

UNITED STATES PATENT OFFICE

2,104,803

PROCESS FOR SEPARATING HIGHER ALIPHATIC ALCOHOLS FROM AQUEOUS EMULSIONS

Clyde O. Henke, Wilmington, Del., and Howard M. Parmelee, Salem, N. J., assignors to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application January 4, 1935,
Serial No. 364

11 Claims. (Cl. 87-28)

This invention relates to the production of higher alcohols and more particularly refers to an improvements in the process for producing higher fatty alcohols by the sodium reduction of fatty acid esters.

It is an object of this invention to expedite and make more economical the production of higher fatty alcohols. A further object is to overcome certain difficulties encountered in the sodium reduction of fatty acid esters. A still further object is to efficiently separate higher alcohol solutions from the mixture of reaction products resulting from the sodium reduction of fatty acid esters. A still further object is to devise an inexpensive method for causing the separation of a strongly alkaline solution of a soap-like compound from a solution of water-insoluble alcohols. Additional objects will become apparent from a consideration of the following description and claims.

These objects are attained according to the herein described invention which broadly comprises the separation of a solution of water-insoluble alcohols from a strongly alkaline aqueous emulsion containing said solution and a soap-like substance by treating the mixture with a surface active material having low emulsifying properties. In a more limited sense the invention pertains to the separation of higher alcohols from the reaction products resulting from the sodium reduction of higher fatty acid esters by adding to said mixture a member of that class of substances commonly known as mercerizing assistants. In its preferred embodiment this invention is directed to the separation of higher fatty alcohol solutions from the reaction products obtained by the sodium reduction of higher fatty esters by adding to said reaction products a hydroxylated aromatic compound of the benzene series and/or a straight or branched chain higher fatty acid containing from 6 to 10 carbon atoms.

The invention may be more readily understood by a consideration of the following illustrative examples:

Example 1

An emulsion resulted from the reduction of spermaceti and contained the following materials:

	Grams
Xylene.....	2000
Mixed methyl cyclohexanols.....	372
Crude cetyl alcohol.....	720
Caustic soda solution 20% sodium hydroxide and a small amount of sodium palmitate.....	1350

This emulsion was very stable. Small samples remained emulsified after they had been saturated with salt and heated for 5 hours.

One gram of o-cresol was mixed with 100 grams of this emulsion and the emulsion immediately separated into two layers.

Example 2

One gram of crude mixed xylenols was mixed with a 100 gram sample of the emulsion described in Example 1 and it then separated immediately into two clear layers. The temperature was 50-70° C.

Example 3

One gram of phenol was mixed with 100 grams of the emulsion described in Example 1. The temperature was 50-70° C. In a short time it had separated into two clear layers.

Example 4

One gram of mixed branched chain fatty acids with 8 to 10 carbon atoms per molecule was mixed with 100 grams of the emulsion described in Example 1. In a short time it separated into two clear layers.

Example 5

An emulsion containing the following materials resulted from the reduction of peanut oil:

	Grams
Xylene.....	1500
Mixed methyl cyclohexanols.....	496
Mixed higher aliphatic alcohols.....	575
Sodium hydroxide solution (20% NaOH) and a small amount of the sodium salts of peanut oil fatty acids.....	1800

After standing at a temperature between 80 and 90° C. for 1½ hours it showed no signs of separating. With the temperature at 78-80° C. 20.8 grams of crude o-cresol was added, and thoroughly mixed with the mass. When the mixing was stopped the mixture separated into two layers within 5 minutes.

Example 6

The reduction of esters from wood distillate acids resulted in a mixture which contained the following materials:

	Grams
Xylene.....	1750
Mixed methyl cyclohexanols.....	134
Mixed higher alcohols from wood distillate acids.....	185
Caustic soda solution (20% sodium hydroxide) and a small amount of sodium soaps of the wood distillate acids.....	565

The mixture formed a very stable emulsion which separated very slowly. 9.9 grams of o-cresol were added, and it separated within 5 minutes.

Example 7

An emulsion resulting from the reduction of spermaceti contained the following materials:

	Grams
Xylene.....	1750
Mixed methyl cyclohexanols.....	372
Crude cetyl alcohol.....	680
Caustic soda solution (20% sodium hydroxide) and a small amount of sodium palmitate.....	1350

This emulsion was very stable. However, when 30 grams of o-cresol were added the emulsion separated into two layers.

It is to be understood that the aforementioned examples are illustrative merely of the manner of carrying out the present invention. The individual reactants and/or mixtures of such reactants as well as the conditions under which they are reacted may be varied widely without departing from the scope of this invention. For example, in place of the emulsions previously referred to other strongly alkaline mixtures containing a solution of water-insoluble alcohols and a soap or a soap-like substance may be treated. The particular water-insoluble alcohols contained in said mixtures may vary widely and are not intended to be limited to the alcohols described in the examples.

In selecting compounds to be used in separating the mixtures comprised herein it has been found that surface active materials having low emulsifying properties are quite satisfactory. These materials are ordinarily, but not essentially, of an acidic character. The class of compounds commonly referred to as mercerizing assistants has been found to be of particular advantage for this purpose. As is well known, cotton may be mercerized with 15-25% sodium hydroxide. Wetting agents which function satisfactorily in this strength caustic assist in the action of the caustic and are herein referred to as mercerizing assistants. A few of the compounds which come within this category are, for instance, sulfuric acid esters of lower alkyl ethers of glycol and glycerine such as the sulfuric acid ester of ethylene glycol mono-(ethyl, propyl or butyl)-ether, sulfuric acid ester of diethylene glycol monoethyl ether, sulfuric acid ester of the monoethyl ether of glycerine; dithiocarbamates such as sodium dipropyl dithiocarbamate, sodium dibutyl dithiocarbamate, sodium ethyl butyl dithiocarbamate, sodium N-N'-dibutyl ethylene diamine di dithiocarbamate; hydroxylated aromatic compounds; fatty acids of high molecular weight, preferably those straight or branched chain acids containing 6 to 10 carbon atoms; methyl-, ethyl- and propyl-esters of naphthenic acids, etc.

Assistants which have been found to be of outstanding value for this purpose are: phenol, cresol, xyleneol, sodium salts thereof and their homologues. Straight and branched chain fatty acids containing from 6 to 10 carbon atoms and their sodium salts have also been found to be quite advantageous. It is to be understood that mixtures of the aforementioned assistants and/or other compounds of the same category may be used in place of individual assistants. The amount of mercerizing assistant which is added to the mixture may vary considerably depending upon the particular assistant or mixture thereof

which is selected as well as upon the mixture to which it is to be added. However, an amount varying from a fraction of 1% to about 3%, based upon the weight of the mixture to be separated, will ordinarily be sufficient.

As previously mentioned, the mixture to be treated in accordance with this invention should be strongly alkaline and should contain soap or a soap-like material solution of water-insoluble alcohols. Where reference is made in the claims to a "soap-like material" this is understood to include soaps such as sodium salts of higher fatty acids. The solution of water-insoluble alcohols ordinarily contains higher fatty alcohols and a solvent such as xylene. Since higher fatty alcohols are particularly contemplated herein a few of them will be described for purposes of illustration. They are: octyl, decyl, lauryl, myristyl, cetyl, stearyl, oleyl, ricinoleyl, linoleyl, etc. alcohols. For optimum results the emulsion in which these water-insoluble alcohols are present with soap-like substances is strongly alkaline. The term "strongly alkaline" is not restricted to any definite range of alkalinity, although for most purposes it may be understood to include an alkalinity corresponding to the presence of from about 15% to about 25% caustic soda.

The use of heat in causing the separation of the mixtures described herein is frequently advantageous. For example, the emulsion to be separated may be heated to temperatures within the range of about 40 to about 95° C. However, it is understood that the aforementioned temperature range is not restrictive and that this invention is applicable where the solution to be treated is at a temperature which falls without said range.

By means of the present invention solutions of water-insoluble alcohols are separated from strongly alkaline emulsions containing soap or soap-like substances. These emulsions are frequently encountered when producing higher fatty alcohols by means of the sodium reduction of higher fatty acid esters. Processes for the sodium reduction of esters are well known and comprise briefly the treatment of such esters with sodium in the presence of hydroxylic compounds as set forth in U. S. Patents 868,252; 1,971,742; 2,019,022; and 2,070,597. These hydroxylic compounds are ordinarily alcohols of primary, secondary and/or tertiary character. Such alcohols may be selected from either the aliphatic, aralkyl and/or hydrocyclic series. Since the present invention is not limited to any particular method of producing the alkaline solutions to be treated it is to be understood that the aforementioned sodium reduction processes are descriptive merely of a few of the many methods in which emulsions to be treated herein may be produced.

Heretofore the previously described solutions were separated by expensive and time-consuming operations. These operations depended upon the use of acids, high temperatures, electrically charged plates, centrifuging, etc. Needless to say the present invention effects a considerable reduction in the cost of this procedure. This invention permits cheap and readily available reagents to be used in either crude or purified form. Moreover, the desired separation is accomplished speedily and effectively.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not

limited to the specific embodiments thereof except as defined in the appended claims.

We claim:

1. A process of breaking an aqueous emulsion which is formed by diluting with water the reaction mixture obtained in the sodium-alcohol reduction of a higher fatty acid ester and which contains a higher aliphatic alcohol, a soap, caustic soda, a hydrocarbon solvent, and water, which comprises admixing said emulsion with an amount of a hydroxylated aromatic compound of the benzene series which is stoichiometrically equivalent to only a small part of the alkali present in the emulsion.

2. A process of breaking an aqueous emulsion which is formed by diluting with water the reaction mixture obtained in the sodium-alcohol reduction of an ester of a higher fatty acid and which contains a higher aliphatic alcohol having eight or more carbon atoms, a soap, caustic soda, a hydrocarbon solvent of the benzene series, and water, which comprises admixing said emulsion with an amount of a hydroxylated aromatic compound of the benzene series which is stoichiometrically equivalent to only a small part of the alkali present in the emulsion.

3. A process of breaking an aqueous emulsion which is formed by diluting with water the reaction mixture obtained in the sodium-alcohol reduction of an ester of a higher fatty acid and which contains a higher aliphatic alcohol having eight or more carbon atoms, a soap, caustic soda, xylene, and water, which comprises admixing said emulsion with an amount of a monohydric mononuclear phenol which is stoichiometrically equivalent to only a small part of the alkali present in the emulsion.

4. A process of breaking an aqueous emulsion which is formed by diluting with water the reaction mixture obtained in the sodium-alcohol reduction of spermaceti and which contains crude cetyl alcohol, sodium palmitate, caustic soda, xylene, and water, which comprises admixing said emulsion with an amount of a monohydric mononuclear phenol which is stoichiometrically equivalent to only a small part of the alkali present in the emulsion.

5. A process as defined in claim 4 in which the phenol used comprises ortho cresol.

6. A process of breaking an aqueous emulsion which is formed by diluting with water the re-

action mixture obtained in the sodium-alcohol reduction of an ester of a higher fatty acid and which contains a higher aliphatic alcohol having eight or more carbon atoms, a soap, caustic soda, xylene, methyl cyclohexanol, and water, which comprises admixing said emulsion with an amount of a monohydric mononuclear phenol which is stoichiometrically equivalent to only a small part of the alkali present in the emulsion.

7. A process as defined in claim 6 in which the phenol used comprises ortho cresol.

8. A process of breaking an aqueous emulsion which is formed by diluting with water the reaction mixture obtained in the sodium-alcohol reduction of spermaceti and which contains crude cetyl alcohol, sodium palmitate, caustic soda, xylene, methyl cyclohexanol, and water, which comprises admixing said emulsion with a monohydric mononuclear phenol which is stoichiometrically equivalent to only a small part of the alkali present in the emulsion.

9. A process as defined in claim 8 in which the phenol used comprises ortho cresol.

10. A process of breaking an aqueous emulsion which is formed by diluting with water the reaction mixture obtained in the alkali metal reduction of a higher fatty acid ester and which contains a higher aliphatic alcohol, a soap, caustic alkali, and water, which comprises admixing said emulsion with an amount which is stoichiometrically equivalent to only a small part of the alkali present in the emulsion, of an acidic wetting agent selected from the group consisting of a hydroxylated aromatic compound of the benzene series and a fatty acid containing from six to ten carbon atoms.

11. A process of breaking an aqueous emulsion which is formed by diluting with water the reaction mixture obtained in the alkali metal reduction of a higher fatty acid ester and which contains a higher aliphatic alcohol, a soap, caustic alkali, and water, which comprises admixing said emulsion with a small amount of a mixture of branched chain aliphatic acids having from eight to ten carbon atoms per molecule, said amount being stoichiometrically equivalent to only a small part of the alkali present in the emulsion.

CLYDE O. HENKE.

HOWARD M. PARMELEE.

CERTIFICATE OF CORRECTION.

Patent No. 2,104,803.

January 11, 1938.

CLYDE O. HENKE, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 9, after "material" insert the words as well as a; page 3, second column, line 18, claim 8, after "with" insert an amount of; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 29th day of March, A. D. 1938.

Henry Van Arsdale,

Acting Commissioner of Patents.

(Seal)