Patented June 3, 1947

2,421,707

UNITED STATES PATENT OFFICE

2,421,707

MONO-SUBSTITUTED DIALKANOL PIPERAZINES

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No Drawing. Application December 29, 1945, Serial No. 638,471

15 Claims. (Cl. 260—268)

1

The present invention relates to new compositions of matter for use as wetting, detersive and dispersing agents and, more particularly, to surface-active compounds of the type of high molecular weight tertiary amino derivatives, and to a process for their production.

Non-soap synthetic surface-active materials have many advantageous and desirable characteristics which recommend their employment for various purposes in industry and for household and personal uses. They have been known and used for many years as wetting, emulsifying, softening and foaming agents, etc., and are also widely used as detergents. The use of these prior art materials as detergents is largely connected with other properties which they exhibit, frequently including capability of forming soluble calcium and magnesium salts, since it is generally recognized by the art that fatty acid soaps have superior detergent characteristics per se. The art has long sought a synthetic detergent which would refute the old saying that "nothing cleans like soap," but, so far as applicant is aware, this search has heretofore been a vain one.

It is an object of the present invention to provide a novel class of surface-active materials having high detersive characteristics.

It is another object of this invention to provide new wetting and detergent compositions of the type of high molecular weight tertiary amino derivatives.

It is also an object of the invention to provide novel surface-active compounds which are water-soluble without containing solubilizing groups derived from polybasic inorganic acids, such as sulphates and sulphonates.

The present invention also contemplates novel organic compositions which provide wetting, detersive, and dispersing characteristics in either acid or alkaline solutions.

A further object of this invention is to provide a novel process for producing new organic surface-active compositions of high detersive characteristics.

Other objects and advantages of the invention will be apparent from the following description.

The organic compositions of the present invention are derivatives of N,N'-dialkanol piperazines.

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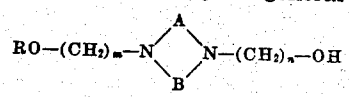
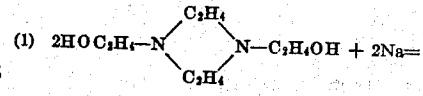
They may be represented by the general formula:

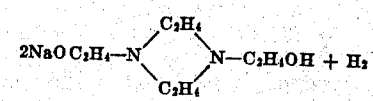


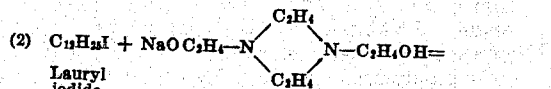
where R is an alkyl or acyl radical having about five to about twenty-three, preferably about eight to about eighteen, carbon atoms; A and B are ethylene radicals wherein any number of hydrogens (none, one or more) may be replaced by alkyl radicals, preferably of not more than two carbon atoms; and m and n are small integers, say 2 to about 5, preferably 2. The carbon chain represented by R may be straight or branched, saturated or unsaturated, and may be either unsubstituted or substituted by substituents such as halogens, hydroxyls, acyl groups, acyloxy groups, alkoxy groups, nitrogen-containing groups, heterocyclic groups, alicyclic groups, aryl groups, etc., although it is generally preferred that substituent groups of hydrophilic character be located near or adjacent to the piperazyl alkoxy group.

Where R is an alkyl or substituted alkyl group, the compound of the invention is an ether. Such novel ethers may be formed by reacting an excess of the N,N'-dialkanol piperazine with an alkali metal (or alkali metal hydride) to produce the alkoxide, and thereafter reacting an excess of the alkoxide with an alkyl halide. The ether is formed in accordance with the following typical equations:

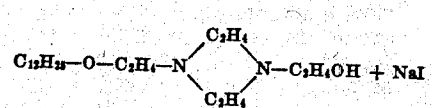


Diethanol piperazine



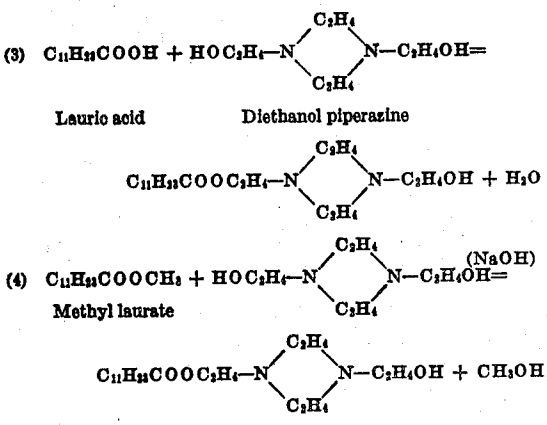


Lauryl iodide



Where R is an acyl or substituted acyl group,

the compound of the invention is an ester. These novel esters may be formed by reacting an excess of the dialkanol piperazine with a suitable carboxylic acid or by treating the dialkanol piperazine with a lower alkyl ester of such carboxylic acid and removing the resulting lower alcohol in an alcoholysis reaction. Typical equations for these alternative reactions are as follows:



Suitable carboxylic acids which may be reacted with N,N'-dialkanol piperazines, as in Equation 3, include lauric acid, myristic acid, palmitic acid, stearic acid, hydroxystearic acid, oleic acid, ricinoleic acid, lauryl succinic acid, isocaprylic acid, caproic acid, α-aminocapric acid, undecylenic acid, linoleic acid, linolenic acid, lignoceric acid, erucic acid, chloropalmitic acid, mixed coconut oil fatty acids, mixed tallow fatty acids, mixtures of any of these acids, etc. Similarly, lower alkyl esters of any of these acids (that is, esters of alcohols having one to about six carbon atoms) may be reacted with dialkanol piperazines as shown in Equation 4, such esters including methyl, ethyl, propyl and isopropyl esters, etc. In like manner, the chlorides, bromides and iodides corresponding to these acids may be employed as in Equation 2 supra to provide the novel piperazyl ethers of the present invention.

Although stoichiometric amounts of the N,N'-dialkanol piperazine, or even less than stoichiometric amounts, may be used in the reactions typified by Equations 1, 3 and 4, yields are improved and undesired by-products are reduced by providing an excess of the dialkanol piperazine. A proportion of about two mols to about five mols of N,N'-dialkanol piperazine to one mol of fatty acid or ester provides satisfactory yields according to Equations 3 and 4, and a proportion of about two mols to about five mols of dialkanol piperazine to one mol of alkali metal is suitable for preparing the alkoxides typified in Equation 1.

The dialkanol piperazines employed for production of the novel esters and ethers of the invention may be symmetrical or mixed. That is, m and n may be the same number or they may be different numbers. In general, it is preferred to employ symmetrical N,N'-dialkanol piperazines, such as N,N'-diethanol piperazine, N,N'-dipropanol piperazine, N,N'-diisopropanol piperazine, 3,6-dimethyl-1,4-di-(β-hydroxy ethyl)-piperazine, 3,6-dimethyl-1,4-di-(β-hydroxy propyl) piperazine, etc., and especially the symmetrical dialkanol piperazines having both hydroxyl groups in omega position with respect to the piperazyl radical. However, mixed piperazines of the type of 1-β-propanol-4-β-ethanol piperazine, 1-β-ethanol-4-γ-butanol piperazine, etc., can also be used.

The monoesters and monoethers of the dialkanol piperazines prepared according to this invention possess uniquely desirable surface-active properties. They are excellent detergents, under certain conditions superior even to fatty acid soaps, and are also valuable as wetting, foaming and lime soap dispersing agents. It is a feature of these novel compositions that they may be used either alone or combined with other surface-active materials, as they are compatible with soaps and/or synthetic surface-active agents of the type of sulphated and/or sulphonated organic compounds. Moreover, the novel compositions herein disclosed exhibit desirable surface-active characteristics in both acid and alkaline media, apparently changing in character, however, from a cationic form to a non-ionized or an anionic form. This discussion of theoretical principles and considerations is intended solely as a suitable explanation of this invention for the benefit of those skilled in the art, and it is in no wise to be considered a limitation of the invention herein described.

The novel compositions provided may be made up in solutions, preferably concentrated, or a dry or partially hydrated solid product may be formed. Adjuvant materials may be admixed with the new compositions to form flakes, granular particles, cakes and other physical forms of the mixture, or such adjuvant materials may be added to solutions of the composition of the invention. Such adjuvant materials may include sodium chloride, sodium sulphate, sodium pyrophosphate, and other builders and fillers employed by the soap and synthetic detergent arts generally, care being taken to avoid the use of any material which would substantially diminish the effectiveness of the new composition. The type of addition agent depends upon the ultimate use of the product.

The following examples, described hereinafter, are merely illustrative of the present invention, and it will be understood that the invention is not limited thereto.

Example I

About 100 parts by weight of lauric acid is admixed with 174 parts of N,N'-diethanol piperazine (that is, 1,4-di(β-hydroxy ethyl) piperazine), and the mixture is heated at some 175° C. for approximately two hours, the pressure being maintained at about 50 millimeters of mercury absolute. A 1% aqueous solution of the resulting product (after filtering to remove excess diethanol piperazine) containing a major proportion of the lauric acid monoester of N,N'-diethanol piperazine foams well, and portions added, respectively, to acid and to alkaline solutions dissolve completely in the acid solution and give a turbid solution on the alkaline side.

The foam stability of the product is demonstrated by the pour foam test described by Ross and Miles in their United States Patent No. 2,315,983. Using a solution of about 0.05% of lauric acid monoester of N,N'-diethanol piperazine in distilled water, the pH of the solution is varied, and a series of pour foam tests are run at 115° F. Maximum foam is produced at pH 4 (212 millimeters).

The detersive efficiency of the product is determined by a standardized launderometer test on cotton soil at 115° F. over a thirty-minute period. At a pH of 10.0 a solution containing about 0.10%

of the monoester and about 0.15% of sodium sulphate in water having 300 parts per million of hardness (calculated as calcium carbonate) gives a detersive efficiency of approximately 71% as compared with a 0.55% solution of tallow soap. Under slightly acidic conditions (pH of 5.0), a detersive efficiency of 71% on the same standard is obtained.

Example II

About 53 parts by weight of the methyl esters of coconut oil fatty acids are heated with 174 parts of N,N'-diethanol piperazine at about 200° C. for two to three hours and in the presence of a small amount of sodium hydroxide as a catalyst. After removing the excess diethanol piperazine, the resulting product comprises in large part the coconut oil fatty acid monoesters of diethanol piperazine. This product is found to be an excellent detergent in either acid or alkaline solution.

Example III

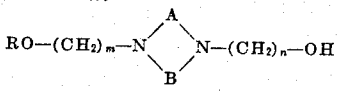
About 174 parts by weight of N,N'-diethanol piperazine is dissolved in 500 parts of xylene, the solution being heated to approximately 135° C. To this hot solution, 11.5 parts of granulated sodium in 100 parts of xylene is slowly added. The reaction mixture is stirred under reflux until all of the sodium has apparently reacted, and about 138 parts of myristyl bromide is then added. Refluxing is continued until the reaction is complete. The crude reaction product is thereafter washed with water to remove sodium bromide and unreacted diethanol piperazine, and the solvent is then removed by distillation and evaporation under reduced pressure. The purified product, comprising principally the mono-myristyl ether of N,N'-diethanol piperazine, foams readily and has fine detersive characteristics in either acid or alkaline aqueous solutions. Both foam and clarity of solution are noted to be better on the acid side.

The properties of the specific compounds of the invention vary to some degree, depending upon the particular starting materials from which they are prepared, but all are surface-active agents having valuable wetting, detersive, emulsifying, softening and foaming characteristics. Besides their unique value as detergents generally, they are especially suitable for use as assistants in the textile and related industries, where they may be employed for softening fabrics, fixing colors, removing grease and oil, penetrating, etc. They may also be advantageously used in the cosmetics industry as emulsifying agents and for stabilizing emulsions.

Although the present invention has been described with reference to particular embodiments and examples, it will be apparent to those skilled in the art that variations and modifications of this invention can be made and that equivalents can be substituted therefor without departing from the principles and true spirit of the invention.

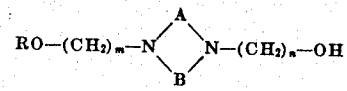
I claim:

1. A piperazine derivative represented by the structural formula:



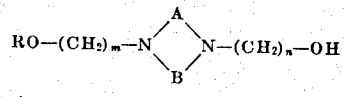
where R is a member of the group consisting of alkyl and acyl radicals having about five to about twenty-three carbon atoms; A and B are members of the group consisting of the ethylene radical and alkyl derivatives thereof wherein any number of hydrogens in the ethylene radical are replaced by alkyl radicals; and m and n are integers of 2 to about 5.

2. A piperazine derivative represented by the structural formula:



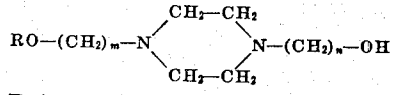
where R is a member of the group consisting of alkyl and acyl radicals having about five to about twenty-three carbon atoms; A and B are members of the group consisting of the ethylene radical and alkyl derivatives thereof wherein any number of hydrogens in the ethylene radical are replaced by alkyl radicals of not more than two carbon atoms; and m and n are integers of 2 to about 5.

3. A piperazine derivative represented by the structural formula:



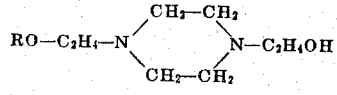
where R is a member of the group consisting of alkyl and acyl radicals having about eight to about eighteen carbon atoms; A and B are members of the group consisting of the ethylene radical and alkyl derivatives thereof wherein any number of hydrogens in the ethylene radical are replaced by alkyl radicals of not more than two carbon atoms; and m and n are integers of 2 to about 5.

4. A piperazine derivative represented by the structural formula:



where R is a member of the group consisting of alkyl and acyl radicals having about five to about twenty-three carbon atoms; and m and n are integers of 2 to about 5.

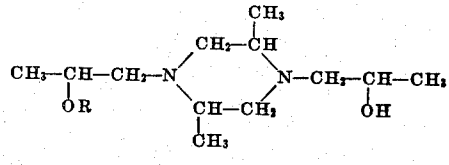
5. A derivative of N,N'-diethanol piperazine represented by the structural formula:



where R is a member of the group consisting of alkyl and acyl radicals having about eight to about eighteen carbon atoms.

6. A surface-active composition comprising the lauric acid monoester of 1,4-di(β-hydroxy ethyl) piperazine.

7. A surface-active composition comprising a derivative of 3,6 - dimethyl - 1,4 - di(β-hydroxy propyl) piperazine, represented by the structural formula:



where R is an acyl radical having about eight to about eighteen carbon atoms.

8. A process for preparing surface-active compositions which comprises reacting an excess of a N,N'-dialkanol piperazine with a member of the group consisting of carboxylic acids and their lower alkyl esters wherein the carboxylic acid radical has about five to about twenty-three car-

bon atoms, and recovering a monoester of the N,N'-dialkanol piperazine.

9. A process for preparing surface-active compositions which comprises heating a N,N'-dialkanol piperazine with a member of the group consisting of carboxylic acids and their lower alkyl esters wherein the carboxylic acid radical has about eight to about eighteen carbon atoms in the proportion of about 2 to about 5 mols of the dialkanol piperazine to 1 mol of the other reactant, removing unreacted dialkanol piperazine, and recovering a monoester of dialkanol piperazine.

10. A process for preparing surface-active compositions which comprises heating N,N'-diethanol piperazine with a fatty acid having about eight to about eighteen carbon atoms per molecule, said diethanol piperazine being present in the proportion of about 2 to about 5 mols per mol of fatty acid, removing unreacted diethanol piperazine, and recovering the fatty acid monoester of N,N'-diethanol piperazine.

11. A process for preparing piperazine derivatives which comprises reacting an excess of a N,N'-dialkanol piperazine with a source of free alkali metal to form a mono-alkoxide, and thereafter reacting an excess of said alkoxide with an alkyl halide to form a monoether of the dialkanol piperazine.

12. A process for preparing piperazine derivatives which comprises heating an excess of a N,N'-dialkanol piperazine with a source of free alkali metal to form a mono-alkoxide, thereafter reacting an excess of said alkoxide with an alkyl halide having about five to about twenty-three carbon atoms per molecule, and recovering the resulting dialkanol piperazine monoether.

13. The process of claim 12 wherein both steps are carried out in an inert organic solvent medium.

14. A process for preparing surface-active compositions which comprises heating a N,N'-dialkanol piperazine with a source of free alkali metal in the proportion of about 2 to about 5 mols of dialkanol piperazine per mol of alkali metal, and thereafter reacting an excess of the resulting monoalkoxide with an alkyl halide having about eight to about eighteen carbon atoms per molecule to form a monoether of the dialkanol piperazine.

15. A process for preparing surface-active compositions which comprises heating in a xylene solution an excess of N,N'-diethanol piperazine with a source of free sodium to form a monosodium alkoxide, thereafter reacting in said xylene solution the monosodium alkoxide with an alkyl bromide having about eight to about eighteen carbon atoms per molecule to form an alkyl monoether of N,N'-diethanol piperazine, removing sodium bromide, unreacted diethanol piperazine and xylene from the reaction mixture, and recovering the monoether therefrom.

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