

PATENT SPECIFICATION

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(54) METHOD AND COMPOSITION FOR THE EMULSIFICATION AND THE DEGRADATION OF PETROLEUM PRODUCTS AND FERTILIZERS THUS OBTAINED

(71) I, GEORGES HENRI SALOMONE/
 of French Nationality, of 16 Avenue Piesse,
 ler de Serbie, Paris 16eme, France, do hereby
 declare the invention for which I pray that a
 patent may be granted to me, 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 method for the emulsification and biodegradation of petroleum products.

Sludges and deposits derived from crude oils and their derivatives give rise to serious technical and economic problems. Thus such sludges and deposits may be fluidised only with difficulty with steam and this operation requires a considerable amount of manual labour together with high prime costs. In any event the use of solvents or steam to remove them give rise to water pollution with consequent harmful effects on the flora and fauna because of the very slow rate of degradation of the hydrocarbons comprising the sludges or deposits.

In British Patent No. 1,200,288 there is described a hydrocarbon emulsifying composition comprising a strong mineral acid, an alkali metal or alkaline earth metal salt and an organic hydrophilic substance, particularly molasses. This product contains from 30 to 70 per cent by weight of the strong mineral acid and has a very acid pH not exceeding 1.8. The diluted emulsion obtained with this product is not toxic to flora and fauna. It has now been found according to the present invention, that petroleum products may be emulsified with a particular composition to give biodegradable compositions which may be degraded to give fertilizer compositions or which may serve as culture media for micro-organisms.

According to the invention, therefore, there
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is provided a method for converting a petroleum product into a biodegradable emulsion which comprises bringing the petroleum product into contact with water and an emulsifying composition comprising:

(a) from 15 to 80 parts by weight of a micro-organism nutrient comprising molasses, cellulose, a sugar beet waste, casein, a malt extract, a proteose (including peptone), an ammonium salt, an amine, an amide and/or vinasse,

(b) from 10 to 50 parts by weight of a surface tension reducing component which is an alkali or alkaline earth metal salt and comprises calcium silicate, sodium silicate, potassium silicate, calcium carbonate, sodium carbonate, potassium carbonate, ammonium carbonate, dibasic sodium phosphate, dicalcium phosphate, and/or a mono- or dibasic ammonium phosphate, and,

(c) a diluent,
 and mixing the components to form an emulsion.

The amount of the micro-organism nutrient and surface tension reducing component may vary depending on the nutritional value and activity of the substances used.

The diluent in the emulsifying composition can be water and the amount of water may vary according to whether a fluid or pasty composition is desired and according to the physical nature of the substances used.

Further, in order to treat petroleum products floating on water the emulsifying composition is suitably in powdery form. In this case the diluent is preferably an absorbent powder which is calcium carbonate or talcum powder. The amount of absorbent powder may vary according to the physical nature of the other substances.

In general, one composition for use in

accordance with the invention will comprise the following:

	Parts by weight
5 Micro-organism nutrient component:	15 to 80
Surface tension reducing component:	10 to 50
Water:	5 to 60

10 When the diluent is an absorbent powder, this may be present in an amount from 150 to 400 per cent by weight of the total weight of the micro-organism nutrient component and the surface tension reducing component.

15 In contrast to the product described in Patent No. 1,200,288 the composition used in accordance with the present invention has an alkaline pH.

20 When an absorbent powder is used as diluent to give a powdery composition, it is preferred in order to increase the oleophilic nature of the composition and facilitate its mixing with petroleum to add a fatty acid in an amount of from 10 to 30 per cent by weight based on the weight of absorbent powder. The fatty acid may be stearic, oleic or palmitic acid.

25 The composition may also contain oligo-elements required for the growth of micro-organisms such as potassium, iron, zinc, magnesium and manganese salts.

30 In the process of the present invention the emulsifying composition containing water as diluent is suitably mixed with the petroleum product in an amount of from 50 to 250 parts by weight of the composition per 100 parts by weight of the petroleum product and the resultant emulsion diluted with water. The dilution water can be fresh, brackish or sea water. The dilution ratio is variable and may be from 5 and 40 times by weight.

40 The emulsion is in itself a fertilizer but its fertilizing properties are obtained only after the degradation of the hydrocarbons so that soils fertilized therewith can be used only after a period of 6 to 12 months.

45 In order to obtain a fertilizer which allows for immediate use of soils fertilized therewith, the diluted preparation is stored and, if necessary, inoculated with micro-organisms, the progress of the biodegradation being checked by gas phase chromatography. It is also possible, in order to assist the development of certain micro-organisms, to first modify the pH of the emulsion by the addition of small amounts of a mineral or organic acid.

50 When the biodegradation is complete, e.g.: after a period of from three to six weeks, the aqueous suspension can be poured onto the soils. The suspension may alternatively be concentrated by evaporation of the water. The biodegradation can also be halted by violent modification of the pH, for example by the addition of a strong acid.

The above mentioned fertilizers can, if de-

sired, also contain other plant nutrients such as potash, phosphates, sulphates or nitrates. In so far as they are not harmful to the development of the micro-organisms causing the biodegradation, these nutrients can be added at any stage whatever, i.e.: to the emulsifying composition or to the emulsion forming the culture medium.

The emulsions forming the culture media for the micro-organisms can also be used as cheap culture media for the industrial culture of certain micro-organisms such as yeasts.

Where the diluent is a solid powder the present invention envisages a process wherein the emulsifying composition is sprinkled onto petroleum products floating on water. The resultant product may be biodegraded to give a fertilizer.

In order that the invention may be well understood the following Examples are given by way of illustration only.

Certain of the emulsifying compositions used in the method of the invention form further embodiments thereof.

Accordingly, one aspect of the invention provides an emulsifying composition comprising (a) from 15 to 80 parts by weight of a micro-organism nutrient comprising molasses, cellulose, a sugar beet waste, a malt extract, a proteose, an ammonium salt, an amine, an amide and/or vinasse; (b) from 10 to 50 parts by weight of a surface tension reducing component which is calcium silicate, sodium silicate, potassium silicate, calcium carbonate, sodium carbonate, potassium carbonate, ammonium carbonate, dibasic sodium phosphate, dicalcium phosphate, and/or a mono- or dibasic ammonium phosphate; and (c) from 5 to 60 parts by weight of water.

Another aspect of the invention provides an emulsifying composition comprising (a) from 15 to 80 parts by weight of a micro-organism nutrient comprising molasses, cellulose, a sugar beet waste, a malt extract, a proteose, an ammonium salt, an amine, an amide and/or vinasse; (b) from 10 to 50 parts by weight of a surface tension reducing component which is calcium silicate, sodium silicate, potassium silicate, calcium carbonate, sodium carbonate, potassium carbonate, ammonium carbonate, dibasic sodium phosphate, dicalcium phosphate and/or a mono- or dibasic ammonium phosphate; and (c) from 150 to 400 per cent by weight (based on the weight of components (a) and (b)) of calcium carbonate or talcum powder.

EXAMPLE 1

A composition comprising:

	Parts by weight
Molasses	100
Sodium silicate	100
Water	100

was prepared.

To 100 parts by weight of residues of heavy fuel oil No. 2, there were added 80 parts by weight of the above liquid composition and the mixture was stirred with the addition of 6000 parts by weight of soft water and 20 parts by weight of phosphoric acid and the resultant emulsion was poured into a storage tank. After 5 weeks a checking by gas phase chromatography revealed complete bio-degradation of the hydrocarbons by natural micro-organisms. The aqueous suspension, after the addition of nitrate and potash was used for spraying sown cereals at the rate of 20 tonnes (1000 Kg) per hectare.

EXAMPLE 2

A composition comprising:

	Parts by weight
Molasses	100
Calcium carbonate	25
Calcium silicate	10
Water	100

was prepared.

100 parts by weight of Iraqi petroleum residues were emulsified by stirring with 60 parts by weight of the above liquid composition and there were added thereto 900 parts by weight of water.

After storing for 4 weeks, the emulsion was used to spray river sand in which cereals had been sown, at a rate of 100 cc of solution per square metre.

The cereals germinated normally.

EXAMPLE 3

A composition comprising:

	Parts by weight
Molasses	100
Dibasic sodium phosphate	10
Calcium carbonate	15
Water	10

was prepared.

This liquid composition was used to emulsify the same quantity by weight of crude oil and there was added to the emulsion four times its weight of brackish water.

This emulsion was used immediately to spray river sand at a rate of 100 grams per square metre. After six months, maize was sown in the treated sand and the maize developed normally.

EXAMPLE 4

A composition comprising:

	Parts by weight
Molasses	100
Sodium silicate	50
Water	50

was prepared.

This pasty preparation was mixed weight

for weight with crude oil recovered from beaches and the mixture was stored in a pit in the form of an emulsion with the addition of 5 times its volume of sea water and of 0.5% nitric acid. After one year, gas phase chromatography showed complete bio-degradation of the hydrocarbons and the product could be used as a fertilizer.

EXAMPLE 5

A pasty composition comprising:

	Parts by weight
Casein	50
Sodium silicate	50
Water	100

was prepared.

The composition was used to emulsify a bottom residue of a fuel oil tank and then oil diluted with a volume of water equal to 10 times the volume of the emulsion. The mixture was stored in the open air for 6 weeks after which its pH was modified by addition of phosphoric and nitric acids to halt the bio-degradation process. After evaporation of a part of the water, the liquid proved an excellent fertilizer.

EXAMPLE 6

A pasty preparation comprising:

	Parts by weight
Malt extract	50
Calcium carbonate	20
Sodium silicate	100
Water	50

was pumped into a double suction stirring pump at the same time as one and a half times its weight of petroleum residues. The emulsion was diluted with brackish water and discharged into a lagoon without any harm to the flora and fauna.

There were also prepared other compositions corresponding to those above partially or totally replacing the molasses with powdered cellulose, finely ground sugar beet wastes and peptone and these compositions gave equivalent results. Likewise, for fertilizers intended for soils poor in ammonium, the salts were replaced totally or partially by mono- or dibasic ammonium phosphates.

EXAMPLE 7

A composition comprising:

	Parts by weight
Molasses	20
Sodium silicate (35° Baumé)	20
Water	20

was prepared.

To 100 parts of this composition were added 40 parts by weight of hydrocarbons

constituted by heavy petroleum residues and the mixture was stirred to give an emulsion which was diluted with about 15 times its volume of cheese factory serum.

- 5 Seven litres of this emulsion were poured into a ten-litre fermenter. The emulsion was inoculated with one gram of yeast of *Torulopsis utilis* stock with suitable aeration and stirring. The yeast developed and after 10 hours, its weight corresponded to 53% of the weight of the molasses used. Gas phase chromatography showed complete bio-degradation of the hydrocarbons. The method could be carried out continuously compensating the degraded elements with application of the composition and hydrocarbon mixture.

EXAMPLE 8

A composition comprising:

	Parts by weight
20 Molasses	25
Natural potassium silicate (sanidine)	30
Water	20

was prepared.

- 25 100 parts by weight of this composition were used to emulsify 50 parts by weight of heavy hydrocarbons and to the emulsion was added about 15 times its volume of water.

- 30 A volume of ten litres of the emulsion was poured into a fifteen-litre fermenter and inoculated with one gram of silico-bacteria of the "Alexandrov" stock. After three weeks the silico-bacteria had proliferated. Decomposition of the natural potassium silicate and an amount of free potassium in the culture medium corresponding to 25% of the natural potassium silicate used were ascertained. Gas phase chromatography showed advanced degradation of the hydrocarbons. The solution formed a good fertilizer rich in potassium.

EXAMPLE 9

A composition comprising:

	Parts by weight
45 Molasses	50
Distillers washes (Vinasse)	50
Sodium silicate	100
Water	100

was prepared.

- 50 The composition was used in the same manner as in Example 1 but complete degradation of the hydrocarbons was obtained after about three weeks.

EXAMPLE 10

A mixture comprising:

	Parts by weight
55 Molasses	25
Distillers washes (Vinasse)	25
Sodium silicate at 35° Baumé	10
Talcum powder	150

- 60 was mechanically stirred.

The powder obtained was used for sprinkling of petroleum floating at the surface of an aquarium. Petroleum was absorbed and carried along by the powder. The emulsified mixture deposited on the bottom of the aquarium has been progressively used up by the flora without any verifiable damage for flora and fauna.

EXAMPLE 11

A mixture comprising:

	Parts by weight
Molasses	20
Distillers washes (Vinasse)	20
Calcium silicate	4
Calcium carbonate	130
Stearic acid	24

was mechanically stirred.

The amount of said powdered product to be used, in the same manner as in Example 10 to absorb the petroleum was reduced by about 40%.

EXAMPLE 12

A mixture comprising:

	Parts by weight
Molasses	20
Distillers washes (Vinasse)	20
Sodium silicate 35°B	8
Talcum powder	130
Oleic acid	20

was mechanically stirred.

The powder obtained was used in the same manner as in Example 11 with fairly the same results.

WHAT I CLAIM IS:—

1. A method for converting a petroleum product into a biodegradable emulsion which comprises bringing the petroleum product into contact with water and an emulsifying composition comprising:

(a) from 15 to 80 parts by weight of a micro-organism nutrient comprising molasses, cellulose, a sugar beet waste, casein, a malt extract, a proteose, an ammonium salt, an amine, an amide and/or vinasse;

(b) from 10 to 50 parts by weight of a surface tension reducing component which is an alkali or alkaline earth metal salt and comprises calcium silicate, sodium silicate, potassium silicate, calcium carbonate, sodium carbonate, potassium carbonate, ammonium carbonate, dibasic sodium phosphate, dicalcium phosphate and/or a mono- or dibasic ammonium phosphate, and,

(c) a diluent, and subsequently mixing them to produce the emulsion.

2. A method as claimed in Claim 1, in which the diluent is water.



constituted by heavy petroleum residues and the mixture was stirred to give an emulsion which was diluted with about 15 times its volume of cheese factory serum.

- 5 Seven litres of this emulsion were poured into a ten-litre fermenter. The emulsion was inoculated with one gram of yeast of *Torulopsis utilis* stock with suitable aeration and stirring. The yeast developed and after 10 hours, its weight corresponded to 53% of the weight of the molasses used. Gas phase chromatography showed complete bio-degradation of the hydrocarbons. The method could be carried out continuously compensating the degraded elements with application of the composition and hydrocarbon mixture.

EXAMPLE 8

A composition comprising:

	Parts by weight
20 Molasses	25
Natural potassium silicate (sanidine)	30
Water	20

was prepared.

- 25 100 parts by weight of this composition were used to emulsify 50 parts by weight of heavy hydrocarbons and to the emulsion was added about 15 times its volume of water.

- 30 A volume of ten litres of the emulsion was poured into a fifteen-litre fermenter and inoculated with one gram of silico-bacteria of the "Alexandrov" stock. After three weeks the silico-bacteria had proliferated. Decomposition of the natural potassium silicate and an amount of free potassium in the culture medium corresponding to 25% of the natural potassium silicate used were ascertained. Gas phase chromatography showed advanced degradation of the hydrocarbons. The solution formed a good fertilizer rich in potassium.

EXAMPLE 9

A composition comprising:

	Parts by weight
45 Molasses	50
Distillers washes (Vinasse)	50
Sodium silicate	100
Water	100

was prepared.

- 50 The composition was used in the same manner as in Example 1 but complete degradation of the hydrocarbons was obtained after about three weeks.

EXAMPLE 10

A mixture comprising:

	Parts by weight
55 Molasses	25
Distillers washes (Vinasse)	25
Sodium silicate at 35° Baumé	10
Talcum powder	150

- 60 was mechanically stirred.

The powder obtained was used for sprinkling of petroleum floating at the surface of an aquarium. Petroleum was absorbed and carried along by the powder. The emulsified mixture deposited on the bottom of the aquarium has been progressively used up by the flora without any verifiable damage for flora and fauna.

EXAMPLE 11

A mixture comprising:

	Parts by weight
Molasses	20
Distillers washes (Vinasse)	20
Calcium silicate	4
Calcium carbonate	130
Stearic acid	24

was mechanically stirred.

The amount of said powdered product to be used, in the same manner as in Example 10 to absorb the petroleum was reduced by about 40%.

EXAMPLE 12

A mixture comprising:

	Parts by weight
Molasses	20
Distillers washes (Vinasse)	20
Sodium silicate 35°B	8
Talcum powder	130
Oleic acid	20

was mechanically stirred.

The powder obtained was used in the same manner as in Example 11 with fairly the same results.

WHAT I CLAIM IS:—

1. A method for converting a petroleum product into a biodegradable emulsion which comprises bringing the petroleum product into contact with water and an emulsifying composition comprising:

(a) from 15 to 80 parts by weight of a micro-organism nutrient comprising molasses, cellulose, a sugar beet waste, casein, a malt extract, a proteose, an ammonium salt, an amine, an amide and/or vinasse;

(b) from 10 to 50 parts by weight of a surface tension reducing component which is an alkali or alkaline earth metal salt and comprises calcium silicate, sodium silicate, potassium silicate, calcium carbonate, sodium carbonate, potassium carbonate, ammonium carbonate, dibasic sodium phosphate, dicalcium phosphate and/or a mono- or dibasic ammonium phosphate, and,

(c) a diluent, and subsequently mixing them to produce the emulsion.

2. A method as claimed in Claim 1, in which the diluent is water.



3. A method as claimed in Claim 2 in which the emulsifying composition comprises from 5 to 60 parts by weight of water.
4. A method as claimed in Claim 2 or Claim 3 in which the emulsifying composition is mixed with the petroleum product at a rate of from 50 to 250 parts by weight of composition per 100 parts by weight of petroleum product.
5. A method as claimed in any one of Claims 2—4 in which the emulsion is subsequently diluted with water.
6. A method as claimed in Claim 5, in which the emulsion is diluted with from 5 to 40 times its weight of water.
7. A method as claimed in Claim 5 or claim 6, in which the pH of diluted emulsion is adjusted by the addition of an acid.
8. A method as claimed in Claim 1 in which the diluent is an absorbent powder which is calcium carbonate or talcum powder and the emulsifying composition is sprinkled onto a petroleum product floating on water.
9. A method as claimed in Claim 8 in which the emulsifying composition contains from 150 to 400 per cent by weight of absorbent powder based on the weight of components (a) and (b).
10. A method as claimed in Claim 8 or Claim 9, in which the emulsifying composition contains from 10 to 30 per cent by weight (based on the weight of absorbent powder) of oleic, palmitic or stearic acid.
11. A method as claimed in Claim 1, substantially as hereinbefore described with reference to the Examples.
12. An emulsion obtained by a method as claimed in any one of the preceding claims.
13. A product obtained by cultivating micro-organisms on an emulsion as claimed in Claim 12.
14. An emulsifying composition comprising (a) from 15 to 80 parts by weight of a micro-organism nutrient comprising molasses, cellulose, a sugar beet waste, a malt extract, a proteose, an ammonium salt, an amine, an amide and/or vinasse; (b) from 10 to 50 parts by weight of a surface tension reducing component which is calcium silicate, sodium silicate, potassium silicate, calcium carbonate, sodium carbonate, potassium carbonate, ammonium carbonate, dibasic sodium phosphate, dicalcium phosphate, and/or a mono- or dibasic ammonium phosphate; and (c) from 5 to 60 parts by weight of water.
15. A composition as claimed in Claim 14, substantially as hereinbefore described.
16. An emulsifying composition comprising (a) from 15 to 80 parts by weight of a micro-organism nutrient comprising molasses, cellulose, a sugar beet waste, a malt extract, a proteose, an ammonium salt, an amine, an amide and/or vinasse; (b) from 10 to 50 parts by weight of a surface tension reducing component which is calcium silicate, sodium silicate, potassium silicate, calcium carbonate, sodium carbonate, potassium carbonate, ammonium carbonate, dibasic sodium phosphate, dicalcium phosphate and/or a mono- or dibasic ammonium phosphate; and (c) from 150 to 400 per cent by weight (based on the weight of components (a) and (b)) of calcium carbonate or talcum powder.
17. A composition as claimed in Claim 16 also containing from 10 to 30 per cent by weight, based on the weight of component (c), of oleic, palmitic or stearic acid.
18. A composition as claimed in Claim 16 substantially as hereinbefore described with reference to the Examples.
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