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PROCESS FOR BREAKING PETROLEUM EMULSIONS

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

Petroleum emulsions are of the water-in-oil type, and 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. They are obtained from producing wells and from the bottoms of oil storage tanks, and are commonly referred to as "cut oil", "roily oil", "emulsified oil" and "bottom settlings".

The object of our invention is to provide a novel, inexpensive and efficient process for separating emulsions of the kind referred to into their component parts of oil and water or brine.

Briefly described, our process consists in subjecting a petroleum emulsion of the water-in-oil type, to the action of a treating agent or demulsifying agent of a particular kind or composition hereinafter described, thereby causing the emulsion to break down and separate into its component parts of oil and water or brine, when the emulsion is permitted to remain in a quiescent state after such treatment.

The treating agent or demulsifying agent used in our process consists of or comprises a halogenated sulfo fatty acid or salt or ester thereof, or a mixture of two or more halogenated sulfo fatty acids or salts or esters thereof.

We are aware that halogenated fatty acids and sulfo fatty acids are members of the class of materials known as modified fatty acids, used extensively in the demulsification of cut oil or emulsified oil. It has been previously proposed to use halogenated derivatives of the fatty acids for the demulsification or resolution of cut oil. Sulfo fatty acids have been in extensive use for a long time for breaking crude oil emulsions. We have discovered that when a halogenated sulfo fatty acid, in the form of an acid or as a salt or ester thereof, is used as a treating agent or demulsifying agent to break petroleum emulsions of the water-in-oil type, it is found to possess demulsifying properties different from either sulfo fatty acids or halogenated fatty acids. The halogenated sulfo fatty acids may treat or resolve crude oil emulsions which are not affected by sulfo fatty acids or halogenated non-sulfo fatty acids. The effect of introducing both the halogen and the sulfo group into a fatty radical does not appear to be cumulative in regard to demulsifying action. For instance, a certain emulsion may be susceptible to resolution by either a non-halogenated sulfo fatty acid or a non-sulfo halogenated fatty acid, and yet not be affected at all by halogenated sulfo fatty acid. In other cases there are emulsions which are affected and resolved much more readily and much more economically by halogenated sulfo fatty acid or salts or esters thereof, than any other reagent or demulsifying agent which is now available. The advantage or superiority of the reagent contemplated by our process is based on its ability to treat certain emulsions better than any other known reagent, and not on the basis that it can supersede the majority of modified fatty acids, sulfo fatty acids, etc., heretofore used extensively in the resolution of petroleum emulsions.

Examples of known halogenated fatty acids are such as described in U. S. Patent No. 1,566,008, dated December 15, 1925, to Carl G. Hinrichs. Examples of sulfo fatty acids such as fatty acid sulfates and fatty sulfonic acids, are described in Industrial and Engineering Chemistry, Analytical Edition, volume 3, page 243, July 15, 1931.

The reagents of our present process are halogenated sulfo fatty acids. The sulfo group may be present as an acid sulfate or as a true sulfonic acid. The halogen may be any suitable member of the halogen family and preferably is bromine or chlorine. In practically every instance, chlorine is most desirable because it is the cheapest available halogen. The reagents contemplated by our invention do not include sulfo aromatic fatty acids which contain a chlorinated or halogenated aromatic residue or nucleus. It is to be understood that a halo-

gen such as chlorine is attached directly to the fatty acid radical, that is, it must be introduced into the fatty acid chain as an addition product or substitution product.

The reagents of our present process can be prepared by a number of methods. One method is to employ an unsaturated hydroxy fatty acid or glyceride such as castor oil, and subject it to the action of chlorine, so that the unsaturated bond becomes saturated with chlorine, and also so that two or more additional hydrogens are replaced by chlorine, so as to produce a tetra or hexachlorricinoleic acid body. This fatty chloride is then sulfonated or sulfated so that sulfuric acid combines with the active alcoholic hydroxyl. The excess of sulfuric acid is removed by washing and the carboxyl hydrogen, if desired, may be neutralized with any suitable base, such as caustic soda, caustic potash, ammonia, etc. It should be pointed out that in the sulfonation or sulfation the glyceride is usually decomposed or hydrolyzed and the carboxyl hydrogen is liberated.

Another method of manufacture involves the use of chlorosulfonic acid for sulfonation or sulfation of unsaturated fatty acids. The sulfation or sulfonation of an unsaturated fatty acid with chlorosulfonic acid does not always yield a chlorosulfo fatty acid. For instance, the treatment of oleic acid with chlorosulfonic acid does not always yield chlorosulfoleic acid. The reaction, as generally conducted, yields only materials free from combined chlorine. However, as pointed out by K. H. Bauer and J. Stockhausen in Seifensieder Zeitung, volume 59, page 34 (1932), it is possible to conduct the reaction so as to obtain chlorosulfoleic acid. Other unsaturated fatty acids or fats or oils such as castor oil, linseed oil, etc. may be substituted for oleic acid.

Another method of producing halogenated sulfo fatty acids depends on the use of a sulfite such as potassium sulfite, in reaction with a salt of a halogenated fatty material. Such procedure is fully described in U. S. Patent No. 1,851,102, to Georg Kalischer and Karl Keller, dated March 29, 1932.

Our preferred reagent or treating agent is produced in the following manner: Castor oil is treated with steam and a suitable fat splitting agent of the kind generally employed for splitting fats and under the conditions generally employed so as to yield polymerized or esterified ricinoleic acid. The fatty material so obtained by hydrolysis and esterification from castor oil is separated from the accompanying water and treated with chlorine until not only has there been an addition of chlorine at the unsaturated bond, but also until there is a substitution of chlorine, so that approximately six chlorine atoms are absorbed for each original ricinoleic molecule. This material is usually referred to as hexachlorinated ricinoleic acid, although it should be noted that the ricinoleic acid is in reality in an esterified form. One hundred pounds of this material are treated with twenty pounds of anhydrous sodium sulfite in the presence of about twelve to thirteen pounds of water, with the addition of a catalyst such as metallic copper or potassium iodide. The amount of the catalyst may vary from a fraction of one percent up to 3 or 4 percent. The entire mixture is heated in an autoclave at approximately 145° to 160° centigrade with constant stirring. The reaction generally is completed within five to fifteen hours. The reaction mass is dissolved in a small quantity of water and filtered. The filtrate contains the halogenated sulfo fatty acid. This is removed from the filtrate by a salting out process. Common salt or sodium sulfate may be added to salt the material out. The halogenated sulforicinoleic acid thus obtained may be used as recovered from the salting out process, or may be neutralized by the addition of a suitable basic material such as caustic soda, caustic potash, or ammonium hydroxide. It may even be esterified with a suitable alcohol such as ethyl, methyl, or propyl alcohol. We prefer to use it in the form of an ammonium salt.

It is to be understood that the use herein of the term halogenated sulfo fatty acids should not be interpreted as being restricted to such bodies in their acidic state, in so much as they may be equally suitable or preferable after neutralization with a basic material or after esterification with an alcohol.

In practicing our process, a treating agent formed wholly or in part of a material of the kind above described, may be brought in contact with emulsion to be treated in any of the numerous ways now employed in the treatment of petroleum emulsions of the water-in-oil type with chemical demulsifying agents, such, for example, as by introducing the treating agent into the well in which the emulsion is produced; introducing the treating agent into a conduit through which the emulsion is flowing; introducing the treating agent into a tank in which the emulsion is stored; or introducing the treating agent into a container that holds a sludge obtained from the bottom of an oil storage tank. In some instances, it may be advisable to introduce the treating agent into a producing well in such a way that it will become mixed with water and oil that are emerging from the surrounding strata, before said water and oil enter the barrel of the well pump or the tubing up through which said water and oil flow to the surface of the ground. After treatment, the emulsion is allowed to stand in a quiescent state, usually in a settling tank, and usually at a

temperature varying from atmospheric temperature to about 200° F., so as to permit the water or brine to separate from the oil, it being preferable to keep the temperature low enough to prevent the volatilization of valuable constituents of the oil. If desired, the treated emulsion may be acted upon by one or more of the various kinds of apparatus now used in the operation of breaking petroleum emulsions, such as homogenizers, hay tanks, gun barrels, filters, centrifuges, or electrical dehydrators.

The amount of treating agent that may be required to break the emulsion may vary from approximately 1 part of treating agent to 500 parts of emulsion, up to 1 part of treating agent to 20,000 or even 30,000 parts of emulsion. The proportion depends on the type of emulsion being treated, and also upon the equipment being used, and the temperature employed. In treating exceptionally refractory emulsions of the kinds known as "tank bottoms" and "residual pit oils", the ratio of 1:500, above referred to, may be required. In treating fresh emulsions, i. e., emulsions that will yield readily to the action of chemical demulsifying agents, the ratio of 1:30,000, above referred to, may be sufficient to produce highly satisfactory results. In general, we have found that for an average petroleum emulsion, a ratio of 1 part of treating agent to 5,000 parts of emulsion will usually be found to produce commercially satisfactory results.

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

1. A process for breaking petroleum emulsions of the water-in-oil type, which consists in subjecting the emulsion to the action of a demulsifying agent containing a halogenated sulfo fatty body, in which the halogen is directly attached to the fatty acid radical.

2. A process for breaking petroleum emulsions of the water-in-oil type, which consists in subjecting the emulsion to the action of a demulsifying agent containing a halogenated sulfo acid body in which the halogen is directly attached to the fatty acid radical, and in the form of a salt.

3. A process for breaking petroleum emulsions of the water-in-oil type, which consists in subjecting the emulsion to the action of a demulsifying agent containing a halogenated sulfo fatty acid body in which the halogen is directly attached to the fatty acid radical and in the form of an ammonium salt.

4. A process for breaking petroleum emulsions of the water-in-oil type, which consists in subjecting the emulsion to the action of a demulsifying agent containing a chlorinated sulfo fatty body, in which the chlorine atom is directly attached to the fatty acid radical.

5. A process for breaking petroleum emulsions of the water-in-oil type, which consists in subjecting the emulsion to the action of a demulsifying agent containing a chlorinated sulfo fatty acid body in which the chlorine atom is directly attached to the fatty acid radical, and in the form of a salt.

6. A process for breaking petroleum emulsions of the water-in-oil type, which consists in subjecting the emulsion to the action of a demulsifying agent containing a chlorinated sulfo fatty acid body in which chlorine atom is directly attached to the fatty acid radical, and in the form of an ammonium salt.

7. A process for breaking petroleum emulsions of the water-in-oil type, which consists in subjecting the emulsion to the action of a demulsifying agent containing a chlorinated sulfo-fatty body in which the chlorine atom is directly attached to the fatty acid radical, and derived from castor oil.

8. A process for breaking petroleum emulsions of the water-in-oil type, which consists in subjecting the emulsion to the action of a demulsifying agent containing a chlorinated sulfo-fatty body in which the chlorine atom is directly attached to the fatty acid radical, and derived from castor oil in the form of a salt.

9. A process for breaking petroleum emulsions of the water-in-oil type, which consists in subjecting the emulsion to the action of a demulsifying agent containing a chlorinated sulfo-fatty body in which the chlorine atom is directly attached to the fatty acid radical, and derived from castor oil in the form of an ammonium salt.

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