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HANDLING 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 through the oil which constitutes the continuous phase of the emulsion. The agents heretofore developed have been of varying degrees of efficiency, but all of them have the drawback of being of limited applicability.

It has now been found that the efficiency of such demulsifying agents, as well as the number of different types of emulsions to which they can be successfully applied, can be increased by making them up by combining different definite types of hitherto known agents. More particularly, it has been found that very effective agents can be compounded by combining a Diels-Alder condensation product of a terpene and maleic anhydride or acid and a substance which will hereinafter be referred to as a reesterified bodied fatty oil. The first of these agents may be termed a deslugger, because it functions especially to break down the sludges which are thrown down from emulsions by agents of the second specified type which, for the purpose of discussion, may be termed sludging agents. Other agents than those specified will act as desludging agents, but with much less efficiency than the particular type specified. Likewise, other agents, such as Diels-Alder condensation products synthesized from fatty acids and fatty oils and maleic anhydride, function as sludging agents but, again, with much less efficiency than the specific class named above.

The preparation of the Diels-Alder condensation products from terpenes and maleic acid or anhydride is described in detail in U. S. Patents 1,993,026, 1,993,027, 1,993,028, 1,993,029, 1,993,030, 1,993,032 and 1,993,033. The terpenes employed in the preparation of these products may have conjugated double bonds or be free from such bonds. Typical terpenes which may be employed are alpha-pinene, beta-pinene, dipentene, d- and l-limonene, terpinolene, alpha-terpinene, and alpha- and beta-phellandrene. The condensation products are preferably employed in the form of esters obtained by reacting the condensation products with mono- or polyhydric alcohols under conditions disclosed in said patents. The preferred derivatives for the purpose of the

present invention are the ethylene glycol esters of the condensation products prepared by condensing turpentine and maleic anhydride. Of the glycol derivatives, those preferred are the di- and tri-ethylene glycol derivatives.

When reference is made to a bodied fatty oil there is meant a fatty oil the molecular weight of which has been increased by oxidation or heat polymerization, or both. Thus, the term includes blown castor oil, blown linseed oil, heat bodied linseed oil, and other blown or heat bodied fatty oils which undergo molecular change upon oxidation or heat. For use in the practice of the present invention, these oils are re-esterified with polyethylene glycols of molecular weights from about 250 to 4,000, depending upon the oil selected. For different oils, different polyglycols are most effective for re-esterification for the purpose of the present invention. It has been found, for example, that nonaethylene glycol produces the best product with heat-bodied linseed oil. For blown castor oil a polyglycol of much higher molecular weight, around 2,000, is employed. If desired, a number of different glycols may be used simultaneously in the re-esterification. During the re-esterification it is helpful to employ a minute amount of caustic soda to catalyze the re-esterification. It may be mentioned that the esterification in the case of any of these fatty oils may take place at the same time the oil is being processed to body it, that is to say, the glycols can be mixed with raw linseed oil and the esterification and bodying carried out simultaneously.

The performance of these mixtures in the demulsification of water in oil emulsions is improved by employing conjointly with them an oil soluble petroleum sulfonic acid in the form of its sodium salt. An oil soluble petroleum sulfonic acid is one which is recovered from the acid oil resulting from the treatment of petroleum oil with concentrated sulfuric acid, as distinguished from the sulfonic acid, which is recovered from the sludge layer resulting from such a sulfuric acid treatment. A particularly effective petroleum sulfonic acid is one which is obtained by washing the acid oil with a limited amount of water and recovering the sulfonic acid from the wash water by first washing out entrained oil with a light paraffinic solvent, then neutralizing the wash water with caustic and separating the water from the resulting sodium sulfonate by distillation.

The proportions in which these various ingredients are compounded may vary over a wide

range, the important factor apparently being the simultaneous presence of the sludging agent and desludging agent. A wide variety of formulae have been employed, depending on the emulsions to be treated. For each type of emulsion it is advisable to experiment with the proportions of the ingredients in order to arrive at the best composition. Ordinarily when the sulfonate is employed it will constitute the predominant ingredient. For most emulsions the desludging agent will be used in smaller amounts than the sludging agent. The various ingredients will mix with each other to form a clear mixture. This mixture will usually require some dilution in order to bring it to a viscosity which permits easy handling. Dilution may be accomplished by adding an aromatic solvent, such as xylene, benzol, or aromatic cuts obtained from petroleum. A certain amount of water will also be tolerated in the mixture. Depending upon the quantity of the sulfonate employed, the water content may range up to about 10%. Of course, it is desirable to use as much water as possible, because the more water employed the less thinner will be required to obtain the desired viscosity. Especially when water is included it is advantageous to neutralize the excess acidity of the Diels-Alder condensation product by the addition of ammonia. This neutralization appears to improve the treating agent.

A convenient way to prepare treating agents according to the present invention is to make up two base mixtures, the one containing 50% of oil soluble sodium petroleum sulfonate, 25% of aromatic diluent, 20% of Diels-Alder condensation product, and 5% of ammonia water, and the second containing 50% of the sodium sulfonate, 25% of the re-esterified bodied oil, 20% of aromatic diluent and 5% of ammonia in water, and combine the two base mixtures in different proportions. The composition made by blending equal parts of the two base mixtures might be said to be a fairly representative treating agent according to the present invention. As has been indicated, in this representative treating agent the preferred Diels-Alder condensation product is that obtained by esterifying with triethylene glycol the condensation product of maleic anhydride with turpentine, and the preferred re-esterified bodied fatty oil is that obtained by combining nonaethylene glycol with heat bodied linseed oil. The latter compound is conveniently formed by heating linseed oil with nonaethylene glycol for about four hours at 450°-480° F.

It will be understood that the demulsifying agents according to the present invention will be used in amounts customarily employed in the art. It may be stated that these composite agents are characterized by effecting a faster, cleaner and more complete break of the oil and water than agents heretofore employed. The composite treating agent is almost universally applicable to emulsions of this type encountered in the field. A great many of the emulsions which can be readily resolved will not respond at all to either the desludging or the sludging agent alone. 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 about 1 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.

It may be helpful to enlarge slightly upon the meaning of the expressions "sludging agent" and "desludging agent." A water-in-oil emulsion is

said to be sludged when the water is thrown down in the form of a sludge or tight emulsion, leaving a supernatant layer of substantially anhydrous oil. A water-in-oil emulsion is said to be desludged when a clear layer of water is thrown down from the emulsion, leaving small particles of water still in the oil in the form of emulsion. In other words, when the emulsion is sludged, clear oil is recovered from it, while when it is desludged clear water is recovered from it, in each case leaving the other component still in an emulsified state. Thus, a sludging agent is one which will break out oil, while a desludging agent is one which will break out water.

It will be understood that the treating agent hereinbefore described is 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 a composite treating agent according to the present invention may be added to the acid employed for the acidizing step.

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

1. A method for resolving a water-in-oil emulsion which comprises treating it with a composition containing a Diels-Alder condensation product, derived from a terpene and an open-chain, polycarboxylic unsaturated acid body reactive in the Diels-Alder synthesis, and a bodied fatty oil re-esterified with a polyalkylene glycol.

2. A method for resolving a water-in-oil emulsion which comprises treating it with a composition containing a Diels-Alder condensation product, derived from a terpene hydrocarbon and maleic acid, and a bodied fatty oil re-esterified with a polyalkylene glycol.

3. A method for resolving a water-in-oil emulsion which comprises treating it with a composition containing an ester derivative of a Diels-Alder condensation product, derived from a terpene and maleic acid, and a bodied fatty oil re-esterified with a polyalkylene glycol.

4. A method for resolving a water-in-oil emulsion which comprises treating it with a composition containing a Diels-Alder condensation product, derived from a terpene and a polycarboxylic unsaturated open-chain acid reactive in the Diels-Alder synthesis, a bodied fatty oil re-esterified with a polyalkylene glycol and an oil soluble petroleum sulfonic acid.

5. A method for resolving a water-in-oil emulsion which comprises treating it with a composi-

tion containing a Diels-Alder condensation product, derived from a terpene and a maleic acid body, a bodied fatty oil re-esterified with a polyethylene glycol and a salt of an oil soluble petroleum sulfonic acid.

6. A composition of matter for use as a demulsifier comprising a Diels-Alder condensation product of a terpene and an open-chain polycarboxylic unsaturated acid body reactive in the Diels-Alder synthesis and a bodied fatty oil re-esterified with a polyalkylene glycol.

7. A composition of matter for demulsifying purposes comprising an ester of a Diels-Alder condensation product, derived from a terpene and an open-chain polycarboxylic unsaturated acid body reactive in the Diels-Alder synthesis and a bodied fatty oil re-esterified with a polyalkylene glycol.

8. A composition of matter for demulsifying purposes comprising a Diels-Alder condensation product, derived from a terpene and an open-chain unsaturated polycarboxylic acid reactive in the Diels-Alder synthesis, a bodied fatty oil re-esterified with a polyalkylene glycol and an oil soluble petroleum sulfonic acid body.

9. A composition of matter for demulsifying purposes comprising an ester of a Diels-Alder condensation product, derived from a terpene and a maleic acid body, a bodied fatty oil re-esterified with a polyalkylene glycol and a salt of an oil soluble petroleum sulfonic acid.

10. A composition according to claim 9 in which the re-esterified fatty oil is a heat bodied linseed oil re-esterified with a polyethylene glycol.

11. A composition according to claim 9 in which the ester of the Diels-Alder condensation product is a glycol ester and the re-esterified bodied fatty oil is a heat bodied linseed oil re-esterified with nonaethylene glycol.

12. A method according to claim 1 in which the re-esterified fatty oil is a heat bodied linseed oil re-esterified with a polyethylene glycol.

13. A method according to claim 3 in which the ester derivative of the Diels-Alder condensation product is a glycol ester and the re-esterified bodied fatty oil is a heat bodied linseed oil re-esterified with nonaethylene glycol.

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