0009] The monoalcohol may have from 1 to 18 carbon atoms, preferably from 1 to 8 carbon atoms, more preferably from 1 to 3 carbon atoms, and it may be linear or branched.

[0010] The monocarboxylic fatty acid may have from 6 to 22 carbon atoms, preferably from 12 to 18 carbon atoms, and it may be linear or branched. The monocarboxylic fatty acid may further contain olefinic unsaturation; saturated C12-C14 and unsaturated C16-C18 monocarboxylic fatty acids and mixtures thereof are most preferred.

[0011] The fatty ester should be liquid at the envisaged operation temperature. Preferably, the fatty ester should have a viscosity below 10 mm2/s, preferably below 5 mm2/s, at 40°C (measured according to DIN standard method 51562). Also, the ester should have a Kauri Butanol value (ASTM test method D1133) of at least 30, preferably at least 40, more preferably at least 50.

[0012] The esters to be used in the compositions of the invention have no acute toxicity (LD50 > 2000), are not irritating and are readily biodegradable. Also, they are not ecotoxic (96 hours LC50 fish > 100 mg/L), non-volatile (vapour tension < 0.1 hPa at 20°) and do not contain aromatic components.

[0013] As surface active agents (also called surfactant), there may be used any non-ionic surfactant or blend having a HLB (hydrophilic/lipophylic balance) value of minimum 7, preferably of 7 to 10, more preferably from 8 to 10, and containing no aromatic ring in its structure. The preferred surface active agents for use in the invention are selected from the group consisting of polyoxyalkylene esters of fatty acids and mixtures thereof, preferably polyoxyethylene and polyoxypropylene esters.

[0014] The surface active agents to be used in the compositions of the invention have no acute toxicity (LD50> 2000), are not irritating, non-volatile (< 0.1 hPa at 20°C), biodegradable, and do not contain aromatic components.

[0015] The compositions of the invention contain at least 40 wt% of the fatty esters, preferably at least 55 wt%, more preferably at least 75 wt% and most preferably at least 90 wt%, the remainder of the composition being essentially the surfactant.

[0016] The composition must be liquid at the envisioned operation temperature. Thus, the viscosity of the composition should be of at most 80 mm2/s, preferably at most 50 mm2/s, more preferably at most 30 mm2/s, most preferably at most 10 mm2/s, measured at 40°C.

[0017] The composition is not ecotoxic (96 hours-LC50-fish > 100 mg/l).

[0018] The method of the invention for removing oil from soil essentially consists of the steps of:

(i) applying an effective amount of the composition to the oil-covered surfaces of the soil to form a mixture of oil with said composition;
(ii) washing said mixture with a liquid selected from the group consisting of water and mixtures of water with one or more surface-active agents.

[0019] The application of the composition may be made as usual, e.g. by spraying, by pouring, or with a brush, including allowing the composition to mix with the oil.

[0020] The compositions of the invention have an appropriate combination of viscosity and solvency power to allow a good and fast penetration on the soil while dissolving the oil or other hydrocarbon product to be removed from the surface of the soil. The resulting mixture is easily emulsified in water; thus, the oil or other hydrocarbon product is easily removed from the surface of the soil. This combined effect renders the cleaning operation easier thus shorter, if compared with a cleaning done in traditional ways.

[0021] The formulation has an appropriate combination of viscosity and solvency power to easily mix with the pollutant even in interstices of the soil, and to reduce its viscosity. The resulting mixture is easily emulsified in water, thus allowing to easily disperse the oil and remove it from the surface of the soil.

[0022] The oil spill is thus removed from the surface in the form of an oil-in-water emulsion wherein the oily

phase comprises fatty esters. The dispersed state increases the accessibility to the naturally occurring bacteria that are performing the biodegradation. The biodegradability of the emulsion is increased (with respect to simple emulsions) as a result of the presence of readily biodegradable products (the fatty esters) that stimulate the metabolism of the bacteria.

[0023] The composition of the invention has no adverse effect on the aquatic life (including birds and other animals that come into contact with the water). The method of the invention allows for a faster recovery of the aquatic life.

[0024] The composition and method of the invention are particularly efficient for removing oil from rocky shores and coastlines.

Example 1

[0025] There was prepared a blend of:

- 90 wt% of methyl esters of rapeseed fatty acids, commercially available from TotalFina Oleochemicals under the trade name Radia 7961 (Kauri Butanol value = 56, viscosity = 4.2 mm2/s at 40°C); and
- 10 wt% of polyoxyethylene 400 di-oleate, commercially available from TotalFina Oleochemicals under the trade name Radiasurf 7443 (HLB = 7.4)

[0026] Both components are listed in the INCI (International Nomenclature of Cosmetic Ingredients). Also, the composition was not ecotoxic (96 hours LC50 fish > 100 mg/L), non-volatile (< 0.1 hPa at 20°C), biodegradable, and did not contain aromatic components.

[0027] The composition had a low viscosity (less than 10 mm2/s at 40°C).

[0028] An effective amount of the composition was sprayed on the oiled surfaces of rocks; the composition was allowed to mix with the oil during about 5 minutes, then the rocks were washed with tap water. The oil was completely removed from the rocks.

Example 2

[0029] There was prepared a blend of:

- 90 wt% of isopropyl esters of C12-C18 fatty acids (topped coconut fatty acids), available from TotalFina Oleochemicals under the trade name Radia 30106 (Kauri Butanol value = 51; viscosity = 3.5 mm2/s at 40°C); and
- 10 wt% of polyoxyethylene 400 di-oleate, commercially available from TotalFina Oleochemicals under the trade name Radiasurf 7443 (HLB = 7.4)

[0030] The composition had a viscosity of 4.5 mm2/s at 40°C.

[0031] Similar results were obtained.

Claims

1. Composition for the cleaning of oil-covered soil, essentially consisting of a mixture of (i) one or more fatty esters and (ii) one or more surface-active agents.

2. Composition according to claim 1, wherein the fatty ester is the ester of a monofunctional alcohol having from 1 to 18 carbon atoms and a monocarboxylic fatty acid having from 6 to 22 carbon atoms.

3. Composition according to claim 2, wherein the fatty ester is the ester of a monofunctional alcohol having from 1 to 3 carbon atoms and a monocarboxylic fatty acid selected from the group consisting of saturated acids having 12 to 14 carbon atoms, unsaturated acids having from 16 to 18 carbon atoms, and mixtures thereof.

4. Composition according to any one of claims 1 to 3, wherein the fatty ester has a viscosity below 10 mm2/s, preferably below 5 mm2/s, and /or a Kauri Butanol value of at least 30, preferably at least 40, more preferably at least 50.

5. Composition according to any one of claims 1 to 4, wherein the surface-active agent is non-ionic and has a HLB of at least 7, preferably 7 to 10, more preferably 8 to 10.

6. Composition according to claim 5, wherein the surface-active agent is selected from the group consisting of polyalkylene esters of fatty acids and mixtures thereof.

7. Composition according to any one of claims 1 to 6, wherein the fatty acid esters represent at least 40 wt%, preferably at least 55 wt%, more preferably at least 75 wt% and most preferably at least 90 wt%.

8. Composition according to any one of claims 1 to 7 having a viscosity the viscosity of at most 80 mm2/s, preferably at most 50 mm2/s, more preferably at most 30 mm2/s, most preferably at most 10 mm2/s, measured at 40°C.

9. Use of the composition according to any one of claims 1 to 8 in the cleaning of oil-covered soil.

10. Method for removing oil from a soil, essentially consisting of the steps of:

    (i) applying an effective amount of the composition according to any one of claims 1 to 8 to the oil-covered surfaces to form a mixture of oil with said composition;
    (ii) washing said mixture with a liquid selected

from the group consisting of water and mixtures of water with one or more surface-active agents.

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EUROPEAN SEARCH REPORT

Application Number
EP 00 10 0834

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	EP 0 971 012 A (INST FRANCAIS DU PETROL) 12 January 2000 (2000-01-12) * claims *	1-5,7,9, 10	C11D1/825 //C11D1:66, C11D1:74
A	* page 2, line 34 - page 3, line 14 *	6,8	
X	FR 2 700 342 A (ELF AQUITAINE ;LABO BIOLOG VEGETALE YVES ROCHER) 13 July 1994 (1994-07-13)	1-4,7,10	
A	* abstract * * claims * * examples 2,4 * * page 10, line 11 - page 13, line 7 *	8,9	
A	WO 95 17244 A (UNION OIL CO) 29 June 1995 (1995-06-29) * claims 1,4-11,21-23,40-42,47,48 * * examples 55-59,62,68-71 * * page 23, line 12 - page 25, line 32 *	1,9,10	
A	GB 1 280 259 A (SHELL) 5 July 1972 (1972-07-05) * claims * * examples *	1,6,9,10	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C11D C02F B09C
A	US 4 224 152 A (LEPAIN ANDRE O) 23 September 1980 (1980-09-23) * claims * * examples *	1,9,10	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	24 August 2000	Neys, P

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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O : non-written disclosure
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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 00 10 0834

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The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

24-08-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0971012 A	12-01-2000	FR 2781497 A	28-01-2000
FR 2700342 A	13-07-1994	AT 158811 T	15-10-1997
		AU 5835994 A	15-08-1994
		CA 2153665 A	21-07-1994
		DE 69405980 D	06-11-1997
		EP 0690908 A	10-01-1996
		FR 2700341 A	13-07-1994
		WO 9416043 A	21-07-1994
		NO 952737 A	04-09-1995
		NZ 259534 A	26-05-1997
WO 9517244 A	29-06-1995	US 5634984 A	03-06-1997
		AT 162427 T	15-02-1998
		AU 684309 B	11-12-1997
		AU 7714394 A	10-07-1995
		BR 9408417 A	05-08-1997
		CA 2179720 A	29-06-1995
		CN 1142786 A	12-02-1997
		DE 69408167 D	26-02-1998
		DE 69408167 T	30-07-1998
		EP 0735919 A	09-10-1996
		ES 2114226 T	16-05-1998
		US 5723423 A	03-03-1998
		US 5788781 A	04-08-1998
		US 5780407 A	14-07-1998
GB 1280259 A	05-07-1972	AU 462487 B	26-06-1975
		AU 3657271 A	14-06-1973
		BE 776006 A	16-03-1972
		CA 943034 A	05-03-1974
		DE 2160698 A	29-06-1972
		ES 397736 A	01-04-1975
		FR 2117481 A	21-07-1972
		HK 18276 A	09-04-1976
		IT 946110 B	21-05-1973
		NL 7116770 A	13-06-1972
		NO 137482 B	28-11-1977
		PH 9831 A	02-04-1976
		SE 376598 B	02-06-1975
		ZA 7108181 A	30-08-1972
US 4224152 A	23-09-1980	FR 2413460 A	27-07-1979
		CA 1095369 A	10-02-1981
		DE 2855158 A	12-07-1979
		GB 2011368 A,B	11-07-1979

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 00 10 0834

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

24-08-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4224152 A		IT 1101592 B	07-10-1985
		JP 1395680 C	24-08-1987
		JP 54135677 A	22-10-1979
		JP 62000757 B	09-01-1987
		NO 784351 A,B,	29-06-1979
		PT 68980 A	01-01-1979

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82