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PROCESS AND AGENT FOR BREAKING PETROLEUM EMULSIONS

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The present invention is directed to a method for breaking water-in-oil emulsions, and particularly to a new composition for the resolution of such emulsions.

A great many agents have been developed for the breaking of water-in-oil emulsions, which are widely encountered in both the arts of producing and refining oil. These emulsions comprise fine droplets of water or brine dispersed in a more or less permanent state throughout the oil which constitutes the continuous phase of the emulsion. The problem of resolving these emulsions is a serious one, and attempts to solve it have resulted in the development of the most diverse types of agents of varying degrees of efficiency. So variegated have been the treating agents developed that it has been impossible to lay down any general rule to serve as a guide in the development of new treating agents.

According to the present invention petroleum emulsions, particularly those of the water-in-oil type, are effectively resolved by the action of fatty derivatives of higher alkylene glycols, especially polyethylene glycols. The lower polymers of the alkylene glycols do not yield fatty derivatives which have practical effectiveness for the resolution of these emulsions. For example, the fatty derivatives of the mono-, di-, and tri-ethylene glycols are either completely ineffective or must be used in prohibitive quantities to effect substantial demulsification. The most generally suitable and powerful demulsifying materials are derived from polyglycols of the type formula

$$R(OC_2H_4)_xOH$$

in which R is hydrogen or an alkyl group and x has a value from 4 to 50. Among the derivatives of polyethylene glycols, those derived from nonaethylene glycol appear to be the most effective, followed closely by derivatives of hexaethylene glycol. With certain fatty materials, however, polyglycols of higher molecular weight, such as 1500–2000, may yield the most effective derivatives for demulsifying purposes.

The fatty material employed to produce the polyglycol derivative may be selected from the class of fatty oils and fatty acids. Acids such as oleic, ricinoleic, linoleic, stearic, palmitic, etc., and fatty materials from which these acids are derived may be reacted with the polyglycols to produce the desired treating agents. Especially effective agents are obtained by reacting the polyglycols with fatty oils, such as linseed oil, cottonseed oil, tung oil, oiticica, China-wood oil, castor oil, and the like. Mixtures of such oils may

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be employed to produce the derivatives. Likewise, mixtures of polyglycols may be employed. The fatty material selected to react with the polyglycols need not have any free acidity, but may be a neutral ester, such as a glyceride, when the reaction is carried out at an elevated temperature for a considerable time, because under these conditions re-esterification or partial replacement of the hydroxyls of the glycerol in the fatty material by hydroxyls of the polyglycol will take place. In this way a very considerable percentage of the polyglycols can be reacted with neutral glycerides or other esters of fatty acids.

The effectiveness of these fatty derivatives of polyglycols is considerably increased by either preparing them under or subjecting them after preparation to conditions which are suitable for the thickening, either by oxidation or polymerization, of the fatty material. Because this treatment results in an increase in molecular weight of the fatty material, it may be referred to as a polymerization. This polymerization can be effected in a variety of ways, such as by heating alone, by blowing with air or oxygen during heating, or by heating in the presence of a catalyst. For example, with certain fatty materials, such as tung oil and oiticica oil and fatty acids derived from these oils which have a strong inherent tendency to polymerize when heated, the polyglycol is added to the starting material and the polymerization and esterification are conducted simultaneously simply by heating for a prolonged period. While certain of the drying oils, such as linseed oil, may also be polymerized by heating, it is desirable in handling such oils to effect the polymerization either by blowing with air at elevated temperature or by heating with sulfur. In this case the esterification may be conducted simultaneously with the polymerization or before it or after it.

The polyglycols may be reacted with fatty bodies of high molecular weight, such as blown castor oil, blown corn oil, heat polymerized linseed oil, or the like. Again, it is possible to use combinations of different fatty acids and fatty materials together with polyglycols so as to produce a product of high molecular weight. For example, esters of the higher polyglycols with ricinoleic acid may be reesterified with fatty acids derived from tung oil and the thermal polymerization or condensation of the tung oil fatty acid hydrocarbon radicals with one another leads to the formation of high molecular weight polymerized bodies. In any case, the degree of polymerization should be controlled so as to avoid the

production of a gel-like product, or one which has unduly limited solubility in conventional solvents. All of the fatty derivatives of polyglycols employed according to the present invention are freely soluble in aromatic solvents and to a more limited extent in petroleum solvents, such as kerosene. The greater the degree of polymerization, the less soluble is the derivative in the oil phase of the emulsion.

The polyglycols which are employed in the preparation of demulsifying agents according to the present invention are readily available. Polyethylene glycols, for example, are formed as by-products in the manufacture of ethylene glycol itself. By varying the conditions of manufacture, the reaction can be influenced in the direction of the production of polyglycols. For example, when ethylene oxide is reacted with water the formation of polyglycols is favored by maintaining a ratio of mols of ethylene oxide to mols of water greater than 1. It is also possible to prepare these polyglycols from the monoglycols by successive stages of dehydration. Whereas the monoglycols and their dimers and trimers are soluble in aromatics only to a limited extent, the higher polyglycols are soluble in all proportions. As the molecular weight of polyethylene glycol is increased its melting point rises, so that a polyethylene glycol having a molecular weight of about 1500 has a melting point of about 35° C. For use in the preparation of the derivatives employed according to the present invention, it is not necessary that the higher polyethylene glycols be separated into close fractions of narrow molecular weight limits, but a fraction including a large number of polymers may be employed.

In order to determine the effect of the degree of polymerization of the glycol on the demulsifying properties of the fatty derivative, a variety of oleic acid esters were prepared by reacting 1, 1½, and 2 mols of oleic acid with 1 mol each of di-ethylene glycol, tri-ethylene glycol, tetraethylene glycol, hexaethylene glycol, and nonaethylene glycol. In each case the reaction was carried out by heating the mixture for four hours at 450–480° F. Demulsifying tests made with these esters showed that the esters derived from the nonaethylene glycol were by far the best and that those derived from hexaethylene glycol were next best. The esters derived from tetraethylene glycol exhibited the minimum demulsifying power which could be tolerated, and the esters of the lower polyethylene glycol were ineffective. The ester derived from two mols of oleic acid and one mol of nonaethylene glycol was much more effective than the esters produced from one mol and 1½ mols of oleic acid per mol of nonaethylene glycol. When this most effective ester was prepared under conditions which resulted in polymerization, its effectiveness was greatly increased.

An ester prepared by heating two mols of linseed oil fatty acids and one mol of nonaethylene glycol for four hours at 450–480° F. behaved as a demulsifier very much like the unoxidized (unpolymerized) ester of oleic acid. When the same ester was prepared in the presence of cobalt naphthenate while blowing a steady stream of air through the reaction mixture, the product was very dark in color and exhibited greatly enhanced demulsifying power.

Another highly polymeric and very highly effective material was prepared by reacting 85 per cent of ester derived by reacting two mols of linseed oil fatty acids with one mole of nonaethylene glycol and 15 per cent of flowers of sulfur. The ester was heated up to about 350° F. and the sulfur was added slowly and stirred into the reaction mixture thoroughly. The heating was continued for about 15 minutes when all the sulfur appeared to have combined. The color of the reaction product became very dark and the viscosity was greatly increased. The product of this reaction is a highly effective demulsifier, much more effective than the linseed oil fatty acid nonaethylene glycol ester from which it was derived. On the emulsions tested, it proved to be effective at ⅕ the concentration which was required of the simple ester for the same effectiveness.

To obtain a highly polymerized ester by simple heating, two mols of China-wood oil fatty acids were heated with one mol of nonaethylene glycol for four hours at 450° F. in a closed vessel. The product of the reaction was a highly viscous liquid which exhibited strong demulsifying powers.

A series of derivatives corresponding to those prepared from oleic acid were also prepared from ricinoleic acid which, because of its hydroxy groups, was capable of yielding products of different molecular structure from those obtained from oleic acid. The results in general were about the same, the derivative of nonaethylene glycol being the best and that from hexaethylene glycol being the second best.

The experiments reported above served to indicate, in a general way, the manner in which the demulsifying potency of the esters varies with their molecular structure and weight.

Example I

Sixty-nine parts of oiticica oil and 31 parts of polyethylene glycol having an average molecular weight of about 400 were heated at 540° F. for 2 hours. The product was a viscous fluid easily soluble in xylene but essentially insoluble in kerosene.

The oiticica oil and polyethylene glycols are not soluble in one another at ordinary temperatures and it is only after reaction that a mixture of oiticica oil and a higher polyethylene glycol gives a clear solution at ordinary temperatures.

The above described high molecular weight reaction product of a higher polyethylene glycol and oiticica oil is an excellent demulsifier at very low concentrations for a wide variety of crude petroleum emulsions, being far more effective than oiticica oil, polymerized oiticica oil or the polyethylene glycol from which it was produced. While it has been found that this material is very generally useful it will suffice to give one specific example of its application to a characteristic crude oil emulsion from wells Nos. 16 and 19 from the R. M. White lease in the Anahuac, Texas, field (emulsion containing 70% oil and 30% emulsified brine). This emulsion is very stable and will not separate to an appreciable degree when allowed to stand at ordinary temperatures for several months. This demulsifying material was added in the ratio of one part of chemical to 7,000 parts of the emulsion, the mixture shaken thoroughly and allowed to stand at 115° F. for 15 minutes. A complete resolution of the emulsion into its component parts of oil and brine was effected.

This demulsifying material can also be used to advantage in combination with other demulsifying materials. A blend which proved to be very economical as well as exceptionally effective and

rapid in treating the above emulsion is composed of equal parts of the ester material, a water-soluble sludge layer petroleum sulfonate, and an oil soluble petroleum sulfonate together with solvents to combine these components into a homogeneous fluid compound.

Example II

A material which behaves as a demulsifying agent very much like the material of Example I is derived by reacting 70 parts of a heavy blown castor oil with 30 parts of a polyethylene glycol having an average molecular weight of about 400 by heating and agitating together at 520° F. for 1 to 5 hours, 2 hours yielding a highly satisfactory product.

Example III

A highly effective material, more effective on some emulsions than the material of Example I, is derived by heating at 520° F. for 2 hours a mixture of 70% blown castor oil and 30% of a polyethylene glycol having an average molecular weight of 1500.

Example IV

Two mols of tung oil fatty acids and one mol of nonaethylene glycol were heated together at 450–480° F. for 4 hours. The product of this reaction was a very viscous oil which was easily soluble in xylene, but not appreciably soluble in kerosene. The very high viscosity indicated that polymerization had proceeded to an extensive degree. As a demulsifier this material is effective to a very low concentration.

Example V

Nineteen parts of nonaethylene glycol, 55 parts of ricinoleic acid, and 25 parts of tung oil fatty acids were caused to esterify and polymerize by heating at 480° F. for 5 hours. The reaction product was mobile and completely soluble in xylene but soluble in kerosene only at low dilutions, such as one part in five parts of kerosene, but not soluble at higher dilutions such as one part to 15 parts of kerosene. This material shows its demulsifying effect at very low concentrations. In some cases this material is more satisfactorily used in conjunction with other demulsifying materials such as oil-soluble petroleum sulfonates, sludge layer petroleum sulfonates, soaps, sulfonated vegetable or animal oils, sulfo-fatty aromatic materials, alkylated naphthalene sulfonic bodies, etc.

Example VI

Twenty-seven per cent of nonaethylene glycol, 35% tung oil fatty acids and 38% ricinoleic acid were reacted together by heating at 480° F. for 4 hours. The product of the reaction was a viscous oil which was soluble in all proportions of xylene, but was soluble in kerosene to only a limited extent. It was soluble in three volumes of kerosene, but only partly soluble in five volumes of kerosene. It was a powerful demulsifier showing its effect when applied in very low concentrations.

Example VII

Equi-molecular proportions of oiticica oil (76 parts) and hexaethylene glycol (24 parts) are reacted together by heating at 520° F. for 3 hours. The product of the reaction is a viscous liquid which is soluble in xylene in all proportions, but soluble to only a limited extent in kerosene, and insoluble in water. This material is an excellent

demulsifier which is generally applicable to a wide variety of emulsions. As a demulsifier for an Anahuac, Texas, field emulsion (R. M. White lease, wells Nos. 16 and 19) which contains 80% oil and 20% emulsified brine and remains stable for several months when allowed to stand, this material is an excellent demulsifier. When applied in the ratio of one part of chemical to 10,000 parts of emulsion at 115° F. shaken and then allowed to stand, the oil and the water separate completely within 30 minutes into clear oil and clear brine with only a trace of emulsion between the two layers. Admixtures containing this material together with water-soluble petroleum sulfonates are particularly effective in breaking down this Anahuac emulsion quickly at low temperatures.

It will be understood that the demulsifying agents according to the present invention will be used in amounts customarily employed in the art. These agents will ordinarily be employed in the form of solutions in aromatic solvents or other commercial solvents. In actual figures, the amount of treating agent employed may vary from about one part of treating agent to 1,000 parts of emulsion, up to one part of treating agent to 30,000 parts of emulsion. Usually one part of treating agent to 10,000 parts of emulsion will be satisfactory.

The treating agents of the present invention are useful also in the desalting of oil. It is, of course, recognized that the water customarily associated with crude oil in the form of a water-in-oil emulsion is brine, so that when the emulsion is demulsified the oil may, in a sense, be said to be desalted. There is also in the oil, however, a quantity of salt which apparently exists in the form of minute crystals which is not removed in the demulsifying operation and which requires a separate operation, referred to as desalting. This latter operation is ordinarily one in which the oil is washed with hot water, and during the operation emulsion troubles are frequently encountered. It is highly beneficial to add a demulsifying agent of the type hereinbefore described to the wash water in this desalting operation.

There are other operations, both in the art of producing oil and in the art of refining oil, in which water-in-oil emulsions are formed. A common operation in which emulsion troubles are encountered is that of acidizing oil-producing formations. In this operation the treating agents of the present invention may be added to the acid employed in the acidizing step.

The nature and objects of the present invention having been thus described and illustrated, what is claimed as new and useful and is desired to be secured by Letters Patent is:

1. A method for resolving a water-in-oil emulsion which comprises adding to it a substance obtained by reacting a fatty material selected from the group consisting of fatty oils and fatty acids with a polyethylene glycol containing at least 8 carbon atoms, the fatty material being present in said substance in a thickened form induced by a treatment selected from the group consisting of oxidation and polymerization.

2. A method for resolving a water-in-oil emulsion which comprises adding to it a substance obtained by reacting a fatty material selected from the group consisting of fatty oils and fatty acids with a polyalkylene glycol containing at least 8 carbon atoms, the fatty material being present in said substance in a thickened form in-

duced by a treatment selected from the group consisting of oxidation and polymerization.

3. A method according to claim 1 in which the fatty material is linseed oil.

4. A method according to claim 1 in which the polyethylene glycol is nonaethylene glycol.

5. A method according to claim 1 in which the fatty material is tung oil.

6. A method according to claim 1 in which the fatty material is linseed oil and the polyethylene glycol is nonaethylene glycol.

7. A method according to claim 2 in which the fatty material is linseed oil.

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