Patented Nov. 30, 1943

2,335,554

UNITED STATES PATENT OFFICE

2,335,554

PROCESS AND REAGENT FOR RESOLVING EMULSIONS

Truman B. Wayne, Houston, Tex.

No Drawing. Application July 29, 1938, Serial No. 222,057

8 Claims. (Cl. 252—334)

This invention relates to the art of resolving petroleum emulsions of the character commonly encountered in the production, handling and refining of petroleum.

The principal object of this invention is to provide an improved process and reagents for treating petroleum emulsions to separate them into their component parts of oil and water.

The present invention is based on the discovery that derivatives of a particular type of cyclic sulfonic acid derived from the sulfonation of highly aromatic crude oils or crude oil fractions, when condensed with non-hydroxy alkyl or aralkyl amines to form either the salt through ordinary neutralization reactions, or the acyl derivative through acylation of such amines, are particularly effective demulsifiers for certain petroleum emulsions. Ordinary petroleum sulfonic acids derived from the sludges and oil layers in petroleum refining processes contain mixtures of many substances in addition to considerable proportions of the so-called "mahogany," or oil-soluble sulfonic acids, and the "green," or water-soluble sulfonic acids. The various tarry and partially polymerized unsaturates commonly present in such sulfonates are very detrimental to the preparation of the amino derivatives herein described because they form insoluble products with the amines used in preparing my products.

I am aware that many patents and publications have described methods for the preparation, purification, and use of various petroleum sulfonates. These are obtained as by-products from lubricating oil manufacture in petroleum refineries, and also from the manufacture of white medicinal mineral oils, and similar products used in other fields. In all instances, however, these sulfonates are by-products from other operations and little or no care is exercised in their manufacture to obtain products more suitable for their several uses. Considerable purification is obtained by further processing to eliminate undesirable impurities where these mineral oil sulfonates are used as detergents and wetting agents for textile materials, but ordinarily such care is not taken, nor has it been considered necessary, in adapting mineral oil sulfonates to petroleum dehydration.

Various patents have been issued covering petroleum sulfonic acids and their various metallic salts as petroleum demulsifiers, of which United States Letters Patent No. 1,299,385 to Rogers is generally considered as the pioneer patent. The Reddish Patent No. 1,780,144 describes reaction products of mineral oil sulfonic acids and hydroxy-amines. This patent disclosed the use of mono, di, or tri alkyl and/or aryl hydroxy amines as neutralizing agents for mineral oil sulfonic acids of either the "mahogany" or "green" acid types, or mixtures of the two types. It is stated that Reddish's product is highly soluble in "oil, water, alcohol, ketones, as well as in others." (Lines 50–51, page 2.)

The hydroxy-amines are soluble in water but totally insoluble in oil. Hence it is readily apparent that it is only the hydroxy-amine salts of the oil-soluble "mahogany" sulfonates which could possibly possess any oil solubility, and they would have this property only through retaining much of the oil soluble characteristics of the "mahogany" sulfonate. Since the function of the hydroxy-amines is that of promoting water solubility because of their own water soluble, oil insoluble, character, it is evident that they could not increase the oil solubility of the oil insoluble, fully water soluble "green" acid sulfonates. If a mixture of these two types of petroleum sulfonic acids is neutralized with mono, di, or tri ethanolamine, one would expect the oil solubility of the mixture to decrease while the water solubility increases. Any oil solubility possessed by any fraction of the mixture would result from the influence of the original oil soluble mahogany acid sulfonate content.

The preceding discussion, therefore, makes it clear that a result not contemplated in the prior art is accomplished by my present process wherein highly purified and strictly water soluble, oil insoluble, "green" acid sulfonates are condensed with alkyl or aralkyl amines having three or more carbon atoms in each alkyl or aralkyl group, and results in the production of an oil soluble reaction product. Instead of forming clear greenish to reddish colored water solutions, my new reagents produce highly colloidal, water-wettable, suspensions of the reagent in contact with water, and are freely soluble in petroleum hydrocarbons when freed from dissolved water.

The most effective reagents are usually prepared from highly water soluble "green" acids condensed with oil soluble amines having five or more carbon atoms in each alkyl group. In this manner the great affinity for water exhibited by sulfonic acids characterized by a high organic sulfur content is modified by the highly oil soluble characteristics of the amine, and results in a

product possessing a proper balance of hydrophilic and hydrophobic qualities, and only a limited solubility in water.

The water soluble petroleum sulfonic acid used in preparing my reagent may be prepared from the lower sludge layer, or "B" layer as it is commonly termed. This sludge may be obtained from lubricating oil stock or is preferably prepared especially from selected aromatic crudes. If derived from lubricating oil manufacture, it is preferably prepared according to the process described by Humphreys and Rogers in their U. S. Patent No. 1,474,933, dated November 20, 1923. The sodium sulfates obtained from the final alcohol extraction may be acidified with sulfuric acid to remove the sodium, and the free acid recovered. Or the oil free sodium sulfonate solution prepared by repeated extraction of the aqueous solution with naphtha for the removal of oil, may be acidified to free the sulfonic acids. This solution of free sulfonic acids may then be directly used in my subsequent procedure. Other similar procedures wherein tarry and/or oil soluble constituents are carefully removed from the "green" acid fraction are entirely suitable. A suitable procedure is outlined in Example I.

Among suitable amines are the primary, secondary, and tertiary propyl, butyl, amyl, hexyl and octyl amines. Cycloalkyl amines such as cyclohexylamine are particularly well suited. Higher amines such as cetylamine are also contemplated. The higher the molecular weight of the amine, the more oil solubility it confers on the amine salt or acyl derivative. Aralkyl amines such as benzylamine, and its higher homologues, are useful, particularly those having alkyl side-chains with three to eight carbon atoms.

In order to illustrate specifically the new type of condensation product contemplated for use in accordance with the present invention, I have set forth below several examples of the type of product suitable for use. However, it is to be understood that I do not confine myself to the specific chemicals, or proportions thereof, set forth in these examples, as it will be readily apparent that equivalents of these specific chemicals and their various derivatives, or other proportions may be employed without departing from the spirit of the invention or the scope of the appended claims.

It will also be understood that the reagents may be employed for purposes analogous to those herein described. It will, of course, be understood that the reagents may be employed for preventing the formation of petroleum emulsions in a manner understood by those skilled in this art.

Example I

400 parts of a highly aromatic crude oil obtained from the Sam Fordyce field in South Texas are treated with 50 parts of 98% sulfuric acid at 25° C. The acid and oil are intimately mixed by means of a high speed stirring apparatus while the temperature rises slightly. After the reaction is complete as is indicated by a fall in temperature, the sludge is settled, preferably with the aid of centrifugal force, and the oil layer is withdrawn. To this oil layer, now freed from unsaturates which polymerize readily, is added 1000 parts of 20% oleum, at 40° C., and the temperature is gradually raised to 70° C. where sulfonation proceeds with the evolution of some sulfur dioxide.

The acid mass is next added to 1000 parts of cold water, cooling if necessary to prevent decomposition, until the addition is complete. The mass is then heated to the boiling point and allowed to settle. The oil layer is removed, and the combined water and sludge layers are extracted twice with light petroleum distillate to remove oil and mahogany sulfonates. The mass is then allowed to subside and stratify. The acid layer is drawn off and the "green" acid sludge layer is analyzed for organically combined sulfur, free sulfuric acid acidity and water. An amount of cyclohexylamine equivalent to the sulfonic acid acidity is added and the mass is heated nearly to the boiling point. The oil soluble amino compound rises to the top and nearly all of the free acid and water will appear in a lower layer which is drawn off, and the oil soluble cyclohexylamine salt is recovered.

Example II

300 parts of sulfur dioxide extract, derived from the refining of kerosene distillates, are added to the recovered product from Example I, and the mass is heated at temperatures ranging from 150°–200° C. to form the corresponding cyclohexyl amide by dehydration of the amine salt. The solvent is either distilled out or allowed to remain as a diluent.

Example III

The same as Example I or II except that monoamylamine is used instead of cyclohexylamine.

Example IV

The water soluble sulfonic acid, prepared as in Example I, is neutralized with di-octylamine.

Example V

The corresponding di-octyl sulfonamide is prepared from the amine salt prepared according to Example IV, using the procedure outlined in Example II involving dehydration of the corresponding amine salt.

Example VI

Same as Example I or II except that benzyl amyl amine is used instead of cyclohexylamine.

The term "N-alkylated sulfonamide" contemplates broadly the N-alkylated monosulfonamides and disulfonamides, inclusively. As is well known to those skilled in organic chemistry, N-alkylated monosulfonamides may be prepared from either primary or secondary alkylamines by substituting one hydrogen atom by a sulfonic acid radical or its equivalent. N-alkylated disulfonamides may be prepared only from primary alkylamines since the reaction involves substitution of two hydrogen atoms of the primary amine by two sulfonic acid radicals or their equivalents.

Thus, if in Example I, II or III, only one-half of the quantity of primary amine required to neutralize the sulfonic acid acidity were added and the dehydration reaction is carried out in the presence of sulfuric acid and a high-boiling solvent at an elevated temperature, the reaction product may contain a mixture of mono- and disulfonamides which are readily separated from the free sulfuric acid and sulfonic acids present in the reaction mass. However, if a di-alkylated secondary amine, such as dioctylamine disclosed in Examples IV and V were used, only the monosulfonamide could result from the initially formed alkylamine salt.

An equivalent of the sulfonic acids used in the preceding examples is their corresponding sulfonyl chlorides which react to form N-alkylated sulfonamides directly.

The term "water-wettable" as used in the specification and claims refers to the characteristic of the product which enables it to be readily wetted by water and which is usually accompanied by some degree of hydration of the product in contact with the aqueous phase of the emulsion. When the product segregates at the interface of the emulsion and is adsorbed at the interfacial film where the hydrophobe body responsible for the emulsion exists, the water-wettable property of this product counteracts the effect of the hydrophobe present in the emulsion and thus effects its resolution.

The term "oil soluble" is used to include the property of colloidal dispersion in the oil phase.

It will further be understood that in the preparation of the water soluble petroleum sulfonic acid which is used as a base for reaction with the amine, there may be present minor fractions which are oil soluble; the expression "substantially water soluble" is therefore used.

The improved treating agents prepared in accordance with the present invention are used in small percentages, viz., in the proportion of one part of treating agent to from 2,000 to 20,000 parts (or, in some cases, as high as 30,000 parts) of petroleum emulsion, either by adding the concentrated product directly to the emulsion or after diluting with water or oil in the conventional manner. The treating agents may be used in any of the numerous ways commonly employed in the treatment of petroleum emulsions as will be apparent.

I claim:

1. A petroleum demulsifying composition which comprises as a component the N-alkylated sulfonamide of a water-soluble, oil-insoluble petroleum sulfonic acid.

2. A petroleum demulsifying composition which comprises as a component the N-aralkylated sulfonamide of a water-soluble, oil-insoluble petroleum sulfonic acid.

3. The process of breaking petroleum emulsions comprising, incorporating therein a small percentage of a petroleum demulsifying composition having as a component the N-alkylated sulfonamide of a water-soluble, oil-insoluble petroleum sulfonic acid.

4. The process of breaking petroleum emulsions comprising, incorporating therein a small percentage of a petroleum demulsifying composition having as a component the N-aralkylated sulfonamide of a water-soluble, oil-insoluble petroleum sulfonic acid.

5. A petroleum demulsifying composition which comprises as a component the N-alkylated disulfonamide of a water-soluble, oil-insoluble petroleum sulfonic acid.

6. A petroleum demulsifying composition which comprises as a component the N-alkylated monosulfonamide of a water-soluble, oil-insoluble petroleum sulfonic acid.

7. A petroleum demulsifying composition which comprises as a component the N-aralkylated disulfonamide of a water-soluble, oil-insoluble petroleum sulfonic acid.

8. A petroleum demulsifying composition which comprises as a component the N-aralkylated monosulfonamide of a water-soluble, oil-insoluble petroleum sulfonic acid.

TRUMAN B. WAYNE.