

PATENT SPECIFICATION

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(54) COMPOSITION FOR THE ELIMINATION OF MINERAL OIL PRODUCTS BY BIODEGRADATION

(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 metals salts thereof. These compositions give stable emulsions and 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 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 a vinasse in combination with at least one oleophilic fatty acid.

According to a preferred feature of the present invention, a basic element is added to the composition and is selected from potassium hydroxide, sodium hydroxide, ammonia and their basic salts, in a quantity such that the pH of the composition is substantially 7 to 7.5.

The vinasse used in the composition is preferably a magnesium or potassium residuary liquor obtained from a sugar refinery or a residuary liquor obtained from the production of glutamic acid.

An amino-acid may be used to enrich the vinasse in nitrogen and may be selected from glutamic acid, glycocoll, tyrosine, leucine, proline, lysine, valine, betaine, histidine and alanine or may be natural sources rich in amino-acids such as casein, or mixtures thereof.

The fatty acids utilised are preferably fatty

[Price 33p]

Price 75p

acids which are liquid at ambient temperature, such as caproic acid, octoic acid, caprylic acid and oleic acid.

In order to improve the stability of the emulsion, certain non-toxic and biodegradable emulsifiers may be added, such as sodium oleylisethionate, sodium methylamineoethane-sulphonate, sodium lauryl sulphate, secondary sulphonated paraffins, sulphonated alpha-olefins, sarcosinates, 2-amino-2-hydroxymethyl-1,3-propanediol, aminomethylpropanol, ethoxylated fatty alcohol and polyoxyethyleneglycol oleate.

The composition is preferably constituted by a vinasse enriched in amino-acids to which there is added 6 to 20% by weight of fatty acid. The quantity of base or basic salt added depends on the basicity of the added agent and the acidity of the vinasse enriched in amino-acids and fatty acids. In general, it is 8 to 20% by weight of the vinasse, enriched with amino-acids and fatty acids. The quantity of the emulsifier added to the above composition may amount up to 5% by weight.

To make the composition sufficiently fluid for spraying 20 to 50% by weight of water is added. It is possible but not desirable to dilute the composition even more.

For certain applications, particularly for the protection of beaches from oil deposits, it is necessary to bring the composition into the form of a paste. In order to do this, a small quantity of water is added to the composition and mineral charges are added thereto, for example, calcium phosphate or calcium carbonate.

If necessary, it may also be brought into the form of a powder by increasing the content of mineral charges.

The composition according to the present invention is desirably used in a ratio of 25 to 60 parts by weight to 100 parts by weight of petroleum products.

Various examples of compositions according to the present invention will be described hereinafter.

EXAMPLE 1

The following constituents are added in the following order and mixed well together:—

Magnesium vinasse from	
sugar refinery	100 parts by weight
Crude glutamic acid	
(85%)	20 parts by weight
Octoic acid	20 parts by weight
Ammonia at 22° Be	16 parts by weight
Water	44 parts by weight

100 gr. of crude mineral oil were poured onto the surface of a tank containing 100 litres of sea water reproducing a marine ecological micro-medium and 50 gr. of the

composition were sprayed on the layer of mineral oil so formed. An emulsion was formed which remained in suspension in the upper layers, a feature which is of interest since it concerns the most oxygenated layers. The flora continued to develop normally. A sea bird dipped in the above tank, then rinsed by immersion in a trough of sea water, showed no adhesion of the emulsion.

The biodegradation was monitored by chromatography in a gaseous phase. The speed of degradation varied as a function of the various factors such as temperature, aeration and natural concentration of the medium in micro-organisms. Comparison with reference tanks showed that it was at least twenty times faster than natural biodegradation. Under conditions corresponding to temperate seas, it was completed within one to three months.

EXAMPLE 2

In the same manner as Example 1, a composition was prepared formed by:—

Potassium vinasse from	
sugar refinery	100 parts by weight
Crude glutamic acid	15 parts by weight
Oleic acid	10 parts by weight
Caustic potash	
lye d = 1.34	16 parts by weight
Water	59 parts by weight

This composition, used in the same manner as in Example 1, gave similar results.

EXAMPLE 3

The same composition was prepared as in Example 1, but by replacing the 16 parts of ammonia with 60 parts by weight of diammonium phosphate. The composition was used in the same manner as in Example 1 with similar results.

EXAMPLE 4

Preparation was effected in the same manner as in Example 1, that is to say, by the addition in the following order, of the constituents with stirring between successive additions:—

Vinasse from the	
preparation of	
glutamic acid	100 parts by weight
Crude glutamic acid	10 parts by weight
Octoic acid	10 parts by weight
Caustic soda	
lye at 36° Be	16 parts by weight
Water	64 parts by weight

This composition was used in the same manner as in Example 1 in a ratio of 45 parts to 100 parts of mineral oil products.

EXAMPLE 5

The same composition was prepared as in Example 4, but by replacing the 10 parts of crude glutamic acid by 10 parts of soluble casein. The composition was used in a ratio of 40 parts by weight to 100 parts of mineral oil products.

EXAMPLE 6

In the composition of Example 4, there were added three parts by weight of sodium oleylisethionate before adding the water. Used in the same manner as that in Example 4, the composition gave a finer emulsion.

EXAMPLE 7

The following composition was prepared by successive additions with stirring between the various additions:—

20	Magnesium vinasse from sugar refinery	100 parts by weight
	Casein	10 parts by weight
	Octoic acid	10 parts by weight
25	Caustic potash lye d = 1.34	16 parts by weight
	Sodium methylaminocethane sulphate	1 part by weight
	Sodium lauryl sulphate	2 parts by weight
30	Water	63 parts by weight

This composition utilized in a ratio of 40 parts by weight to 100 parts by weight of mineral oil products gave as fine an emulsion as in Example 6.

EXAMPLE 8

The following composition was prepared in the same manner as in Example 7:—

40	Glutamic acid vinasse	100 parts by weight
	Crude glutamic acid	10 parts by weight
	Octoic acid	10 parts by weight
	Caustic soda lye at 36° Be	16 parts by weight
45	Sodium Oleylisethionate	2 parts by weight
	Sodium lauryl sulphate	4 parts by weight
	Water	58 parts by weight

This composition was utilized in a ratio of 30 parts by weight to 100 parts of mineral oil products.

In the foregoing, it has been proposed to use the compositions for spraying on oil slicks on the surface of layers of water, but these compositions can also be used for the biodegradable emulsifying of residues on the bottom of tanks by stirring with these residues, followed by dilution in water and for cleaning surfaces soiled by petroleum products or for other similar purposes. The composition may be less diluted for some of these applications. Although the composition is particularly intended to maintain the biodegradable character of the emulsion during

the dispersion thereof in a large volume of water, the slightly diluted emulsion particularly that obtained from residues on the bottom of tanks, may be subjected to biodegradation in a confined medium the products of the biodegradation having a certain fertilising action.

The composition may also be used in a pasty form, for instance, so as to be disposed in a line at the limit of the tide on beaches threatened by oil slicks.

EXAMPLE 9

A pasty composition was prepared by mixing in succession and in the following order:

Vinasse from the preparation of glutamic acid	100 parts by weight
Octoic acid	9 parts by weight
Polyoxyethyleneglycol oleate	22 parts by weight
Caustic soda lye at 36° Be	13 parts by weight
Calcium phosphate	13 parts by weight
Calcium carbonate	44 parts by weight
Water	20 parts by weight

In a hydrographic research tank, a line of the pasty composition was deposited on a layer of sand and then an oil slick was advanced towards it. Under the effect of the artificial swell, the oil slick reaching the beach was emulsified with the composition and the emulsion, similar to these obtained with other compositions, was dispersed in the surface layers, the emulsion deposited on the sand being naturally washed by the swell.

The composition proved to be effective in a ratio of 25 parts by weight to 100 parts by weight of mineral oil products.

The above compositions, given by way of example only, may be modified in many ways without departing from the scope of the present invention as defined in the claims. Thus the addition of water to enable the composition to be sprayed may be completely or partially effected at the place of use.

WHAT WE CLAIM IN:—

1. A composition for bringing mineral oil products into the form of a biodegradable emulsion comprising a vinasse in combination with at least one oleophilic fatty acid.
2. A composition as claimed in claim 1, also comprising a basic element selected from potassium hydroxide, sodium hydroxide, ammonia and their basic salts in a quantity such that the pH of the composition is substantially 7 to 7.5.
3. A composition as claimed in claim 1 or 2 in which the vinasse is a magnesium or potassium residuary liquor obtained from a sugar refinery or a residuary liquor obtained from the preparation of glutamic acid.

EXAMPLE 5

The same composition was prepared as in Example 4, but by replacing the 10 parts of crude glutamic acid by 10 parts of soluble casein. The composition was used in a ratio of 40 parts by weight to 100 parts of mineral oil products.

EXAMPLE 6

In the composition of Example 4, there were added three parts by weight of sodium oleylisethionate before adding the water. Used in the same manner as that in Example 4, the composition gave a finer emulsion.

EXAMPLE 7

The following composition was prepared by successive additions with stirring between the various additions:—

Magnesium vinasse from sugar refinery	100 parts by weight
Casein	10 parts by weight
Octoic acid	10 parts by weight
Caustic potash lye d = 1.34	16 parts by weight
Sodium methylaminoethane sulphate	1 part by weight
Sodium lauryl sulphate	2 parts by weight
Water	63 parts by weight

This composition utilized in a ratio of 40 parts by weight to 100 parts by weight of mineral oil products gave as fine an emulsion as in Example 6.

EXAMPLE 8

The following composition was prepared in the same manner as in Example 7:—

Glutamic acid vinasse	100 parts by weight
Crude glutamic acid	10 parts by weight
Octoic acid	10 parts by weight
Caustic soda lye at 36° Be	16 parts by weight
Sodium Oleylisethionate	2 parts by weight
Sodium lauryl sulphate	4 parts by weight
Water	58 parts by weight

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the dispersion thereof in a large volume of water, the slightly diluted emulsion particularly that obtained from residues on the bottom of tanks, may be subjected to biodegradation in a confined medium the products of the biodegradation having a certain fertilising action.

The composition may also be used in a pasty form, for instance, so as to be disposed in a line at the limit of the tide on beaches threatened by oil slicks.

EXAMPLE 9

A pasty composition was prepared by mixing in succession and in the following order:

Vinasse from the preparation of glutamic acid	100 parts by weight
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Calcium phosphate	13 parts by weight
Calcium carbonate	44 parts by weight
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In a hydrographic research tank, a line of the pasty composition was deposited on a layer of sand and then an oil slick was advanced towards it. Under the effect of the artificial swell, the oil slick reaching the beach was emulsified with the composition and the emulsion, similar to these obtained with other compositions, was dispersed in the surface layers, the emulsion deposited on the sand being naturally washed by the swell.

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WHAT WE CLAIM IN:—

1. A composition for bringing mineral oil products into the form of a biodegradable emulsion comprising a vinasse in combination with at least one oleophilic fatty acid.

2. A composition as claimed in claim 1, also comprising a basic element selected from potassium hydroxide, sodium hydroxide, ammonia and their basic salts in a quantity such that the pH of the composition is substantially 7 to 7.5.

3. A composition as claimed in claim 1 or 2 in which the vinasse is a magnesium or potassium residuary liquor obtained from a sugar refinery or a residuary liquor obtained from the preparation of glutamic acid.



4. A composition as claimed in claim 1, 2 or 3 also comprising an amino-acid to enrich the vinasse in nitrogen.
5. A composition as claimed in claim 4, in which the amino-acid is selected from glutamic acid, glycocoll, tyrosine, leucine, proline, lysine, valine, betaine, histidine and alanine, or natural sources rich in amino acids such as casein, or a mixture thereof.
- 10 6. A composition as claimed in any preceding claim, in which the fatty acid is liquid at ambient temperature and is at least one of caproic acid, octoic acid, caprylic acid and oleic acid.
- 15 7. A composition as claimed in any preceding claim, in which the vinasse contains 6 to 20% by weight of the fatty acid.
- 20 8. A composition as claimed in any preceding claim additionally comprising at least one non-toxic and biodegradable emulsifier selected from sodium oleylisethionate, sodium methylaminoethane sulphonate, sodium lauryl sulphate, a secondary sulphonated paraffin, a sulphonated alpha-olefin, a
- 25 sarcosinate, 2-amino-2-hydroxy methyl-1, 3-propanediol, aminomethylpropanol, ethoxylated fatty alcohol, and polyoxyethylene-glycol oleate.
9. A composition as claimed in claim 8 comprising up to 5% by weight of emulsifier.
10. A composition as claimed in any preceding claim, which has added to it 20 to 50% by weight of water.
11. A composition as claimed in any one of claims 1 to 9, which has been made pasty 35 by the addition of a mineral charge and a small quantity of water.
12. A composition for bringing mineral oil products into the form of a biodegradable emulsion substantially as hereinbefore described and exemplified. 40
13. A biodegradable emulsion comprising 100 parts by weight of mineral oil products to 25 to 60 parts by weight of the composition as claimed in any one of claims 1 to 12. 45

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