

# PATENT SPECIFICATION

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## (54) METHOD AND COMPOSITION FOR EMULSIFYING PETROLEUM PRODUCTS WITH A VIEW TO PREPARING A CULTURE MEDIUM FOR MICRO-ORGANISMS

(71) I, GEORGES HENRI SALOMONE, of French Nationality of 14 Avenue Pierre 1er 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 emulsifying petroleum products to prepare culture media for micro-organisms.

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 fluidified 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 these gives rise to water pollution with consequent harmful effects on the flora and fauna because of very slow rate of degradation of the said hydrocarbons.

In British Patent No. 1,200,288, there is described a hydrocarbon emulsifying composition comprising a strong mineral acid, an alkali or alkaline earth metal salt and an organic, hydrophilic substance, particularly molasses. This product contains from 30 to 70% 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.

In copending application No. 20991/71 (Serial No. 1353945), there is described a method for the emulsification and biodegradation of petroleum products using an emulsifying composition comprising three components namely (a) a microorganism nutrient component (b) an alkali or alkaline earth metal salt as surface tension reducing component and (c) a diluent, which composition has an essentially basic character.

It has now been found, in accordance with

the present invention, that petroleum products may be converted into emulsions which may be used as culture media for micro-organisms using an emulsifying composition comprising (a) a micro-organism nutrient component and (b) an organic acid.

According to the invention, therefore, there is provided a method of converting a petroleum product into a biodegradable emulsion which comprises mixing the petroleum product with an emulsifying composition comprising:—

(a) from 20 to 50 parts by weight of a micro-organism nutrient component comprising molasses, cellulose, sugar beet waste, casein, a malt extract and/or proteose (including peptone); and

(b) from 30 to 50 parts by weight of an organic acid component comprising lactic, acetic, citric, gluconic, glutamic, itaconic and/or oxalic acid and emulsifying the mixture with water.

The emulsifying composition can also contain an alkali or alkaline-earth metal salt, particularly in the case where it is necessary to control the pH of the final emulsion for use as a culture medium for micro-organisms. If desired there can be added to the composition a small percentage, not exceeding 10% by weight, of a strong mineral acid.

The amount of the different constituents can vary depending on their nutritional value and activity.

The composition, for use in accordance with the invention, will comprise the following:

|                                     |                          |
|-------------------------------------|--------------------------|
| Micro-organism nutrient             | 20 to 50 parts by weight |
| Organic acid                        | 30 to 50 parts by weight |
| Alkali or alkaline-earth metal salt | 0 to 30 parts by weight  |

The organic acid can be a cheap, commercially available acid and is lactic, acetic, citric, gluconic, glutamic, ita-

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conic or oxalic acid. These acids can be in the pure form or in the form of industrial wastes containing them, such as cheese factory serum, brewery mash or fermentation residues from the production of citric or glutamic acid.

The alkali or alkaline-earth metal salt can be a non-toxic salt reducing surface tension. In particular calcium, sodium, ammonium or potassium, silicates, sulphates, sulphites, hyposulphites, carbonates, phosphates, phosphites, chlorides, nitrates, nitrites, lactates, acetates, oxalates, glutamates and citrates can be used. These salts can be in the pure form or as contained in industrial wastes.

In the method of the invention the emulsifying composition is suitably mixed with the petroleum product at a rate of from 40 to 1,000 parts by weight of composition per 100 parts by weight of petroleum product and the whole then diluted with water suitably at a dilution of the order of 1 to 30 times.

The emulsion obtained may form a culture medium for micro-organisms and can have added to it compounds which can be decomposed or solubilized by the micro-organisms such as metal salts or oxides, particularly in the form of low grade ores or minerals. This culture medium can be used for the industrial culture of micro-organisms such as edible yeasts intended for human or animal nutrition, bacteria or fungi intended for the manufacture by fermentation of certain products such as citric acid, gluconic acid or glutamic acid, or bacteria or fungi capable of solubilizing compounds, for example the silico-bacteria which liberate potassium from natural potassium silicates, thio-bacteria for producing sulphuric acid from reduced sulphur products, the sulphate-reducing bacteria for producing sulphur from starting sulphates and sulphites and the various microorganisms used for the enrichment of low grade minerals, as well as to assist the bio-degradation of substances which are difficult to decompose.

The culture media can, after partial or total degradation be used as fertilizers or as base constituents for fertilizers to which can be added fertilizing components such as potash, sulphates, phosphates or nitrates. These fertilizing components can be added to the composition or to the emulsion if they are not harmful to the development of the micro-organisms.

The emulsifying composition used in the invention forms another embodiment thereof and accordingly, the invention also provides an emulsifying composition comprising:—

(a) from 20 to 50 parts by weight of a micro-organism nutrient component comprising molasses, cellulose, sugar beet

waste, casein, a malt extract and/or proteose; and

(b) from 30 to 50 parts by weight of an organic acid component comprising lactic, acetic, citric, gluconic, glutamic, itaconic and/or oxalic acid.

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

#### EXAMPLE 1

A composition comprising:

|                     |                     |
|---------------------|---------------------|
| Molasses            | 80 parts by weight  |
| Lactic acid         | 100 parts by weight |
| Dicalcium phosphate | 60 parts by weight  |

was prepared. To 100 parts by weight of petroleum residues were added 120 parts by weight of the above composition and the mixture was stirred with the addition of 15 times its volume of water. The emulsion was poured into a ten-liter fermenter and inoculated with one gram of yeast of *Torulopsis utilis* stock. The yeast developed and after 10 hours, it was possible to recover an amount of yeast equal to about 50% of the weight of the molasses used. A check by gas phase chromatography showed marked degradation of the hydrocarbons. The culture medium was used as fertilizer.

#### EXAMPLE 2

A composition comprising:

|                                |                     |
|--------------------------------|---------------------|
| Molasses                       | 40 parts by weight  |
| Lactic acid                    | 100 parts by weight |
| Potassium phosphate            | 20 parts by weight  |
| Sulphate in the form of gypsum | 40 parts by weight  |

was prepared. The composition was used to emulsify crude oil at the rate of 200 parts by weight of the composition for 100 parts by weight of the petroleum wastes and 5000 parts by weight of water.

The emulsion placed in a fermenter under anaerobic conditions served as culture medium for *Vibrio desulfuricans*. After 4 weeks the transformation of the calcium sulphate into sulphur was ascertained, the production of precipitated sulphur corresponding to 42% of the sulphur contained at the beginning in the form of sulphate.

#### EXAMPLE 3

The same composition as in Example 1 was prepared, but replacing the lactic acid by the same quantity, by weight, of acetic acid. This composition was used in the same manner and under the same conditions with, however, an increase in the percentage of the composition for the emulsification of petroleum residues. The emulsion obtained, greatly diluted, was used as fertilizer for a micaceous sand. After having been inoculated

with silico-bacteria and left at rest for six months, the soil showed an enrichment in potassium liberated from the mica. It was sown with cereal which sprouted normally without any deficiency in phosphate, calcium or potassium.

#### EXAMPLE 4

In the composition in accordance with Example 3, the 80 parts by weight of molasses were replaced by 60 parts by weight of peptone. Three tonnes (1000 Kg) of the composition were used to emulsify an equivalent weight of bunker hydrocarbon residues with the addition of 10 volumes of sea water. The emulsion was discharged in a port environment without any modification of the flora or fauna and without any petroleum deposit on the jetties.

#### EXAMPLE 5

With a composition comprising:

Lactic acid 100 parts by weight  
Molasses 80 parts by weight

80 parts by weight of crude oil were emulsified with the addition of 5000 parts by weight of soft water. There was added to the emulsion 100 parts by weight of natural manganese dioxide and this was inoculated with a *Cladosporium herbarium* fungus. After 30 days in a fermenter with stirring and suitable aeration, 20% of the manganese was found solubilized in the culture medium and 0.7% thereof had accumulated in the mycelium. The separation was effected by filtration.

#### EXAMPLE 6

The following composition was prepared:

Casein 30 parts by weight  
Lactic acid 10 parts by weight  
Dairy serum 90 parts by weight  
Natural calcium sulphate (anhydrite) 30 parts by weight

20 parts by weight of crude oil were emulsified with this composition and, after dilution with water, there was cultivated in this medium, under anaerobic conditions, *Vibrio desulfuricans* inoculated with five millimeters of a fresh culture of *Vibrio desulfuricans* per ten litres of solution. After five weeks the sulphur precipitated in consequence of the transformation of the calcium sulphate corresponded to 40% of the sulphur contained at the beginning in the form of sulphate.

#### EXAMPLE 7

A composition containing:

Molasses 90 parts by weight  
Lactic acid 54 parts by weight  
Calcium sulphite 60 parts by weight  
Phosphoric acid 20 parts by weight  
was prepared.

100 parts by weight of this composition were used to emulsify 100 parts by weight of petroleum residues and the emulsion was diluted to 15 times its volume with water. The emulsion was inoculated in a fermenter with thio-bacteria. 70% of the sulphur contained in the calcium sulphite was transformed into sulphuric acid which was recovered by elimination of the solid material by filtration and concentration of the filtrate.

#### WHAT I CLAIM IS:—

1. A method of converting a petroleum product into a biodegradable emulsion which comprises mixing the petroleum product with an emulsifying composition comprising:—

(a) from 20 to 50 parts by weight of a micro-organism nutrient component comprising molasses, cellulose, sugar beet waste, casein, a malt extract and/or proteose; and

(b) from 30 to 50 parts by weight of an organic acid component comprising lactic, acetic, citric, gluconic, glutamic, itaconic and/or oxalic acid,

and emulsifying the mixture with water.

2. A method as claimed in Claim 1 in which the organic acid component is in the form of an industrial waste.

3. A method as claimed in Claim 1 or Claim 2 in which the emulsifying composition also contains up to 30 parts by weight of an alkali or an alkaline earth metal salt component comprising a silicate, sulphate, sulphite, hyposulphite, carbonate, phosphate, phosphite, chloride, nitrate, nitrite, lactate, acetate, oxalate, glutamate or citrate of calcium, sodium, potassium, or the ammonium ion.

4. A method as claimed in Claim 3 in which the alkali or alkaline earth metal salt component is in the form of an industrial waste.

5. A method as claimed in any one of the preceding claims in which the emulsifying composition is mixed with the petroleum product at a rate of from 40 to 1,000 parts by weight of emulsifying composition per 100 parts by weight of petroleum product.

6. A method as claimed in Claim 1 substantially as hereinbefore described with reference to the Examples.

7. An emulsion when obtained by a process as claimed in any one of Claims 1-6.

8. A method of cultivating micro-organisms which comprises adding one or more nutrients to an emulsion as claimed in Claim 7 and subsequently culturing a micro-organism in the resultant culture medium.

9. A method as claimed in Claim 8 in which a natural potassium silicate is added

with silico-bacteria and left at rest for six months, the soil showed an enrichment in potassium liberated from the mica. It was sown with cereal which sprouted normally without any deficiency in phosphate, calcium or potassium.

#### EXAMPLE 4

In the composition in accordance with Example 3, the 80 parts by weight of molasses were replaced by 60 parts by weight of peptone. Three tonnes (1000 Kg) of the composition were used to emulsify an equivalent weight of bunker hydrocarbon residues with the addition of 10 volumes of sea water. The emulsion was discharged in a port environment without any modification of the flora or fauna and without any petroleum deposit on the jetties.

#### EXAMPLE 5

With a composition comprising:  
Lactic acid 100 parts by weight  
Molasses 80 parts by weight  
80 parts by weight of crude oil were emulsified with the addition of 5000 parts by weight of soft water. There was added to the emulsion 100 parts by weight of natural manganese dioxide and this was inoculated with a *Cladosporium herbarium* fungus. After 30 days in a fermenter with stirring and suitable aeration, 20% of the manganese was found solubilized in the culture medium and 0.7% thereof had accumulated in the mycelium. The separation was effected by filtration.

#### EXAMPLE 6

The following composition was prepared:  
Casein 30 parts by weight  
Lactic acid 10 parts by weight  
Dairy serum 90 parts by weight  
Natural calcium sulphate (anhydrite) 30 parts by weight  
20 parts by weight of crude oil were emulsified with this composition and, after dilution with water, there was cultivated in this medium, under anaerobic conditions, *Vibrio desulfuricans* inoculated with five millimeters of a fresh culture of *Vibrio desulfuricans* per ten litres of solution. After five weeks the sulphur precipitated in consequence of the transformation of the calcium sulphate corresponded to 40% of the sulphur contained at the beginning in the form of sulphate.

#### EXAMPLE 7

A composition containing:  
Molasses 90 parts by weight  
Lactic acid 54 parts by weight  
Calcium sulphite 60 parts by weight  
Phosphoric acid 20 parts by weight  
was prepared.

100 parts by weight of this composition were used to emulsify 100 parts by weight of petroleum residues and the emulsion was diluted to 15 times its volume with water. The emulsion was inoculated in a fermenter with thio-bacteria. 70% of the sulphur contained in the calcium sulphite was transformed into sulphuric acid which was recovered by elimination of the solid material by filtration and concentration of the filtrate.

#### WHAT I CLAIM IS:—

1. A method of converting a petroleum product into a biodegradable emulsion which comprises mixing the petroleum product with an emulsifying composition comprising:—

(a) from 20 to 50 parts by weight of a micro-organism nutrient component comprising molasses, cellulose, sugar beet waste, casein, a malt extract and/or proteose; and  
(b) from 30 to 50 parts by weight of an organic acid component comprising lactic, acetic, citric, gluconic, glutamic, itaconic and/or oxalic acid,  
and emulsifying the mixture with water.

2. A method as claimed in Claim 1 in which the organic acid component is in the form of an industrial waste.

3. A method as claimed in Claim 1 or Claim 2 in which the emulsifying composition also contains up to 30 parts by weight of an alkali or an alkaline earth metal salt component comprising a silicate, sulphate, sulphite, hyposulphite, carbonate, phosphate, phosphite, chloride, nitrate, nitrite, lactate, acetate, oxalate, glutamate or citrate of calcium, sodium, potassium, or the ammonium ion.

4. A method as claimed in Claim 3 in which the alkali or alkaline earth metal salt component is in the form of an industrial waste.

5. A method as claimed in any one of the preceding claims in which the emulsifying composition is mixed with the petroleum product at a rate of from 40 to 1,000 parts by weight of emulsifying composition per 100 parts by weight of petroleum product.

6. A method as claimed in Claim 1 substantially as hereinbefore described with reference to the Examples.

7. An emulsion when obtained by a process as claimed in any one of Claims 1-6.

8. A method of cultivating micro-organisms which comprises adding one or more nutrients to an emulsion as claimed in Claim 7 and subsequently culturing a micro-organism in the resultant culture medium.

9. A method as claimed in Claim 8 in which a natural potassium silicate is added



to the emulsion which is subsequently inoculated with silico bacteria.

10. A method as claimed in Claim 8 in which sulphur compounds are added to the emulsion which is subsequently inoculated with thio-bacteria.

11. A method as claimed in Claim 8 in which sulphates or sulphites are added to the emulsion which is subsequently inoculated with sulphate-reducing bacteria.

12. A method as claimed in Claim 8 in which a low grade ore is added to the emulsion which is subsequently inoculated with micro-organisms solubilizing the metal contained in the ore.

13. A method as claimed in Claim 8 substantially as hereinbefore described.

14. Bio-degraded products when obtained by a method as claimed in any one of Claims 8-13.

15. An emulsifying composition comprising:—

(a) from 20 to 50 parts by weight of a micro-organism nutrient component com-

prising molasses, cellulose, sugar beet waste, casein, a malt extract and/or proteose; and

(b) from 30 to 50 parts by weight of an organic acid component comprising lactic, acetic, citric, gluconic, glutamic, itaconic and/or oxalic acid.

16. A composition as claimed in Claim 15 also containing up to 30 parts by weight of an alkali or alkaline earth metal salt component comprising a silicate, sulphate, sulphite, hyposulphite, carbonate, phosphate, phosphite, chloride, nitrate, nitrite, lactate, acetate, oxalate, glutamate or citrate of calcium, sodium, potassium or the ammonium ion.

17. A composition as claimed in Claim 15 substantially as hereinbefore described.

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