

PATENT SPECIFICATION

(11) 1 426 646

1 426 646

- (21) Application No. 6804/73 (22) Filed 12 Feb. 1973
 (31) Convention Application No. 7205894 (32) Filed 22 Feb. 1972 in (19)
 (33) France (FR)
 (44) Complete Specification published 3 March 1976
 (51) INT CL² B01F 17/14 C02B 9/02 C11D
 10/02/(C11D 10/02 1/72
 3/20 3/30 3/36 3/38)



- (52) Index at acceptance

BIV 2A3 3BX 3DX 3E 3F
 C1C 210 242 243 251 252 254 30X 407
 C5D 6B11A 6B12N1 6B12N4 6B8 6C8

(54) COMPOSITION FOR THE ELIMINATION OF MINERAL OIL ESPECIALLY PETROLEUM PRODUCTS BY BIOLOGICAL DEGRADATION /

(71) We, **BANQUE POUR L'EXPANSION INDUSTRIELLE "BANEXI"**, of 1, Boulevard Haussmann, Paris 9eme, France; a Societe Anonyme organised under the laws of France, do hereby declare 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 particularly described in and by the following statement:

The present invention relates to a composition for bringing mineral oil, especially petroleum, products into the form of a biodegradable emulsion.

Compositions have already been proposed for bringing mineral oil products into the form of a biodegradable emulsion, these compositions having a base of organic substances capable of supplying to micro-organisms, materials such as carbohydrates or hydrophilic polypeptides, various residual wash liquors (vinasses), casein, etc., together with emulsifying agents or various chemical substances such as mineral or organic acids or the alkali or alkaline earth metal salts thereof. These compositions give stable emulsions and they are perfectly biodegradable, particularly when the biodegradation is effected in a closed medium.

In fact, in order to be biodegradable, an emulsion of mineral oil, especially petroleum products must not be toxic and it must contain sources of carbon, nitrogen and phosphorus in sufficient quantity to ensure, for the micro-organisms, the elements necessary for the constitution of living matter. The biodegradation of mineral oil products results from the use, by the micro-organisms, of the hydrocarbons as a source of carbon and it is necessary that the composition used for emulsifying should contain considerable sources of nitrogen and sources of phosphorus in a smaller quantity. These sources of nitrogen and

phosphorus exist in previously proposed compositions, but the emulsion is made utilising water-soluble oleophilic agents and the nitrogenous or phosphorus elements are not closely bound to the hydrocarbon molecules. In every case the nitrogenous and phosphorus elements are dispersed in the dilute emulsion. If this dilution is contained as in the case of biodegradation effected in a tank or the like, for example, for a biodegradation intended to transform the hydrocarbons into fertilising materials or in the case of the use of the emulsion as a culture medium for the micro-organisms, said micro-organisms find the nitrogenous and phosphated elements within their immediate reach. On the other hand, in the case of very extensive dilution, for example in the case of discarded material discharged into the river or sea, the content of nitrogen and phosphorus in the medium surrounding the hydrocarbon molecules is insufficient to permit the growth of micro-organisms.

According to the present invention there is provided a composition for bringing mineral oil products into the form of a biodegradable emulsion, comprising lecithin in combination with at least one non-toxic and entirely biodegradable emulsifier selected from sodium oleylisethionate, sodium methyl aminoethane sulphonate, sodium lauryl sulphate, a secondary sulphonated paraffin, a sulphonated alpha-olefin, a sarcosinate, 2-amino-2-hydroxymethyl-1, 3-propanediol, aminomethylpropanol, an ethoxylated C₁₀-C₁₂ fatty alcohol and polyethyleneglycol oleate, with the proviso that said polyethyleneglycol oleate emulsifier is utilised in admixture with at least one of:—

(a) another of said emulsifiers;

(b) a solvent compatible with hydrocarbons and without toxic action selected from propyleneglycol,

50

55

60

65

70

75

80

85

90

dipropyleneglycol and petroleum solvents deprived of aromatic fractions; or
(c) a mineral charge to produce a paste or powder.

5 The lecithin ensures the supply of nitrogen and phosphorus and it can be enriched with nitrogen by addition of 11-amino-undecanoic acid, of formula $H_2N-(CH_2)_{10}-COOH$.

10 If desired, the composition may contain other biodegradable organic bodies, in particular organic acids such as lactic acid, which simultaneously represents a vehicle for bringing the 11-amino-undecanoic acid
15 into solution, amino acids such as glutamic acids, glycocoll, tyrosine, leucine, proline, lysine, valine, betaine, histidine and alanine or amino acid sources such as vinasses and casein, or fatty acids such as caproic, octoic,
20 caprylic and oleic acids.

The composition may be brought into liquid form, in particular so as to be atomised or applied through a nozzle, by
25 addition of water or of a solvent more compatible than water with hydrocarbons but without toxic action such as propylene glycol, di-propylene glycol and petroleum solvents deprived of aromatic fractions.

30 The compositions may also be brought into the form of a paste or a powder by the addition of a mineral charge such as calcium phosphate, calcium carbonate or zinc oxide. It is preferable that part of the mineral charge is formed by a metal oxide.

35 Various examples for carrying the invention into practice will be described hereinafter, the percentages given in these examples being parts by weight.

Example 1

40 Five parts of 11-amino-undecanoic acid are dissolved in 15 parts of lactic acid, then ten parts of emulsifier are added, formed by an ethoxylated (50E) fatty alcohol (C10-12), 2 parts of soya lecithin and 68
45 parts of water.

The liquid composition obtained was used for emulsifying crude oil (petroleum) in a ratio of 30 parts of composition to 100 parts of crude oil and sludge oils or in a ratio of 35
50 parts of composition to 100 parts of sludge oil.

55 The emulsions were poured into tanks representing marine ecological micro-media. They remained in the form of fine emulsions in the upper parts of the tanks without modifying the development of the fauna and flora.

60 Biodegradation was observed by chromatography in a gaseous phase. The speed of degradation varied as a function of the various factors such as temperature, aeration and natural richness of the medium in micro-organisms. Comparison with reference tanks show that it was at least

65 twenty times faster than natural biodegradation. Under conditions corresponding to temperate seas, it was completed within one to three months.

Example 2

As emulsifier, 15 parts of the ethoxylated fatty alcohol of Example 1 was added to 5
70 parts of soya lecithin. Dilution was then effected with 80 parts of water. 20 grams of this composition were sprayed on a crude oil slick of 100 gr. floating on the surface of a tank containing sea water, the surface of
75 which was agitated. A fine emulsion was formed having the same characteristics of harmlessness and biodegradability as in Example 1.

Example 3

A composition was prepared containing, in addition to 5 parts of lecithin, 6 parts of a sulphonated alpha-olefin and 8 parts of the ethoxylated fatty alcohol of Example 1 as
85 emulsifiers, and 81 parts of water. The amount of this composition employed is 25 parts to 100 parts of crude oil and 30 parts to 100 parts of sludge oil or No. 2 heavy fuel.

Example 4

3 parts of lecithin and 6 parts of the ethoxylated fatty alcohol of Example 1 were well mixed together forming an emulsifier, then 88 parts of water and three parts of sodium lauryl sulphate were added to the
95 mixture with stirring forming an emulsifier. This composition, used in a ratio of 25 to 35 parts to 100 parts of mineral oil products gave, according to the nature thereof, similar results as in Example 1.

Example 5

5 parts of lecithin, 4 parts of aminomethylpropanol and 87 parts of water were closely mixed together and then there was added 4 parts of sodium lauryl sulphate. This liquid composition was sprayed on an
105 oil slick at the rate of 30 parts to 100 parts of mineral oil products.

Example 6

2 parts of lecithin were mixed with 10
110 parts of octoic acid and then 4 parts of a sulphonated alpha-olefin and 4 parts of the ethoxylated fatty alcohol of Example 1 were added as emulsifier and finally 68 parts of dipropylene glycol was added as solvent. 20
115 kg of the composition was poured into a tank containing 100 kg of petroleum deposits and the mixture was stirred and the walls brushed. The homogeneous mixture obtained was pumped and poured into a tank of water in which an emulsion formed. Progressive biodegradation of the emulsion was observed, the speed of biodegradation being similar to that of the emulsion in
120 Example 1.

Example 7

5 A composition was prepared, formed of 10 parts of lecithin, 40 parts of polyethyleneglycol oleate and 50 parts of white spirit deprived of aromatic fractions. 100 parts of the residues of an oil tanker were stirred with 25 parts of this composition which immediately gave a mixture which was poured into a tank of sea water, the biodegradation of the emulsion being produced in the same manner as above.

Example 8

15 A mixture of 20 parts lecithin, 40 parts of the ethoxylated fatty alcohol of Example 1 and 40 parts of water was prepared. This mixture was stored. When used, the mixture was diluted in a ratio of 100 parts of mixture to 100 parts of sea water and the diluted composition was sprayed onto an oil slick in a ratio of approximately 30 parts to 100 parts of oil. Similar results were obtained as in Example 2.

Example 9

25 A mixture of 10 parts of lecithin, 20 parts of polyethyleneglycol oleate, 20 parts of an ethoxylated (50E) fatty alcohol ($C_{10}-C_{12}$) and 50 parts of dipropyleneglycol was prepared. For treating a fresh oil slick spread over a cement ground, 100 parts of the mixture were diluted with 100 parts of water, the slick was sprayed with the composition and brushed and then rinsed with water. The diluted emulsion was collected and used as aquarium water. The ground was perfect, the fauna and flora in the aquarium showed no sign of degeneration and biodegradation was effected in approximately eight weeks.

Example 10

40 A mixture was prepared containing 10 parts of lecithin, 30 parts of polyethyleneglycol oleate and 60 parts of dipropylene glycol. At the time of use the composition was diluted weight for weight with water and used in the same manner as in Example 2 with similar results.

Example 11

50 A mixture was prepared from 20 parts lecithin, 20 parts of polyethyleneglycol oleate and 6 parts of calcium phosphate, 20 parts calcium carbonate and 34 parts water. The resultant paste was disposed in a line on a beach of white sand in a hydrographic research tank and mineral oil was poured into the tank spreading out into a slick. The oil slick was steered by the currents and the artificial swell towards the beach and the line of composition was driven by the waves to be mixed with the oil, resulting in an emulsion dispersed in the upper layers of

the tank. The emulsion deposited on the sand was washed by the flow and no trace of soiling could be found on the sand. A duck allowed to swim in the tank showed no unusual behaviour nor could any adhesion of emulsion be found on its feathers.

Example 12

8 parts of 11-amino-undecanoic acid were dissolved in 20 parts of lactic acid, then 2 parts lecithin, 100 parts of vinasses from preparation of glutamic acid, 5 parts of 85% crude glutamic acid, 150 parts of water and 4 parts of sodium lauryl sulphate were added. This composition was used in the same manner as in Example 1 and gave similar results with appreciably the same speed of biodegradation.

Example 13

50 parts of zinc oxide and 500 parts of calcium carbonate were added to a mixture of 10 parts of lecithin, 20 parts stearic acid, 30 parts of polyethyleneglycol oleate and 30 parts of white spirit which yielded a powder. This powder was used to dust on an oil slick which resulted in a deposit and the disappearance of the oil slick. The biodegradation of the products contained in this deposit was observed by periodic sampling. Progressive and simultaneous biodegradation of the lecithin, of the stearic acid, the white spirit and the petroleum products, was observed, the consumption of the phosphorus and the nitrogen in the lecithin proceeding within the deposit in parallel with the biodegradation of the oil. The biodegradation was much more rapid than the very slow natural biodegradation of the oil carried along with the powdered chalk, a feature attributed to the presence within the deposit of lecithin and a metal oxide representing a source of oxygen.

The above methods, described merely by way of example, may be modified in many ways without departing from the scope of the present invention as defined in the claims.

WHAT WE CLAIM IS:—

1. A composition for bringing mineral oil products into the form of a biodegradable emulsion, comprising lecithin in combination with at least one non-toxic and entirely biodegradable emulsifier selected from sodium oleylisethionate, sodium methylaminoethane sulphonate, sodium lauryl sulphate, a secondary sulphonated paraffin, a sulphonated alpha-olefin, a sarcosinate, 2-amino-2-hydroxymethyl-1, 3-propanediol, aminomethylpropanol, an ethoxylated $C_{10}-C_{12}$ fatty alcohol and polyethyleneglycol oleate, with the proviso that said polyethyleneglycol oleate



Example 7

A composition was prepared, formed of 10 parts of lecithin, 40 parts of polyethyleneglycol oleate and 50 parts of white spirit deprived of aromatic fractions. 100 parts of the residues of an oil tanker were stirred with 25 parts of this composition which immediately gave a mixture which was poured into a tank of sea water, the biodegradation of the emulsion being produced in the same manner as above.

Example 8

A mixture of 20 parts lecithin, 40 parts of the ethoxylated fatty alcohol of Example 1 and 40 parts of water was prepared. This mixture was stored. When used, the mixture was diluted in a ratio of 100 parts of mixture to 100 parts of sea water and the diluted composition was sprayed onto an oil slick in a ratio of approximately 30 parts to 100 parts of oil. Similar results were obtained as in Example 2.

Example 9

A mixture of 10 parts of lecithin, 20 parts of polyethyleneglycol oleate, 20 parts of an ethoxylated (50E) fatty alcohol ($C_{10}-C_{12}$) and 50 parts of dipropyleneglycol was prepared. For treating a fresh oil slick spread over a cement ground, 100 parts of the mixture were diluted with 100 parts of water, the slick was sprayed with the composition and brushed and then rinsed with water. The diluted emulsion was collected and used as aquarium water. The ground was perfect, the fauna and flora in the aquarium showed no sign of degeneration and biodegradation was effected in approximately eight weeks.

Example 10

A mixture was prepared containing 10 parts of lecithin, 30 parts of polyethyleneglycol oleate and 60 parts of dipropylene glycol. At the time of use the composition was diluted weight for weight with water and used in the same manner as in Example 2 with similar results.

Example 11

A mixture was prepared from 20 parts lecithin, 20 parts of polyethyleneglycol oleate and 6 parts of calcium phosphate, 20 parts calcium carbonate and 34 parts water. The resultant paste was disposed in a line on a beach of white sand in a hydrographic research tank and mineral oil was poured into the tank spreading out into a slick. The oil slick was steered by the currents and the artificial swell towards the beach and the line of composition was driven by the waves to be mixed with the oil, resulting in an emulsion dispersed in the upper layers of

the tank. The emulsion deposited on the sand was washed by the flow and no trace of soiling could be found on the sand. A duck allowed to swim in the tank showed no unusual behaviour nor could any adhesion of emulsion be found on its feathers.

Example 12

8 parts of 11-amino-undecanoic acid were dissolved in 20 parts of lactic acid, then 2 parts lecithin, 100 parts of vinasses from preparation of glutamic acid, 5 parts of 85% crude glutamic acid, 150 parts of water and 4 parts of sodium lauryl sulphate were added. This composition was used in the same manner as in Example 1 and gave similar results with appreciably the same speed of biodegradation.

Example 13

50 parts of zinc oxide and 500 parts of calcium carbonate were added to a mixture of 10 parts of lecithin, 20 parts stearic acid, 30 parts of polyethyleneglycol oleate and 30 parts of white spirit which yielded a powder. This powder was used to dust on an oil slick which resulted in a deposit and the disappearance of the oil slick. The biodegradation of the products contained in this deposit was observed by periodic sampling. Progressive and simultaneous biodegradation of the lecithin, of the stearic acid, the white spirit and the petroleum products, was observed, the consumption of the phosphorus and the nitrogen in the lecithin proceeding within the deposit in parallel with the biodegradation of the oil. The biodegradation was much more rapid than the very slow natural biodegradation of the oil carried along with the powdered chalk, a feature attributed to the presence within the deposit of lecithin and a metal oxide representing a source of oxygen.

The above methods, described merely by way of example, may be modified in many ways without departing from the scope of the present invention as defined in the claims.

WHAT WE CLAIM IS:—

1. A composition for bringing mineral oil products into the form of a biodegradable emulsion, comprising lecithin in combination with at least one non-toxic and entirely biodegradable emulsifier selected from sodium oleylisethionate, sodium methylaminoethane sulphonate, sodium lauryl sulphate, a secondary sulphonated paraffin, a sulphonated alpha-olefin, a sarcosinate, 2-amino-2-hydroxymethyl-1, 3-propanediol, aminomethylpropanol, an ethoxylated $C_{10}-C_{12}$ fatty alcohol and polyethyleneglycol oleate, with the proviso that said polyethyleneglycol oleate

emulsifier is utilised in admixture with at least one of:—

(a) another of said emulsifiers;

5 (b) a solvent compatible with hydrocarbons and without toxic action selected from propyleneglycol, dipropyleneglycol and petroleum solvents deprived of aromatic fractions; or

10 (c) a mineral charge to produce a paste or powder.

2. A composition as claimed in claim 1 also comprising 11-amino-undecanoic acid.

15 3. A composition as claimed in claim 1 or 2, additionally containing one or more biodegradable organic acids or amino-acid sources.

4. A composition as claimed in claim 3, in which the organic acid is lactic acid.

20 5. A composition as claimed in claim 3, in which the organic acid is an amino acid selected from glutamic acid, glycocoll, tyrosine, leucine, proline, lysine, valine, betaine, histidine and alanine.

25 6. A composition as claimed in claim 3 in which the amino acid source is selected from vinasses and casein.

30 7. A composition as claimed in claim 3, in which the organic acid is a fatty acid selected from caproic, octoic, caprylic and oleic acid.

8. A composition as claimed in any preceding claim when diluted with water.

9. A composition as claimed in any one of claims 1 to 7 additionally containing a solvent compatible with hydrocarbons and without toxic action, selected from propyleneglycol, dipropyleneglycol and petroleum solvents deprived of aromatic fractions, when not already present.

10. A composition as claimed in any one of claims 1 to 7 made in the form of a paste or powder by the addition of a mineral charge, when not already in such form.

11. A composition as claimed in claim 10 in which at least part of the mineral charge is a metal oxide.

12. A composition for bringing mineral oil products into the form of a biogradable emulsion substantially as hereinbefore described and exemplified.

POTTS, KERR & CO.,
Chartered Patent Agents,
9, Warwick Court,
London, WC1R 5DJ.
and
15, Hamilton Square,
Birkenhead,
Merseyside, L41 6BR.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1976.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

