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(54) COMPOSITION FOR EMULSIFYING HYDROCARBONS

(71) I, GEORGE HENRI SALOMONE, a French citizen, 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:—

This invention is concerned with improvements in and relating to compositions for emulsifying hydrocarbons with fresh water, brackish water or sea water.

The mining of muds and deposits for crude oil and derivatives thereof presents some important and serious technological and economic problems. It is only with difficulty that these muds and deposits can be rendered fluent with steam, and this operation requires a considerable effort at high cost. The use of solvents and the mining of muds fluidized with steam create continuous water pollution which kills vegetation and animal life. Restoring the land and water thus polluted by such products also presents important technological problems.

It is an object of the present invention to provide a composition to emulsify crude oil and residuals of the same, with fresh water, brackish water or sea water.

According to the invention there is provided a composition for emulsifying hydrocarbons, especially crude oil, with water which comprises a mixture of a strong mineral acid, an alkali metal salt, an ammonium salt or an alkaline earth metal salt, and a hydrophilic organic substance. Suitably the compositions of the invention consist only of the ingredients listed above.

Preferably, the composition contains from 30 to 70% by weight of the strong mineral acid, from 15 to 35% by weight of the ammonium salt, alkali metal salt or alkaline earth metal salt, and from 15 to 35% by weight of the hydrophilic organic substance.

As the strong mineral acid, acids such as phosphoric, hydrochloric, nitric, sulphuric and hydrofluoric acids may be employed.

The alkali metal salt, ammonium salt or alkaline earth metal salt is preferably a salt

with the mineral acid used in the composition. However, alkali metal salts or alkaline earth metal salts of other strong mineral acids such as fluorides, difluorides, chlorides, sulphates, phosphates and nitrates, may be used alone or in admixture. The metals forming the salts include sodium, potassium, lithium, calcium, strontium and barium. If desired, the composition may contain two or more salts.

The organic hydrophilic substance may suitably be a carbohydrate or a hydrophilic polypeptide. Examples of carbohydrates which may be employed in the composition of the invention are saccharose, unrefined sugar and molasses. The polypeptide may be, for example, a peptone such as pancreatic peptone. One or more hydrophilic organic substances may be employed in the compositions of the invention.

Preferably, when the product is to be used in the cleaning of ferrous metal containers, the strong mineral acid used is phosphoric acid and the salt is an alkali metal phosphate or alkaline earth metal phosphate. Phosphoric acid has the advantageous effect of lightly phosphatizing the metal surfaces with which it comes in contact; and this, in the presence of mineral oils, protects the ferrous metal. A preferred composition according to the invention, consists essentially of 30 to 70% by weight of technically pure 75% phosphoric acid, 15 to 35% by weight of tribasic calcium phosphate, and 15 to 35% by weight of molasses.

For cleaning stone surfaces, beaches and the like, the preferred acid is hydrofluoric acid.

The composition according to the invention, when mixed under agitation with hydrocarbons in an amount of about 50 to 70 parts by weight of composition to 100 parts by weight of the residual products to be eliminated, yields a stable emulsion which may be mixed with water to any desired dilution.

The invention also provides a method of emulsifying a hydrocarbon oil which comprises contacting said oil with a composition

[Price 5s. 0d. (25p)]

as described above; agitating the mixture of hydrocarbon oil and composition and diluting the agitated mixture with water.

In order that the invention may be well understood, the following Examples of compositions according to the present invention are given by way of illustration only.

EXAMPLE 1

		Parts by weight
10	Hydrofluoric acid	48
	Ammonium bifluoride	9
	Ammonium sulphate	9
	Barium chloride	9
15	Saccharose	10
	Unrefined sugar	15

EXAMPLE 2

		Parts by weight
20	Phosphoric acid	52
	Dibasic calcium phosphate	24
	Unrefined sugar	24

EXAMPLE 3

		Parts by weight
25	Phosphoric acid	50
	Dibasic calcium phosphate	25
	Pancreatic peptone	25

EXAMPLE 4

		Parts by weight
30	Sulphuric acid	60
	Calcium sulphate	10
	Calcium chloride	10
35	Unrefined sugar	20

EXAMPLE 5

		Parts by weight
40	Hydrochloric acid	40
	Sodium chloride	15
	Tribasic calcium phosphate	15
	Molasses	30

EXAMPLE 6

		Parts by weight
45	Nitric acid	30
	Sodium nitrate	15
	Ammonium sulphate	10
	Calcium chloride	10
50	Saccharose	15
	Molasses	20

The mixture according to Example 1 has been used to clean rocks soiled by petroleum. The composition was applied by brushing to the soiled coastal rocks. The resultant milky layer was removed by natural dilution at the next tide, the rocks having

been cleaned of all the material that soiled them.

The composition according to Example 2 was used in the form of an aqueous paste to emulsify 22 pounds of petroleum residue from Iraq. The 22 pounds of petroleum residue and 13.2 pounds of composition according to the invention were pumped in a double-acting positive displacement pump and the resulting compressed homogeneous paste was diluted with water.

To study the action of the composition of the invention on marine vegetation, there were established dilutions at three different concentrations very much higher than the concentrations encountered in practice, which, at the time of dumping is at most 5% and which immediately diminishes by admixture with the water which receives the dumped material, whether sewerage or river or sea water. These concentrations were respectively, 10, 25 and 50% of the homogeneous paste. Twelve different species of fungi were cultivated in these various media: *Sterigmatocystis nigra*, *Aspergillus amstelodami*, *Aspergillus flavus*, *Penicillium brevicompactum*, *Penicillium cyclopium*, *Paecilomyces varioti*, *Acrostalagmus koningi*, *Chaetomium globosum*, *Myrothecium verrucaria*, *Stachybotrys atra*, *Memnoniella echinata* and *Penicillium funiculosum*. The fungi developed normally as concentrations of 10 to 25% of the composition. Growth was, however, retarded at a concentration of 50%.

The same composition was the subject of an experiment to determine its effect on diving birds. To this end, two quarts of crude oil were emulsified with one quart of composition according to the present invention and 25 quarts of water. Two ducks were immersed in this solution. They did not seem to be in the least incommoded and swam normally. Their feathers did not stick together and were not rendered wettable. Out of the water, the birds dried normally.

The composition according to Example 3 was used to clean a steel vessel containing about 110 pounds of No. 2 heavy fuel oil. The emulsification of this heavier material required 82 pounds of composition according to the invention. After vigorous agitation, 50 gallons of water were introduced by means of a hose onto the vessel so as to effect a first dilution. The mixture was pumped out and passed into a sewer with an additional 400 gallons of water so as to ensure a harmless concentration. The walls of the vessel were entirely clean.

WHAT I CLAIM IS:—

1. A composition for emulsifying hydrocarbons with water, comprising a mixture of a strong mineral acid, an ammonium salt or a salt of an alkali metal or alkaline earth

as described above; agitating the mixture of hydrocarbon oil and composition and diluting the agitated mixture with water.

In order that the invention may be well understood, the following Examples of compositions according to the present invention are given by way of illustration only.

EXAMPLE 1

	Parts by weight
10 Hydrofluoric acid	48
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	Parts by weight
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EXAMPLE 3

	Parts by weight
25 Phosphoric acid	50
Dibasic calcium phosphate	25
Pancreatic peptone	25

EXAMPLE 4

	Parts by weight
30 Sulphuric acid	60
Calcium sulphate	10
Calcium chloride	10
35 Unrefined sugar	20

EXAMPLE 5

	Parts by weight
40 Hydrochloric acid	40
Sodium chloride	15
Tribasic calcium phosphate	15
Molasses	30

EXAMPLE 6

	Parts by weight
45 Nitric acid	30
Sodium nitrate	15
Ammonium sulphate	10
Calcium chloride	10
50 Saccharose	15
Molasses	20

The mixture according to Example 1 has been used to clean rocks soiled by petroleum. The composition was applied by brushing to the soiled coastal rocks. The resultant milky layer was removed by natural dilution at the next tide, the rocks having

been cleaned of all the material that soiled them.

The composition according to Example 2 was used in the form of an aqueous paste to emulsify 22 pounds of petroleum residue from Iraq. The 22 pounds of petroleum residue and 13.2 pounds of composition according to the invention were pumped in a double-acting positive displacement pump and the resulting compressed homogeneous paste was diluted with water.

To study the action of the composition of the invention on marine vegetation, there were established dilutions at three different concentrations very much higher than the concentrations encountered in practice, which, at the time of dumping is at most 5% and which immediately diminishes by admixture with the water which receives the dumped material, whether sewerage or river or sea water. These concentrations were respectively, 10, 25 and 50% of the homogeneous paste. Twelve different species of fungi were cultivated in these various media: *Sterigmatocystis nigra*, *Aspergillus amstelodami*, *Aspergillus flavus*, *Penicillium brevicompactum*, *Penicillium cyclopium*, *Paeclomyces varioti*, *Acrostalagmus koningi*, *Chaetomium globosum*, *Myrothecium verrucaria*, *Stachybotrys atra*, *Memnoniella echinata* and *Penicillium funiculosum*. The fungi developed normally as concentrations of 10 to 25% of the composition. Growth was, however, retarded at a concentration of 50%.

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The composition according to Example 3 was used to clean a steel vessel containing about 110 pounds of No. 2 heavy fuel oil. The emulsification of this heavier material required 82 pounds of composition according to the invention. After vigorous agitation, 50 gallons of water were introduced by means of a hose onto the vessel so as to effect a first dilution. The mixture was pumped out and passed into a sewer with an additional 400 gallons of water so as to ensure a harmless concentration. The walls of the vessel were entirely clean.

WHAT I CLAIM IS:—

1. A composition for emulsifying hydrocarbons with water, comprising a mixture of a strong mineral acid, an ammonium salt or a salt of an alkali metal or alkaline earth



metal, and a hydrophilic organic substance.

2. A composition as claimed in claim 1, in which said acid is present in an amount of from 30 to 70% by weight, said salt is present in an amount of from 15 to 35% by weight, and said hydrophilic organic substance is present in an amount of from 15 to 35% by weight.

3. A composition as claimed in claim 1 or claim 2, in which said acid is phosphoric, hydrochloric, nitric, sulphuric or hydrofluoric acid.

4. A composition as claimed in any one of the preceding claims, in which said salt is a fluoride, difluoride, chloride, sulphate, phosphate or nitrate.

5. A composition as claimed in any one of the preceding claims in which said salt is a salt of sodium, potassium, lithium, calcium, strontium or barium.

6. A composition as claimed in any one of the preceding claims in which two or more of said salts are present.

7. A composition as claimed in any one of the preceding claims in which said hydrophilic organic substance is a carbohydrate or a hydrophilic peptide.

8. A composition as claimed in claim 7 in which said organic substance is sac-

charose, unrefined sugar, molasses or pancreatic peptone.

9. A composition as claimed in any one of the preceding claims in which said salt is a salt of the strong mineral acid which is used in the composition.

10. A composition as claimed in claim 2, in which said strong mineral acid is phosphoric and said salt is an alkali metal or alkaline earth metal phosphate.

11. A composition as claimed in claim 10 in which said strong mineral acid is phosphoric acid, said salt is dibasic calcium phosphate, and said hydrophilic organic substance is unrefined sugar.

12. A composition as claimed in claim 1 substantially as hereinbefore described with reference to any one of the Examples.

13. A method of emulsifying a hydrocarbon oil which comprises contacting said oil with a composition as claimed in any one of the preceding claims; agitating the mixture of hydrocarbon oil and composition and diluting the agitated mixture with water.

14. A method as claimed in claim 13 substantially as hereinbefore described.

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