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METHOD OF, AND COMPOSITIONS FOR USE IN, CLEANSING THE INTERIOR SURFACES OF TANKS AND THE LIKE

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This invention concerns a method of cleansing the surfaces of tanks, chambers, pipe lines, heat exchangers, and like confined spaces, for example, the interior surfaces of ships' and other storage tanks and containers, all of which are herein regarded as being included by the word "tanks."

By "cleansing" is meant the substantial removal of oily deposits from such surfaces. By "oily deposits" is meant deposits which are not homogeneously miscible with or soluble in water, and which primarily comprise deposits of, or including, crude mineral oils, crude tar oils, shale oils, saponifiable oils and fats, and derivatives of all these oils and fats and any crystals or other foreign matter or bodies mixed therewith or adhering thereto.

Thus the invention is especially concerned with the cleansing of the internal surfaces of tanks for any of the said oils or fats or derivatives of the same after the discharging of tanks or preparatory to the inspection and/or repair and/or refilling of the tanks with the same or a different oil or fat.

More particularly the invention is primarily concerned with a tank cleaning method (hereinafter referred to as "a method of the type specified") wherein an aqueous cleansing liquid is projected by nozzles on to the surfaces to be cleaned and this liquid, together with the oily deposits removed by the cleansing liquid from said surfaces and entrained in the liquid, is returned to a separating vessel for the gravitational separation of the entrained substances from the cleansing liquid whereafter the latter is recycled for re-use in cleansing operations.

Such a method is described and claimed in British Patent No. 696,631, the cleansing liquid in that case comprising a synthetic surface active or wetting agent in an aqueous solution in conjunction, if required, with one or more electrolytes, e.g. sodium chloride, sodium nitrate and sodium sulphate, to vary the properties, e.g. the specific gravity, of the cleansing liquid to suit the particular type of oily deposit which is to be removed from the surfaces to be cleaned.

However, it is desired to provide a method of tank cleansing which will enable the separation process to be speeded up and the capacity of the plant thereby increased and also to enable the water content of the recovered oil to be reduced still further than is possible with the aqueous detergent cleansing liquids referred to in the said Patent No. 696,631.

In extensive experiments which have been carried out in an endeavor to achieve this object, the effect of using a great many alternative forms of surface active agents and mixtures of the same with other surface active agents and/or other substances has been tried in widely varying conditions. These extensive experiments had, of course, to be made with the many varied types of oils and fats and their derivatives above referred to, since not all the different substances respond in the same way to the same surface active agent. Obviously, the optimum surface active agent or agents used should be that or those which would be substantially universally applicable.

Of the very large number of surface active agents which have been tried as aforesaid, only certain specific agents

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were found to give the desired improved results and then only when used in a particular manner.

Thus, according to this invention, there is provided an improved method of cleansing tanks which comprises washing the surfaces of such tanks with a cleansing liquid and then permitting the mixture of cleansing liquid and removed oily deposit to stratify and the oil and aqueous phases thereof to separate in the presence of a surface-active agent of such a character and in such a state that it is preferentially taken up by the oil phase of the said mixture and which, when so taken up by the oil, will promote the coalescence of the latter and thereby assist the separation of the oil phase from the aqueous phase of the mixture.

The washing of the tank surfaces is preferably effected by using the above described method in a tank cleaning method of the type specified, wherein the cleansing liquid is brought into contact with, e.g. projected on to, the tank surfaces to be cleansed and the mixture of this cleansing liquid and the removed deposits is then passed to a separating vessel wherein the said gravitational stratification and separation is effected, the separated oils being discharged from said vessel and at least the major part of the separated cleansing liquid being recycled for further tank cleansing purposes.

According to a further feature of the invention, the surface active agent employed may be preferentially soluble in the oil phase of the mixture of removed oily deposits and aqueous cleansing liquid.

It has been found that a surface active agent of the non-ionic type is particularly suitable for carrying out the method of this invention and it has been found that very satisfactory results are obtained when using a surface active agent comprising a polyglycol ether and preferably either a polyglycol ether comprising a polypropylene polyethylene oxide (for example the type sold under the trademark Fomescol) or a condensation product of stearyl or octadecyl alcohol with twenty-eight molecules of ethylene oxide (for example, the type sold under the trademark Solopol NK).

It has also been found to be of advantage to heat, during the cleansing operations, the cleansing liquid and also to heat the mixture returned to the separating vessel and in some cases further to heat the oil/water emulsion and oil layer in the separating vessel, and to assist the separation it is found particularly advantageous to employ a surface active agent of which the solubility decreases in the aqueous phase with increase in temperature, i.e. that the surface active agent should have a negative solubility coefficient in the aqueous phase.

It will be appreciated that with a surface active agent having a negative solubility coefficient, the heating of the liquid or emulsion increases the preferential solubility of the surface active agent in the oil phase.

Heating the emulsion or oil in the separating vessel and in the cleansing circuit generally if desired also serves to reduce the viscosity of the oil and aqueous phases and thus to assist in the separation.

The presence of the surface active agent is particularly important in the separating vessel but at least a proportion of such surface active agent may be included in the circulating and recycled cleansing liquid.

Preferably, the quantity of surface active agent is such that its concentration in the oil separating in the separating vessel is between 0.05 and 0.5% wt./wt. The quantity of surface active agent to be added therefore depends on how much oil is present and, in practice, it is found desirable to introduce additional quantities of the surface active agent into the system thereby to maintain the concentration of the surface active agent at the required level to suit the particular operations being performed.

The specific polyglycol ether surface active agents above referred to are soluble in the aqueous phase of the said mixture at ambient temperature.

Moreover such surface active agents have a cloud point (that is the temperature at which the solubility of the surface active agent decreases sharply) not higher than the temperature at which the gravitational stratification and separation of the oil and aqueous phases of the said mixture is effected and this is a very desirable characteristic.

It is found in by far the great majority of cleansing operations that it is very advantageous to avoid the aqueous phase of the said mixture attaining, at least in the separating vessel, a pH substantially exceeding 7, it being desirable to maintain the aqueous phase in the separating vessel neutral and preferably somewhat acid. Indeed the pH is very desirably maintained between 7 and 4.5 and a very advantageous pH value has been found to be about 6.

It has also been found highly desirable, and in some cases essential, to include in the cleansing liquid one or more electrolytes of a freely soluble character both to sustain the coagulating or coalescing action of the surface active agent and to adjust the specific gravity of the aqueous phase to suit the separation required.

Any suitable electrolyte or mixture of electrolytes may be chosen but conveniently one or more salts of inorganic acids is or are chosen, for example, one or more of the following:

Sodium phosphates
Sodium sulphate
Sodium nitrate
Sodium chloride
Sodium carbonate
Sodium metasilicate

The salt or salts chosen would be selected appropriately according to the pH of the aqueous phase. The electrolytes may be used in any proportion according to the specific purpose for which the cleansing liquid is required. Generally, a proportion of between 5% and 15% wt./wt. is found to be convenient.

Conveniently the electrolyte comprises sodium chloride and in that case the cleansing liquid may consist of sea water, with or without additional sodium chloride.

If the cleansing liquid is not at the required pH then it is suitably adjusted and if necessary buffered.

Where the cleansing liquid could be corrosive to the metals it would contact when used in the cleansing operation (and particularly the metal of the separating vessel and of the recycling, heating and projecting plant) a suitable corrosion inhibitor is conveniently included and this may, for example, comprise potassium or sodium chromate.

Alternatively, for example, the said corrosion inhibitor may comprise a mixture of sodium fluoride and sodium chromate (for example, within the range of relative concentrations by weight of 1/3 fluoride to 2/3 chromate and 1/6 fluoride to 5/6 chromate). The latter mixture is convenient when the pH of the aqueous phase is between 5 and 6.5.

In order that the invention may be more readily understood one embodiment of the method will now be described by way of example with reference to the cleaning of the interior surface of a ship's oil tank.

In this embodiment, the cleansing liquid is made up from water in which is dissolved a paste consisting of the following constituents:

Sodium chloride (NaCl)-----	Kg. 2020
Sodium chromate (Na ₂ CrO ₄)-----	16
Phosphoric acid (32% wt./wt. P ₂ O ₅)-----	160
Sodium hydroxide 100% (NaOH) as a 45% wt./wt. solution -----	43

155 kg. of the above mixture are dissolved in 1 m.³ of water.

16 kg. of the above paste are added to each m.³ of the cleansing liquid to increase the specific gravity by 0.01 (i.e. to correct the specific gravity of 14 m.³ of the liquid from 1.07 to 1.09 approximately 450 kg. of the paste should be added).

A cleansing liquid formed as above described and having a specific gravity of 1.09 will have a pH of 6.0. It will be an equimolar solution of mono- and di-sodium phosphate at 23.3 mmol. per litre, containing also 131 gm. sodium chloride and 1 gm. sodium chromate per litre.

To the cleansing liquid is added a polyglycol ether, conveniently "Solopol NK," in such quantity that it will be present in a concentration of approximately between 0.1 and 0.2% of active ingredient in the oil separated in the separating vessel. The cloud point of the Solopol NK in this solution will be about 70° to 75° C.

The above described cleansing liquid is supplied to a projecting nozzle or nozzles introduced into a tank to be cleansed, the cleansing liquid being supplied to such nozzle at a temperature of about 70° to 75° C. and being manoeuvred in the tank in such manner that the cleansing liquid is projected against the interior wall surfaces of the tank and removes the oily deposits therefrom.

The mixture of cleansing liquid and entrained oily deposits is withdrawn from the tank continuously and passed in to a separating vessel (containing cleansing liquid) at such a flow rate as to avoid agitation of the contents of the separating vessel and the creation of turbulence in such vessel.

The mixture of cleansing liquid and oily deposits is heated on the way to the separating vessel and the separated oil or oil-containing layer may also be heated in the separating vessel, the temperature of separation being higher than the cloud point of the surface active agent. As well as assisting in the separation of the aqueous from the oil phase, the heating serves to keep liquid any substances, for example waxy substances, which might solidify.

The mixture is allowed to separate by gravitation in the separating vessel, the oil floating to the surface of the liquid in such vessel and the cleansing liquid which separates out being removed from the separating vessel and recirculated to the nozzle for further and immediate re-use, the rate of recirculation of the re-generated cleansing liquid being so related to the rate at which the mixture is received by the separating vessel, that the level of the cleansing liquid/oil interface in the separating vessel always remains substantially the same whilst the liquid itself remains substantially quiescent. Thus, for example, part of the cleansing liquid in the separating vessel may be withdrawn therefrom and returned thereto reflux fashion, such refluxed cleansing liquid being re-heated if desired.

Additional quantities of the surface active agent are added at any convenient part of the plant whenever it is necessary for the purpose of maintaining the separated cleansing liquid sufficiently clean for the cleansing operations being performed.

In a second example, the cleansing liquid comprises water in which is dissolved a paste made up of the following constituents:

Sodium chloride (NaCl)-----	kg-----	100
Sodium chromate (Na ₂ CrO ₄)-----	kg-----	1
Sodium hydroxide 100% (NaOH)-----	kg-----	3.00
Phosphoric acid (32% wt./wt. P ₂ O ₅)-----	kg-----	11.1
Water -----	m. ³ -----	1

Whilst in the above two examples, the cleansing liquid is buffered using equimolar proportions of mono- and di-sodium phosphates, in alternative examples the cleansing liquid may be buffered using equimolar proportions of di- and tri-sodium phosphates at about equivalent concentrations.

In a further example, the phosphates may be replaced by equal weights of sodium metasilicate and sodium carbonate.

Although the surface active agent which has been referred to in the above quoted examples is Solopol NK, it should be understood that this may be replaced by Fomescol without other changes being necessary in the composition. In the solution Fomescol will have a cloud point of approximately 50° C.

We have found that by using the method above described it has been possible in many instances to reduce the water content of the separated oil to a value as low as 0.05 to 0.5%. It has been possible to cleanse a 100 m.³ tank with an internal surface area of about 130 m.² in two to three hours, the linear velocity of the cleansing liquid through the separating vessel, having a horizontal cross-sectional area of 4 m.², being about 10 m./hr.

Whilst the above described method may conveniently be carried out in the plant of British Patent No. 696,631, various modifications may be made in such plant.

Thus, for example, a de-aerator is conveniently used when the mixture is withdrawn from the tank by means of a pump which might result in the discharge of air into such mixture.

In a further modification, at least some of any solids that may be present in the said mixture may be extracted from the mixture before it enters the separating vessel.

In another variation, ballast water may be pumped into an oily water separator and the free oil may be subsequently subjected to the method of the invention for the removal of further water and suspended sediments, if any.

We claim:

1. A method of cleansing tanks which comprises the steps of washing the interior surfaces of such tanks with an aqueous cleansing liquid; passing the mixture of cleansing liquid and removed oily deposits to a separating vessel; allowing such mixture to stratify and the oil and the aqueous phases thereof to separate in the presence of a polyglycol ether having a negative solubility coefficient with respect to said aqueous phase, the mixture being maintained at a temperature at least as high as the cloud point of the aqueous solution of the polyglycol ether and the aqueous phase being maintained at a pH not substantially exceeding 7, withdrawing the separated oil from the separating vessel; and recycling at least the major part of the cleansing liquid for further tank cleansing purposes.

2. A method of cleansing tanks which comprises the steps of washing the interior surfaces of such tanks with an aqueous cleansing liquid; passing the mixture of cleansing liquid and removed oily deposits to a separating vessel; allowing such mixture to stratify and the oil and the aqueous phases thereof to separate in the presence of a surface active agent chosen from the group consisting of a polypropylene polyethylene oxide and condensation products of stearyl and octadecyl alcohol with 28 molecules of ethylene oxide and having a negative solubility coefficient with respect to said aqueous phase, the mixture being maintained at a temperature at least as high as the cloud point of the aqueous solution of the polyglycol ether, withdrawing the separated oil from the separating vessel; and recycling at least the major part of the cleansing liquid for further tank cleansing purposes.

3. A method of cleansing tanks which comprises the steps of projecting on to the interior surfaces of such tanks an aqueous cleansing liquid including a polyglycol ether having a negative solubility coefficient with respect to the aqueous phase; passing the mixture of cleansing liquid and removed oily deposits to a separating vessel; allowing such mixture to stratify and the oil and the aqueous phases thereof to separate, the mixture being maintained in the separating vessel at a temperature at least as high as the cloud point of the aqueous solution of the polyglycol ether; and recycling at least the major

part of the cleansing liquid for further tank cleansing purposes.

4. A method of cleansing tanks which comprises the steps of projecting on to the interior surfaces of such tanks an aqueous cleansing liquid including a polyglycol ether having a negative solubility coefficient with respect to the aqueous phase, sodium chloride, sodium chromate, phosphoric acid and sodium hydroxide; passing the mixture of cleansing liquid and removed oily deposits to a separating vessel; allowing such mixture to stratify and the oil and the aqueous phases thereof to separate, the mixture being maintained in the separating vessel at a temperature at least as high as the cloud point of the aqueous solution of the polyglycol ether; withdrawing the separated oil from the separating vessel; and recycling at least the major part of the cleansing liquid for further tank cleansing purposes.

5. A method of cleansing tanks which comprises the steps of projecting on to the interior surfaces of such tanks an aqueous cleansing liquid including a polyglycol ether having a negative solubility coefficient with respect to the aqueous phase, sodium chloride, sodium chromate, and di- and tri-sodium phosphates; passing the mixture of cleansing liquid and removed oily deposits to a separating vessel; allowing such mixture to stratify and the oil and the aqueous phases thereof to separate, the mixture being maintained in the separating vessel at a temperature at least as high as the cloud point of the aqueous solution of the polyglycol ether; withdrawing the separated oil from the separating vessel; and recycling at least the major part of the cleansing liquid for further tank cleansing purposes.

6. A method of cleansing tanks which comprises the steps of projecting on to the interior surfaces of such tanks an aqueous cleansing liquid including a polyglycol ether having a negative solubility coefficient with respect to the aqueous phase, sodium chloride, sodium chromate, sodium metasilicate and sodium carbonate; passing the mixture of cleansing liquid and removed oily deposits to a separating vessel; allowing such mixture to stratify and the oil and the aqueous phases thereof to separate, the mixture being maintained in the separating vessel at a temperature at least as high as the cloud point of the aqueous solution of the polyglycol ether; withdrawing the separated oil from the separating vessel; and recycling at least the major part of the cleansing liquid for further tank cleansing purposes.

7. A method of cleansing tanks which comprises the steps of projecting on to the interior surfaces of such tanks an aqueous cleansing liquid having a specific gravity of 1.09 and including a polyglycol ether having a negative solubility coefficient with respect to the aqueous phase, passing the mixture of cleansing liquid and removed oily deposits to a separating vessel; allowing such mixture to stratify and the oil and the aqueous phases thereof to separate, the mixture being maintained in the separating vessel at a temperature at least as high as the cloud point of the aqueous solution of the polyglycol ether; withdrawing the separated oil from the separating vessel; and recycling at least the major part of the cleansing liquid for further tank cleansing purposes.

8. A method of cleansing tanks which comprises the steps of washing the interior surfaces of such tanks with an aqueous cleansing liquid; passing the mixture of cleansing liquid and removed oily deposits to a separating vessel; allowing such mixture to stratify and the oil and the aqueous phases thereof to separate in the presence of a polyglycol ether having a negative solubility coefficient with respect to said aqueous phase, the mixture being maintained at a temperature at least as high as the cloud point of the aqueous solution of the polyglycol ether and so buffering the cleansing liquid that the pH does not exceed 7; withdrawing the separated oil from the separating vessel; and recycling at least the major part of the cleansing liquid for further tank cleansing purposes.

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9. A method of cleansing tanks which comprises the steps of washing the interior surfaces of such tanks with an aqueous cleansing liquid including at least one electrolyte of a freely soluble character to adjust the specific gravity of the aqueous phase to suit the separation required; passing the mixture of cleansing liquid and removed oily deposits to a separating vessel; allowing such mixture to stratify and the oil and the aqueous phases thereof to separate in the presence of a polyglycol ether having a negative solubility coefficient with respect to said aqueous phase, the mixture being maintained at a temperature at least as high as the cloud point of the aqueous solution of the polyglycol ether and the aqueous phase being maintained at a pH not substantially exceeding 7; withdrawing the separated oil from the separating vessel; and recycling at least the major part of the cleansing liquid for further tank cleansing purposes.

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10. The method of claim 9, in which the polyglycol ether is present in a concentration of approximately 0.1 to 0.2% in the oil separated in the separating vessel.

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