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PROCESS FOR BREAKING PETROLEUM EMULSIONS

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This invention relates primarily to the resolution of petroleum emulsions.

One object of our invention is to provide a novel process for resolving petroleum emulsions of the water-in-oil type, that are commonly referred to as "cut oil," "roily oil," "emulsified oil," etc., and which comprise fine droplets of naturally-occurring waters or brines dispersed in a more or less permanent state throughout the oil which constitutes the continuous phase of the emulsion.

Another object is to provide an economical and rapid process for separating emulsions which have been prepared under controlled conditions from mineral oil, such as crude petroleum and relatively soft waters or weak brines. Controlled emulsification and subsequent demulsification under the conditions just mentioned, is of significant value in removing impurities, particularly inorganic salts, from pipeline oil.

The compounds used as the demulsifying agent of our process, are the oxyalkylation products derived by the oxyalkylation of compounds sometimes referred to as "acyl-aryl-sulphonimids." (See U. S. Patent No. 1,145,499, dated July 15, 1915 to Bückel.) Such sulphonimids represent the product obtained by the introduction of two acyl radicals into the ammonium radical, one acyl radical being derived from a high molal detergent-forming monocarboxy acid, and the other acyl radical being derived from an aryl sulfonic acid. Since the word "acyl" can properly be employed to describe both such acidic radicals, it is convenient to use the word "acyl" in a limited sense to refer to the acyl radical derived from a carboxy acid.

The expression "detergent-forming monocarboxy acids" has been frequently employed in the literature to designate certain high molal acids having at least 8 and not more than 32 carbon atoms, and characterized by the fact that they combine with alkali to form soap or soap-like materials. The commonest examples are higher fatty acids derived from animal, vegetable, or marine sources. Other well-known examples include resinic acids, such as abietic acid, naturally-occurring petroleum acids such as those obtained by the oxidation of petroleum hydrocarbons, waxes and the like, and form certain naturally-occurring waxes. Such monocarboxy detergent-forming acids may be cyclic or acyclic. They may be saturated or unsaturated. Included also are derivatives which do not eliminate the soap-forming property and which are obviously chemical equivalents of the unmodified

acid. For instance, chlorinated oleic acid will serve as satisfactorily as oleic acid. Hydrogenated abietic acid is as satisfactory as the material prior to hydrogenation. Brominated naphthenic acid is as satisfactory as the naphthenic acid itself. This also applies to similar derivatives obtainable from oxidized petroleum acids, wax acids, etc.

The aryl group may be monocyclic or polycyclic. In the polycyclic type the rings may be separated or fused. One or more alkyl radicals may be substituted in aromatic nucleus, for instance, derivatives may be obtained from toluene, xylene, cymene, methylnaphthalene, diisopropylnaphthalene, amylnated naphthalene, and similar aromatics, in which the alkyl side chain may contain as many as twenty carbon atoms. Other non-functional substituents may also be present. The usual procedure is to react the selected aromatic compound with chlorosulfonic acid, or use any other suitable reactant to obtain the sulphonchloride. The sulphonchloride is then reacted with ammonia to yield the sulphonamid. As to a more complete list of suitable aromatic compounds, see U. S. Patent No. 2,248,342, dated July 8, 1941, to De Groote and Wirtel. This patent includes, among others, aromatic compounds obtained by introducing the octadecyl radical into the aromatic nucleus. Such radical can be introduced into benzene, naphthalene, diphenyl into a substituted benzene, a substituted naphthalene, or a substituted diphenyl.

Another procedure for obtaining aromatic sulphonchlorides depends upon reaction with the corresponding sulfonic acid, certain non-metallic halides, such as sulphurchlorides, or phosphorous chlorides being employed. One can prepare numerous substituted aromatic sulfonic acids in the manner described in U. S. Patent No. 2,278,167, dated March 31, 1942, to De Groote and Keiser. It is, of course, understood that unsubstituted aromatic sulfonic acids may be employed, and in fact, in some instances are available as inexpensive by-products. The manufacture of the acyl chlorides presents no particular difficulty, especially when manufactured from high molal saturated monocarboxy acids. Reference is made to the manufacture from saturated fatty acids, from naphthenic acids, wax acids obtained from naturally-occurring waxes, oxidized petroleum acids, etc. Some of the procedures employed for preparing the high molal acyl chlorides are not as satisfactory when unsaturated acids such as oleic acids are employed.

Thus, sulphurchloride may serve satisfactorily for preparing the acyl chloride from stearic acid, but is not as satisfactory, if oleic acid is used. Phosphorous chlorides, for instance, phosphorous pentachloride, may be used equally satisfactorily, as a rule, with either saturated acids, or monoethylenic acids. The same is true of thionyl chloride. As to such procedures, see aforementioned Bückel patent. When the high molal acids are of the polyethylenic type, or contain some other functional group, in addition to a single ethylene linkage, other difficulties may be encountered and special methods may be required.

When a sulphonamid, particularly a monocyclic sulphonamid free from nuclear substituted alkyl radicals, or having, at the most, short chain alkyl radicals present, is treated with suitable acidyl chloride, one obtains practically a quantitative yield of the acidyl-aryl-sulphonimid. This procedure is so simple that it may be readily illustrated by the procedure described in the aforementioned Bückel patent. The short alkyl chain or chains preferably have less than 6 carbon atoms.

ACIDYL-ARYL-SULPHONIMID

Example 1

98 kilos of sodium benzenesulfonamid are heated in an oil bath for about 1-2 hours at about 100-120° C., with 152 kilos of stearic acid chlorid. When recrystallized from alcohol, the crude product melts at 104° C.

ACIDYL-ARYL-SULPHONIMID

Example 2

85 kilos of para-toluenesulfonamid are heated on the water bath in presence of an indifferent solvent such, for instance, as carbon tetrachloride, with 137 kilos palmitic acid chloride, until the evolution of hydrochloric acid ceases. When crystallized from alcohol the product thus obtained melts at 100-102° C.

Thus, in view of what has been said, it is obvious that one can readily obtain acidyl-aryl-sulphonimids of the type



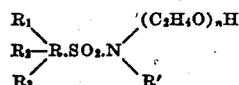
in which R₁, R₂, and R₃ represent hydrogen atoms or alkyl radicals containing one to twenty carbon atoms. R is an aromatic nucleus of the monocyclic or polycyclic type, and R' is an acidyl radical obtained from a high molal detergent-forming monocarboxy acid having at least 8 carbon atoms and not more than 32 carbon atoms.

We have found that if an acidyl-aryl-sulphonimid of the kind above described is treated with an oxyalkylating agent in the customary manner employed to oxyalkylate a phenol, a high molal acid, or the like, one obtains a variety of valuable compounds which may be water-insoluble, or water-miscible, or water-soluble, depending upon the nature of the oxyalkylating agent used, and the molar proportion of oxyalkylating agent to sulphonimid. The presence of the two acyl radicals, one of which is a sulfonyl radical, in the sulphonimid molecule, makes the imid acidic. Such compounds combine with alkalies to give salts. Compare with the well-known Hinsberg reaction. Thus, essentially, the same procedure may be employed in oxyalkylation as

is used in the treatment of high molal sulfonic acids. For instance, see U. S. Patent No. 2,208,581, dated July 23, 1940, to Hoeffelmann. Briefly stated, the procedure employed is to treat the anhydrous sulphonamid with a suitable alkylating agent containing a reactive ethylene oxide ring. As typical examples of applicable compounds may be mentioned glycerine epichlorhydrin, glycidol alcohol, ethylene oxide, propylene oxide, butene-2-oxide, butene-1-oxide, isobutylene oxide, butadiene oxide, butadiene dioxide, chloroprene oxide, isoprene oxide, decene oxide, styrene oxide, cyclohexylene oxide, cyclopentene oxide, etc. The reactive olefine oxide which we prefer to employ is propylene oxide, butylene oxide, glycidol and methyl glycidol, and especially ethylene oxide.

The compound obtained by reaction in equimolar proportions yields a valuable type of compound. For instance, one which shows some valuable properties as a demulsifier, but is of value for other purposes, such as a wax hardener, emulsifier, rust inhibitor, etc. Such compound may be employed as an intermediate for subsequent reactions with sulfuric acid, phosphoric acid, polybasic acids, such as maleic acid, phthalic acid, etc. If a comparatively larger proportion of oxyalkylating agent per mole of sulphonimid is employed, for instance, 5 to 10 moles of ethylene oxide, the hydrotropic property and hydrophile property are greatly enhanced. If 20-60 moles of the oxyalkylating agent, particularly ethylene oxide, is employed, one may obtain water-solubility, provided that the molal weight of the initial sulphonimid is not too large. Generally speaking, a minimum of two moles of ethylene oxide must be introduced for each carbon atom in the sulphonamid. Sometimes a smaller amount can be employed to obtain water-solubility, where, in other instances, as many as four moles per mole of carbon atom must be introduced.

Considering momentarily compounds derived from ethylene oxide, they may be depicted in the following manner:



in which all the characters have their previous significance and *n* may represent any number from 1 to 60.

In view of what has been said, it hardly appears necessary to include examples beyond stating that oxyalkylation can generally be conducted under mild conditions of reaction. For instance, a temperature of 100-125° C. is usually satisfactory; secondly, pressure of less than 200 pounds per square inch gauge pressure is usually satisfactory, the reaction may take place in a comparatively short period, for instance, two hours or less, but in other instances as long as twenty hours may be employed. The reaction is conducted by using a suitable apparatus that insures intimate contact between the oxyalkylating agent and the sulphonimid. After the introduction of the first molecule of ethylene oxide or oxyalkylating agent, acidity has disappeared, and the subsequent stages are sometimes suitably catalyzed by the presence of a small amount of alkali, such as caustic soda, sodium methylate, soap, or the like, which may be present to the extent of one tenth of 1% to one-half of 1%. Compare with the oxyalkylation of high molal alcohols.

OXYALKYLATED ACIDYL-ARYL-SULPHONIMID

Example 1

Stearyl benzene sulphonimid sodium salt is dissolved in any suitable solvent, such as benzene or alcohol, and treated with dry hydrochloric acid gas so as to liberate the imid with the precipitation of salt. The salt is filtered off and the solvent evaporated. One pound mole of the imid so obtained is treated with one pound mole of ethylene oxide so as to produce the corresponding substituted nitrogen-linked hydroxyethyl stearyl benzene sulphonimid.

OXYALKYLATED ACIDYL-ARYL-SULPHONIMID

Example 2

The substituted imid obtained in the manner described in the preceding example is mixed with two tenths of 1% of sodium methylate and then subjected to further oxyethylation with 5 pound moles of ethylene oxide for each pound mole of the substituted imid.

OXYALKYLATED ACIDYL-ARYL-SULPHONIMID

Example 3

The same procedure is followed as in the preceding example, except that 10-20 pound moles of ethylene oxide are used for each pound mole of the substituted imid.

OXYALKYLATED ACIDYL-ARYL-SULPHONIMID

Example 4

Palmityl paratoluene sulphonimid obtained in the manner previously described, is substituted for stearyl benzene sulphonimid in Examples 1-3, preceding.

OXYALKYLATED ACIDYL-ARYL-SULPHONIMID

Example 5

The same procedure is followed as in Examples 1-3, preceding, except that the sulphonimid is derived from mixed high molal fatty acid chlorides of the kind available in the open market, and the sulphonimid is derived from cymene.

As has been suggested, one need not employ the sulphonimid derived from a single fatty acid, but one may employ the imid derived from a mixture of fatty acids, and especially, from the mixture obtained by the hydrogenation of naturally occurring fats or oils. For instance, unsaturated naturally occurring oils, such as olive oil, teaseed oil, soyabean oil, cottonseed oil, etc., may be hydrogenated and then subjected to saponification or hydrolysis. The mixture of fatty acids so obtained or the mixture obtained from palm oil, or palm kernel oil, may be converted into a corresponding acyl chloride and employed in the present instance. Attention is again directed to the fact that it is our preference to use an oxyalkylating agent having not over 4 carbon atoms, i. e., ethylene oxide, propylene oxide, butylene oxide, glycidol, and methyl glycidol.

Conventional demulsifying agents employed in the treatment of oil field emulsions are used as such, or after dilution with any suitable solvent, such as water; petroleum hydrocarbons, such as gasoline, kerosene, stove oil, a coal tar product, such as benzene, toluene, xylene, tar acid oil, cresol, anthracene oil, etc. Alcohols, particularly aliphatic alcohols, such as methyl alcohol, ethyl alcohol, denatured alcohol, propyl alcohol, butyl

alcohol, hexyl alcohol, octyl alcohol, etc., may be employed as diluents. Miscellaneous solvents, such as pine oil, carbon tetrachloride, sulfur dioxide extract obtained in the refining of petroleum, etc., may be employed as diluents. Similarly, the material or materials herein described may be admixed with one or more of the solvents customarily used in connection with conventional demulsifying agents. Moreover, said material or materials may be used alone, or in admixture with other suitable well-known classes of demulsifying agents.

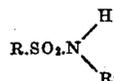
It is well known that conventional demulsifying agents may be used in a water-soluble form, or in an oil-soluble form, or in a form exhibiting both oil and water solubility. Sometimes they may be used in a form which exhibits relatively limited oil-solubility. However, since such reagents are sometimes used in a ratio of 1 to 10,000, or 1 to 20,000, or even 1 to 30,000, such an apparent insolubility in oil and water is not significant, because said reagents undoubtedly have solubility within the concentration employed. This same fact is true in regard to the material or materials herein described.

We desire to point out that the superiority of the reagent or demulsifying agent employed in our herein described process for breaking petroleum emulsions, is based upon its ability to treat certain emulsions more advantageously and at a somewhat lower cost than is possible with other available demulsifiers, or conventional mixtures thereof. It is believed that the particular demulsifying agent or treating agent herein described will find comparatively limited application, so far as the majority of oil field emulsions are concerned; but we have found that such a demulsifying agent has commercial value, as it will economically break or resolve oil field emulsions in a number of cases which cannot be treated as easily or at so low a cost with the demulsifying agents heretofore available.

In practising our process, a treating agent or demulsifying agent of the kind above described is brought into contact with or caused to act upon the emulsion to be treated, in any of the various ways, or by any of the various apparatus now generally used to resolve or break petroleum emulsions with a chemical reagent, the above procedure being used either alone or in combination with other demulsifying procedure, such as the electrical dehydration process.

Having thus described our invention, what we claim as new and desire to secure by Letters Patent is:

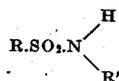
1. A process for breaking petroleum emulsions of the water-in-oil type, characterized by subjecting the emulsion to the action of a demulsifying agent comprising an oxyalkylated derivative of an acidyl-aryl-sulphonimid of the formula:



in which R is an aromatic nucleus, and R' is an acidyl radical obtained from a high molal detergent-forming monocarboxy acid having at least 8 carbon atoms and not more than 32 carbon atoms; said derivative being obtained by means of an oxyalkylating agent having a reactive ethylene oxide ring.

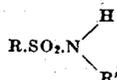
2. A process for breaking petroleum emulsions of the water-in-oil type, characterized by subjecting the emulsion to the action of a demulsi-

fyng agent comprising an oxyalkylated derivative of an acidyl-aryl-sulphonimid of the formula:



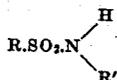
in which R is an aromatic nucleus, and R' is an acidyl radical obtained from a high molal detergent-forming monocarboxy acid having at least 8 carbon atoms and not more than 32 carbon atoms; said derivative being obtained by means of an oxyalkylating agent having a reactive ethylene oxide ring; said oxyalkylating agent having not more than 4 carbon atoms.

3. A process for breaking petroleum emulsions of the water-in-oil type, characterized by subjecting the emulsion to the action of a demulsifying agent comprising an oxyalkylated derivative of an acidyl-aryl-sulphonimid of the formula:



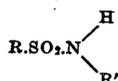
in which R is an aromatic nucleus having at least 1 alkyl side chain containing less than 6 carbon atoms, and R' is an acidyl radical obtained from a high molal detergent-forming monocarboxy acid having at least 8 carbon atoms and not more than 32 carbon atoms; said derivative being obtained by means of an oxyalkylating agent having a reactive ethylene oxide ring; said oxyalkylating agent having not more than 4 carbon atoms.

4. A process for breaking petroleum emulsions of the water-in-oil type, characterized by subjecting the emulsion to the action of a demulsifying agent comprising an oxyalkylated derivative of an acidyl-aryl-sulphonimid of the formula:



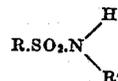
in which R is a monocyclic aromatic nucleus having at least 1 alkyl side chain containing less than 6 carbon atoms, and R' is an acidyl radical obtained from a high molal detergent-forming monocarboxy acid having at least 8 carbon atoms and not more than 32 carbon atoms; said derivative being obtained by means of an oxyalkylating agent having a reactive ethylene oxide ring; said oxyalkylating agent having not more than 4 carbon atoms.

5. A process for breaking petroleum emulsions of the water-in-oil type, characterized by subjecting the emulsion to the action of a demulsifying agent comprising an oxyalkylated derivative of an acidyl-aryl-sulphonimid of the formula:



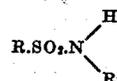
in which R is a monocyclic aromatic nucleus having at least 1 alkyl side chain containing less than 6 carbon atoms, and R' is an acidyl radical obtained from a higher fatty acid having at least 8 and not more than 32 carbon atoms; said derivative being obtained by means of an oxyalkylating agent having a reactive ethylene oxide ring; said oxyalkylating agent having not more than 4 carbon atoms.

6. A process for breaking petroleum emulsions of the water-in-oil type, characterized by subjecting the emulsion to the action of a demulsifying agent comprising an oxyalkylated derivative of an acidyl-aryl-sulphonimid of the formula:



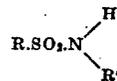
in which R is a monocyclic aromatic nucleus having at least 1 alkyl side chain containing less than 6 carbon atoms, and R' is an acidyl radical obtained from an unsaturated higher fatty acid having at least 8 and not more than 32 carbon atoms; said derivative being obtained by means of an oxyalkylating agent having a reactive ethylene oxide ring; said oxyalkylating agent having not more than 4 carbon atoms.

7. A process for breaking petroleum emulsions of the water-in-oil type, characterized by subjecting the emulsion to the action of a demulsifying agent comprising an oxyethylated derivative of an acidyl-aryl-sulphonimid of the formula:



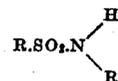
in which R is a monocyclic aromatic nucleus having at least one alkyl side chain containing less than six carbon atoms, and R' is an acidyl radical obtained from an unsaturated higher fatty acid having at least 8 and not more than 32 carbon atoms; said oxyethylated derivative being of the water-insoluble type.

8. A process for breaking petroleum emulsions of the water-in-oil type, characterized by subjecting the emulsion to the action of a demulsifying agent comprising an oxyethylated derivative of an acidyl-aryl-sulphonimid of the formula:



in which R is a monocyclic aromatic nucleus having at least one alkyl side chain containing less than 6 carbon atoms, and R' is an acidyl radical obtained from an unsaturated higher fatty acid having at least 8 and not more than 32 carbon atoms; said oxyethylated derivative being of the water-miscible type.

9. A process for breaking petroleum emulsions of the water-in-oil type, characterized by subjecting the emulsion to the action of a demulsifying agent comprising an oxyethylated derivative of an acidyl-aryl-sulphonimid of the formula:



in which R is a monocyclic aromatic nucleus having at least one alkyl side chain containing less than 6 carbon atoms, and R' is an acidyl radical obtained from an unsaturated higher fatty acid having at least 8 and not more than 32 carbon atoms; said oxyethylated derivative being of the water-soluble type.

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