

UNITED STATES PATENT OFFICE

2,248,342

PROCESS FOR BREAKING PETROLEUM EMULSIONS

Melvin De Groote, University City, and Arthur F. Wirtel, Kirkwood, Mo., assignors to Petrolite Corporation, Ltd., Wilmington, Del., a corporation of Delaware

No Drawing. Application November 22, 1940,
Serial No. 366,552

14 Claims. (Cl. 252—344)

This invention relates primarily to the treatment of emulsions of mineral oil and water, such as petroleum emulsions, for the purpose of separating the oil from the water.

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 of our invention 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.

We have found that the particular chemical compounds or reagents employed as the demulsifier in our herein described process for resolving petroleum emulsions, may also be used for other purposes, for instance, as a break inducer in doctor treatment of the kind intended to sweeten gasoline. See U. S. Patent No. 2,157,223, dated May 9, 1939, to Sutton. Said chemical compounds are also of value as surface tension depressants in the acidization of calcareous oil-bearing strata by means of strong mineral acid, such as hydrochloric acid. Similarly, some of said chemical compounds are effective as surface tension depressants or wetting agents in the flooding of exhausted oil-bearing strata.

As to using compounds of the kind herein described as flooding agents for recovering oil from subterranean strata, reference is made to the procedure described in detail in application for Patent Serial No. 322,534, filed March 6, 1940 (which subsequently issued as U. S. Patent No. 2,233,381, dated February 25, 1941, to De Groote and Keiser); Serial No. 322,535, filed March 6, 1940 (which subsequently issued as U. S. Patent No. 2,233,382, dated February 25, 1941, to De Groote and Keiser); and Serial No. 322,536, filed March 6, 1940 (which subsequently issued as U. S. Patent No. 2,226,119, dated December 24, 1940, to De Groote and Keiser). As to using compounds of the kind herein described as emulsifiers, or in particular as surface tension depressants in combination with mineral acid for

acidization of oil-bearing strata, reference is made to co-pending applications for Patents Serial No. 322,537, filed March 6, 1940, by De Groote and Keiser; Serial No. 323,418, filed March 11, 1940, by De Groote and Keiser; and Serial No. 322,538, filed March 6, 1940, by De Groote and Keiser, which last mentioned application resulted in U. S. Patent No. 2,233,383, dated February 25, 1941.

We have discovered that the non-substituted or substituted hexamethylenetetramine alkylates, arylates and aralkylates with any desired acid ion are particularly effective as demulsifiers for oil field emulsions. The manufacture of such materials, particularly, the alkylates and arylates, are well known. (See British Patent No. 424,717, dated February 27, 1935, to Hunsdiecker and Vogt. See also Journal of Biological Chemistry, volume 21, pages 465-475.) Although such materials may be prepared from substituted hexamethylenetetramine, such as a methylated or ethylated derivative, we have found it most feasible to use the non-substituted product, i. e., hexamethylenetetramine, in the preparation of the demulsifiers herein contemplated. We have found, however, that the most desirable demulsifiers are derived from aralkyl derivatives in preference to alkyl derivatives or aryl derivatives. More specifically, we have found that if an aralkyl reactant in which the alkyl group happens to be a methyl group is employed, that reaction with hexamethylenetetramine or a substituted derivative thereof takes place rapidly with comparatively quantitative yields.

Some of the properties of hexamethylenetetramine are indicated by the ordinary ring structure which depicts the four nitrogen atoms as being tertiary amino atoms. The exact nature of the derivatives herein contemplated as demulsifiers is not known, but one suggestion is that the products derived represent quaternary ammonium compounds. Such explanation would appear to indicate what is actually a fact, i. e., in some instances more than one mole of a selected alkyl, aryl or aralkyl reaction can combine with one mole of hexamethylenetetramine, or a substituted hexamethylenetetramine. However, we prefer to react the raw materials in equal molecular proportions, i. e., one pound mole of hexamethylenetetramine and one pound mole, for example, of a selected aralkyl compound, such as an aralkyl halide. Such reactions may be conducted conveniently in the presence of an inert solvent, such as chloroform or the like. Reaction can be conducted at the lowest possible tem-

perature, usually under the boiling point of water, such as a temperature of approximately 70-80° C. In some instances, the temperature of reaction may proceed at a higher temperature, for instance, at or above the boiling point of water, for instance, a temperature as high as 120° to 140° C., provided that there is no decomposition of the desired product of reaction. As is pointed out in the aforementioned British patent, if one employs a halide, for instance, a chloride, to supply the anion, then such anion can readily be exchanged for other negative ions, for example, sulfate, nitrate, acetate, citrate, benzene sulfonate, etc. One procedure that may be employed is to dissolve the chloride, for example, in alcohol, and add a saturated solution of sodium acetate or the like with precipitation of sodium chloride in the form of the acetate type of compound. Another procedure which is sometimes adaptable is to liberate the free base in solution, i. e., the type of compound in which the chloride, for example, is replaced by a hydroxyl. In some instances, the alcoholic solution of the chloride may be treated with a small amount of caustic soda or caustic potash in dry or highly concentrated form, so as to liberate sodium chloride or potassium chloride with the formation of an alcoholic solution of a free base. In many instances the free base does not show marked stability in dry form that is preferable to neutralize the alcoholic solution of the free base with acetic acid, lactic acid, tartaric acid, benzene sulfonic acid, or the like. In such instances where the free base is stable, it may be employed, and the hydroxyl radical may be considered the equivalent of the chloride ion. As has been previously pointed out, it is our preference to use the aralkyl type of reactant, particularly in which the alkyl group is a methyl radical. It is our preference to employ the polycyclic aralkyl compound, rather than the monocyclic, for instance, the naphthylmethyl chloride type, rather than the benzyl chloride type. Furthermore, we prefer to use a type in which the aromatic nucleus has been substituted at least once, and preferably more than once, by an alkyl radical containing at least five carbon atoms, and preferably, 8 to 10, or even 18 to 20 carbon atoms.

As to the type of reactant preferred, it is to be noted that such products are well known compositions of matter. A selected aromatic material, such as benzene, toluene, cymene, naphthalene, anthracene, di-phenyl, phenol, naphthol, hydroxy-diphenyl, or the like, may be treated with an alkyl halide, such as amyl chloride, octylchloride, decyl chloride, dodecyl chloride, cetyl chloride, and octadecyl chloride, so as to give mono or polyalkylated aromatic compounds exemplified by amyl benzene, di-amyl benzene, octyl benzene, octadecyl benzene, amyl naphthalene, di-amyl naphthalene, tri-amyl naphthalene, octyl naphthalene, naphthalene, di-octyl naphthalene, tri-octyl naphthalene, octadecyl naphthalene, di-octadecyl naphthalene, tri-octadecyl naphthalene, etc.

Such alkylated aromatic materials containing methyl, ethyl, propyl and butyl groups, as well as the longer carbon chain alkyl groups, are treated by well known procedure with a formaldehyde solution and concentrated hydrochloric acid. (See U. S. Patent No. 2,166,554, dated July 18, 1939, to Roblin and Hechenbleikner.) Having obtained such substituted methyl chlorides, in which alkylated aromatic nuclei replaces a meth-

yl hydrogen atom, it is only necessary to react such selected compounds with hexamethylenetetramine or the like in the manner previously indicated. The preferred type of demulsifier is prepared as indicated by the following examples:

Example 1

One pound mole of octylbenzyl chloride is reacted with one pound mole of hexamethylenetetramine until reaction is complete. If desired, reaction may take place in presence of an inert solvent, such as chloroform or a selected chlorinated hydrocarbon having a somewhat higher boiling point. The product so obtained is converted into the acetate.

Example 2

Octyl naphthylmethyl chloride is substituted for benzyl chloride in Example 1.

Example 3

Di-amyl naphthylmethyl chloride is substituted for benzyl chloride in Example 1.

Example 4

Decyl naphthylmethyl chloride is substituted for benzyl chloride in Example 1.

Example 5

Di-octyl naphthylmethyl chloride is substituted for benzyl chloride in Example 1.

Example 6

Octadecyl naphthylmethyl chloride is substituted for benzyl chloride in Example 1.

Example 7

Di-octadecyl naphthylmethyl chloride is substituted for benzyl chloride in Example 1.

It is to be understood that the compound herein contemplated may be manufactured in any suitable manner; and one is not dependent upon following the exact procedure previously outlined. In certain instances other reactants might be employed, or else reactants of the kind previously described might be combined in some other manner. It is not intended that the hereto appended claims be limited in any manner whatsoever as to the method of manufacture, unless such method is specifically recited.

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 compounds employed as the demulsifying agent of our process may be admixed with one or more of the solvents customarily used in connection with conventional demulsifying agents. Moreover, said material or compounds 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 compounds employed as the demulsifying agent of our process.

We desire to point out that the superiority of the reagent or demulsifying agent contemplated in our process 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.

The demulsifier herein contemplated may be employed in connection with what is commonly known as down-the-hole procedure, i. e., bringing the demulsifier in contact with the fluids of the well at the bottom of the well or at some point prior to their emergence. This particular type of application is decidedly feasible when the demulsifier is used in connection with acidification of calcareous oil-bearing strata, especially if suspended in or dissolved in the acid employed for acidification.

In the hereto appended claims reference to a halide is intended to include the chloride, bromide, or iodide. Reference to a hexamethylenetetramine is intended to be a generic term which includes the substituted compound. Reference to hexamethylenetetramine is intended to mean the unsubstituted product.

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

1. A process for resolving petroleum emulsions of the water-in-oil type, characterized by subjecting the emulsion to the action of a demulsifier, comprising a member of the class consisting of anion-containing alkylates, arylates and aralkylates of a hexamethylenetetramine.

2. A process for resolving petroleum emulsions of the water-in-oil type, characterized by subjecting the emulsion to the action of a demulsifier, comprising a member of the class consisting of anion-containing alkylates, arylates and aralkylates of hexamethylenetetramine.

3. A process for resolving petroleum emulsions of the water-in-oil type, characterized by subjecting the emulsion to the action of a de-

mulsi-
fifier, comprising an anion-containing aralkylate of hexamethylenetetramine.

4. A process for resolving petroleum emulsions of the water-in-oil type, characterized by subjecting the emulsion to the action of a demulsifier, comprising an anion-containing aralkylate of hexamethylenetetramine in which the anion-linked alkyl group of said aralkylate is a methyl radical.

5. A process for resolving petroleum emulsions of the water-in-oil type, characterized by subjecting the emulsion to the action of a demulsifier, comprising an anion-containing aralkylate of hexamethylenetetramine in which the anion-linked alkyl group of said aralkylate is a methyl radical, and further characterized by the fact that there is present only one aralkyl radical for each hexamethylenetetramine radical.

6. A process for resolving petroleum emulsions of the water-in-oil type, characterized by subjecting the emulsion to the action of a demulsifier, comprising an anion-containing aralkylate of hexamethylenetetramine in which the anion-linked alkyl group of said aralkylate is a methyl radical and the aryl radical thereof is polycyclic, and further characterized by the fact that there is present only one aralkyl radical for each hexamethylenetetramine radical.

7. A process for resolving petroleum emulsions of the water-in-oil type, characterized by subjecting the emulsion to the action of a demulsifier, comprising an anion-containing aralkylate of hexamethylenetetramine in which the anion-linked alkyl group of said aralkylate is a methyl radical and the aryl radical thereof is polycyclic, and further characterized by the fact that there is present only one aralkyl radical for each hexamethylenetetramine radical, and the anion present is an organic acid radical.

8. A process for resolving petroleum emulsions of the water-in-oil type, characterized by subjecting the emulsion to the action of a demulsifier, comprising an anion-containing aralkylate of hexamethylenetetramine in which the anion-linked alkyl group of said aralkylate is a methyl radical and the aryl radical thereof is an alkylated polycyclic radical in which the number of carbon atoms in at least one alkyl side chain is at least 8 and not more than 20, and further characterized by the fact that there is present only one aralkyl radical for each hexamethylenetetramine radical, and the anion present is an organic acid radical.

9. A process for resolving petroleum emulsions of the water-in-oil type, characterized by subjecting the emulsion to the action of a demulsifier, comprising an anion-containing aralkylate of hexamethylenetetramine in which the anion-linked alkyl group of said aralkylate is a methyl radical thereof is a polyalkylated polycyclic radical in which the number of carbon atoms in at least two alkyl side chains is at least 8 and not more than 20, and further characterized by the fact that there is present only one aralkyl radical for each hexamethylenetetramine radical, and the anion present is an organic radical.

10. A process for resolving petroleum emulsions of the water-in-oil type, characterized by subjecting the emulsion to the action of a demulsifier, comprising an anion-containing aralkylate of hexamethylenetetramine in which the anion-linked alkyl group of said aralkylate is a methyl radical and the aryl radical thereof is a

polyalkylated bicyclic radical in which the number of carbon atoms in at least two alkyl side chains is at least 8 and not more than 20, and further characterized by the fact that there is present only one aralkyl radical for each hexamethylenetetramine radical, and the anion present is an organic acid radical.

11. A process for resolving petroleum emulsions of the water-in-oil type, characterized by subjecting the emulsions to the action of a demulsifier, comprising an anion-containing aralkylate of hexamethylenetetramine in which the anion-linked alkyl group of said aralkylate is a methyl radical and the aryl radical thereof is a polyalkylated naphthyl radical in which the number of carbon atoms in at least two alkyl side chains is at least 8 and not over 20, and further characterized by the fact that there is present only one aralkyl radical for each hexamethylenetetramine radical and the anion present is an organic radical.

12. A process for resolving petroleum emulsions of the water-in-oil type, characterized by subjecting the emulsion to the action of a demulsifier, comprising an anion-containing aralkylate of hexamethylenetetramine in which the anion-linked alkyl group of said aralkylate is a methyl radical and the aryl radical thereof is a polyamylated naphthyl radical, and further characterized by the fact that there is present

only one aralkyl radical for each hexamethylenetetramine radical and the anion thereof is an organic radical.

13. A process for resolving petroleum emulsions of the water-in-oil type, characterized by subjecting the emulsion to the action of a demulsifier, comprising an anion-containing aralkylate of hexamethylenetetramine in which the anion-linked alkyl group of said aralkylate is a methyl radical and the aryl radical thereof is a polyhexylated naphthyl radical, and further characterized by the fact that there is present only one aralkyl radical for each hexamethylenetetramine radical and the anion thereof is an organic radical.

14. A process for resolving petroleum emulsions of the water-in-oil type, characterized by subjecting the emulsion to the action of a demulsifier, comprising an anion-containing aralkylate of hexamethylenetetramine in which the anion-linked alkyl group of said aralkylate is a methyl radical and the aryl radical thereof is a polyoctylated naphthyl radical, and further characterized by the fact that there is present only one aralkyl radical for each hexamethylenetetramine radical and the anion thereof is an organic radical.

MELVIN DE GROOTE.
ARTHUR F. WIRTEL.