

UNITED STATES PATENT OFFICE

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PROCESS FOR BREAKING PETROLEUM EMULSIONS

No Drawing.

Application filed March 25, 1932. Serial No. 601,295.

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.

5 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 emulsions. They are obtained from producing wells and from the bottom of oil storage tanks, and are commonly referred to as "cut oil", "roily oil", "emulsified oil" and "bottom settlings".

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

20 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 the kind 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 treatment.

The treating agent or demulsifying agent used in our process consists of or comprises a nitrogenous sulfo fatty acid in which the nitrogen or nitrogen bearing radical, group or residue is substituted in the carboxyl or carboxyl equivalent of the fatty acid derived by combining a sulfo fatty acid with a basic nitrogen compound, such as anilin, an amino compound, an amido compound, etc., or derived by combining a nitrogenous body with a fatty body and then sulfonating the same. In other words, the nitrogen or nitrogen-bearing radical replaces the OH group of the carboxyl, or replaces the $C_3H_5.O_3$ group of a fatty triglyceride with the result that the demulsifying agent may be said to contain a nitrogenous sulfo fatty acid which is to be characterized by direct linkage between the carbon of the carboxyl radical residue of the sulfo fatty acid and the nitrogen of the nitrogenous body.

50 As will subsequently be pointed out, the

treating agent may be used in an acidic state or after neutralization with an inorganic base to produce a salt or in the form of an ester. Therefore, the term "nitrogenous sulfo fatty acid" is used in the generic sense to include not only the described fatty acids as such, but also their salts and esters. The term "sulfo fatty acid" as employed herein is used to denote a fatty acid body in which there is present an acid sulfate group or a true sulfonic group. Such acid sulfate group or sulfonic group may be attached directly to the fatty acid radical, or it may be attached through an intervening aromatic group, as in the case of the conventional sulfo aromatic fatty acid. Sulfuric acid reacts with fatty acids as in the production of commercial Turkey red oil, so as to produce an ester of sulfuric acid, and in which there is present a HSO_4 group and the sulfur atom of the sulfuric acid residue is joined to the fatty group or radical through an intermediate oxygen atom. In the production of true fatty sulfonic acids such as described in U. S. Patent No. 601,603 to Ernst Twitchell, dated March 29, 1898, there is present a HSO_3 group which is united with the fatty radical or group directly by means of the sulfur atom of the sulfonic group and not through an intervening oxygen atom (see Organic Chemistry, Norris, 2d edition, 1922, McGraw-Hill Book Co., page 365, and Industrial and Engineering Chemistry, Analytical edition, volume 3, page 244, 1931). Sulfo aromatic sulfonic acids are described in U. S. Patent No. 628,503 to Ernst Twitchell, dated July 11, 1899. In these latter fatty bodies, the sulfonic group is attached to the aromatic group and not directly to the fatty acid radical. Therefore, the term "sulfo-fatty acid" as herein employed includes the three classes of sulfur-containing fatty materials enumerated.

The production of compounds derived by combining non-sulfo fatty acids with basic nitrogen compounds such as anilin, amino compounds, amido compounds and the like, to produce substances in which the nitrogen or nitrogen bearing radical replaces the hy-

droxyl of the fatty acid carboxyl or its equivalent, has been described in the literature, although their application for the particular purpose of the present invention, that is, the resolution of petroleum emulsions of the water-in-oil type, has never been disclosed or suggested. U. S. Patent 741,585, to Oscar Liebreich, dated October 13, 1903, describes derivatives of fatty acids and anilin, bases of the naphthalene series, aromatic diamines, homologues of the previously mentioned groups, and also monoalkyl derivatives of the bases mentioned and their homologues. U. S. Patent No. 746,638, to Oscar Liebreich, dated December 8, 1903, discloses the manufacture of similar materials. U. S. Patent No. 748,511, to Oscar Liebreich, dated December 29, 1903 discloses fatty compounds in which the basic nitrogenous material is meta-phenylenediamid and the like. U. S. Patent No. 1,475,477 to Carleton Ellis, dated November 27, 1923, describes the manufacture of similar products from oleic acid and such basic nitrogenous material as anilin, para amido phenol, ortho toluidine, xyli-
dine, quinoline, acetamide, diphenylamine, urea, and beta-naphthylamine. The manufacture of similar products is also disclosed in U. S. Patent No. 1,659,150 to Edward A. Nill, dated February 14, 1928.

The treating agent or demulsifying agent used in our process consists of a product derived by reaction of a basic nitrogenous compound, such as the ones employed in the various patents previously enumerated, and a sulfo-fatty acid. They are manufactured in the same manner as the nitrogenous basic compounds described in the above mentioned patents, except that the reaction takes place between the basic nitrogenous compounds and a stable sulfo fatty acid instead of a non-sulfo fatty acid. A second general procedure for producing our treating agent is to produce the nitrogenous compound of an unsaturated fatty acid such as oleic acid or of a hydroxylated fatty acid such as ricino-
leic acid, and then sulfonate the stable nitrogenous derivative of the fatty acid of the kind described in the manner employed in production of Turkey red oils or sulfo aromatic sulfonic acids as employed in the commercial splitting of fats or in the manner employed in the production of true fatty sulfonic acids.

As previously stated, the expression "nitrogenous sulfo fatty acid" is used in the generic sense to include also the salts and esters of the particular nitrogenous sulfo fatty acids herein described. In other words, nitrogenous sulfo fatty acids as such may be used to constitute the treating agent of our process or they may be neutralized prior to use with any suitable basic material such as caustic soda, caustic potash, sodium

carbonate, potassium carbonate, ammonium carbonate, ammonium hydroxide, calcium hydroxide, magnesium carbonate, etc. If desired, such nitrogenous sulfo fatty acids as above described may be converted into esters by conventional reaction methods with suitable alcohols, aromatic or aliphatic, and the resulting esters or ester used to constitute the treating agent of our process. Some of the esters thus obtained may be oil soluble, and some may be water soluble. The salts such as obtained by neutralization with inorganic bases are usually water-soluble, and a few may even be water-insoluble, as in the case of aluminum.

In practising our process, we prefer to use a treating agent or a demulsifying agent obtained or produced by the following procedure: 240 pounds of anilin and 370 pounds of oleic acid are heated under a reflex condenser for 4 hours at 170 to 190° centigrade. The mixture shows considerable darkening during the reaction. When the reaction is substantially complete, it is distilled with steam to remove uncombined anilin. The resultant product should show an acid number of less than 35. This acid number is due to uncombined oleic acid. This uncombined oleic acid can be removed by washing the mixture with caustic soda, which converts the free oleic acid into water-soluble sodium oleate. Subsequent washing is required to remove any excess of alkali and the material should then be dried. The finished product should have an acid number of less than 5, it should be dark brown in color, and have a greasy feel. The melting point should be about 34° centigrade. 400 pounds of the material so described is mixed with 100 pounds of phenol and treated with 500 lbs. of sulfuric acid so as to produce a sulfonic acid in which the sulfonic acid group is attached to the nitrogenous fatty body through an intermediate phenol residue. This material is akin to a fatty sulfonic acid and may be purified from excess of phenol and free sulfuric acid by repeated washings with water under conditions which do not permit the solubility of the nitrogenous sulfo acid. The nitrogenous sulfo fatty acid thus obtained is neutralized with strong ammonium hydroxide and employed in the form of an ammonium salt.

The specific form, state or condition of the treating agent at the time it is used or applied to the petroleum emulsion to be treated is immaterial and may be varied to suit existing conditions. It can be used in substantially anhydrous state or in solutions of any convenient strength. A concentrated solution of the nitrogenous sulfo fatty acid can be emulsified with oil by the agency of any suitable oil-soluble emulsifiers, such as calcium oleate and the resultant mixture used to constitute the treating agent of our

process. The treating agent can be formed entirely from a material of the kind previously described, or it can be formed from such a material in combination with another or other well known treating agents for petroleum emulsions of the water-in-oil type, such as water softeners, modified fatty bodies, or their salts, petroleum sulfonic acids or their salts, or other substances known to have similar demulsifying properties.

In practising our process, a treating agent or demulsifying agent of the kind above described may be brought in contact with the 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, 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 so as to prevent the valuable constituents of the oil from volatilizing. If desired, the treated emulsion may be acted upon by one or the other of 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 on the anhydrous basis that is required to break the emulsion may vary from approximately 1 part of treating agent to 500 parts of emulsion, up to a ratio of 1 part of treating agent to 20,000 parts of emulsion, depending upon the type or kind of emulsion being treated. In treating exceptionally refractory emulsions of the kind commonly referred to as "tank bottoms" or "residual pit oils", the minimum ratio above referred to is often necessary, but in treating fresh emulsions, i. e., emulsions that will yield readily to the action of chemical demulsifying agents, the maximum ratio above mentioned will frequently produce highly satisfactory results.

For the average petroleum emulsion of the water-in-oil type, a ratio of 1 part of treating agent to 5000 parts of emulsion will usually be found to produce commercially satisfactory results.

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, which consists in subjecting the emulsion to the action of a demulsifying agent containing a nitrogenous sulfo fatty acid, characterized by direct linkage between the carbon of the carboxyl radical residue of the sulfo fatty acid and the nitrogen of the nitrogenous body.

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 salt of a nitrogenous sulfo fatty acid, characterized by direct linkage between the carbon of the carboxyl radical residue of the sulfo fatty acid and the nitrogen of the nitrogenous body.

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 water-soluble salt of a nitrogenous sulfo fatty acid, characterized by direct linkage between the carbon of the carboxyl radical residue of the sulfo fatty acid and the nitrogen of the nitrogenous body.

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 an ammonium salt of a nitrogenous sulfo fatty acid, characterized by direct linkage between the carbon of the carboxyl radical residue of the sulfo fatty acid and the nitrogen of the nitrogenous body.

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