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AMINO DERIVATIVES AND PROCESS OF PREPARING THEM

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11 Claims. (Cl. 260—127)

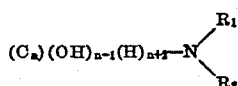
This invention relates to chemical compounds, more particularly chemical compounds which are valuable detergents, and a process for the manufacture thereof. It further relates to a method for increasing the detergent power of treatment liquids, especially such as are employed in the textile and leather industries.

As is well known, various substances, such as, for example, ordinary soaps, that is, the alkali metal salts of the higher fatty acids, are effective in increasing the detergent power and likewise the wetting and penetrating power of neutral aqueous treatment liquids or baths. Such substances are particularly useful in the textile and leather industries. In these industries, however, it may be desirable to treat certain materials with alkaline or acidic baths. In the textile industry, certain types of baths are much more effective for the treatment of specific kinds of fabrics than are others. Thus, in cleaning woolen fibers it is advantageous to use mildly acidic treatment baths, since such fibers may be detrimentally affected by alkalies.

Ordinary soaps are of little value for use in acidic baths, since the alkali metal salts are converted to the insoluble fatty acids. Moreover, heavy metal or alkaline earth metal salts of higher fatty acids are relatively insoluble in aqueous solutions. Hence, where hard water containing salts of magnesium, calcium, and the like is used in aqueous treatment baths, and soaps are added thereto, a relatively large proportion of the soap may be precipitated.

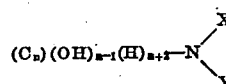
It is an object of the present invention to produce new chemical compounds. A further object is to produce new chemical compounds which are valuable detergent agents, exerting excellent cleansing properties even in the presence of large amounts of acids or salts of heavy or alkaline earth metals. A still further object is the production of new and improved treatment liquids which are especially useful in the textile industry. Another and more specific object is the provision of a method for cleaning woolen fibers and fabrics by means of aqueous acidic treatment baths. A further object is the provision of a new and improved process for producing chemical compounds and treatment liquids of the character above described. Other objects will appear hereinafter.

These objects are accomplished by producing chemical compositions having the formula:



and acid addition products thereof, wherein n is 5 or 6, R_1 is a higher aliphatic radical, having 8 or more carbon atoms, and R_2 is hydrogen or an

aliphatic radical. These products may be obtained in a variety of ways but preferably by combining an alkyl halide with an amine having the formula



in which n is 5 or 6, X is hydrogen, and Y is hydrogen or an aliphatic radical. The resultant product may be further treated with an acid to form an acid addition product (salt) of the amine. Water-soluble compounds of the class described have been found to possess excellent detergent power in aqueous non-alkaline solutions.

While the invention is susceptible of considerable variation and modification in the manner of its practical application, particularly as regards the specific materials used, the proportions thereof and the method of their preparation, the following examples, in which the parts are by weight, will serve to illustrate some of the products falling within the invention and how they may be prepared.

Example I

A mixture consisting of 15 parts of N-glucyl methyl amine, 24 parts of cetyl chloride (obtained from cetyl alcohol, zinc chloride and hydrochloric acid), 12 parts of sodium carbonate, 30 parts of a mixture containing equal proportions of alcohol and benzene, and a trace of potassium iodide was charged into a copper-lined autoclave and maintained at a temperature of about 150° C. for five hours. The reaction mixture was then treated with a large volume of ethyl alcohol, and the inorganic salts which precipitated were removed by filtration. The product comprising substantially N-glucyl-N-methyl cetyl amine was obtained as a cream-colored solid by evaporating the alcoholic filtrate to dryness.

Example II

43.5 parts of the N-glucyl-N-methyl cetyl amine, produced as in Example I, were treated with 10 parts of 37% hydrochloric acid at room temperature, and the resultant addition product was recovered as a resinous solid with a neutral reaction.

Example III

A copper-lined autoclave was charged with a mixture consisting of 15 parts of N-glucyl methyl amine, 30 parts of lauryl bromide (made from lauryl alcohol and hydrobromic acid), 12 parts of sodium carbonate, 30 parts of a 1:1 alcohol-benzene mixture, and a trace of potassium iodide and heated at about 150° C. for about 4 hours. The reaction mixture was dissolved in water and neutralized with hydrochloric acid. It was concentrated to a small volume, a large

volume of ethyl alcohol added, and the inorganic salts removed by filtration. Evaporation of the aqueous alcohol solution yielded the hydrohalide of the N-glucyl-N-methyl lauryl amine as a brownish mass.

Example IV

A reaction mixture consisting of 10 parts of glucyl amine, 15 parts of cetyl chloride, 5 parts of sodium carbonate and a trace of potassium iodide in 50 parts of an aqueous alcohol mixture was heated at about 150° C. for about 5 hours. The reaction mixture was treated with water and neutralized with hydrochloric acid. The insoluble portion which was most probably N:N-di-cetyl-glucyl amine was removed by filtration. The filtrate was concentrated to a small volume, a large volume of ethyl alcohol added, and the inorganic salts were separated by evaporation of the aqueous alcohol solution. A brownish mass consisting principally of the hydrochloride of N-glucyl cetyl amine was obtained.

Example V

About 15 parts of the N-glucyl-N-methyl cetyl amine, obtained as described in Example I, was treated with about 17 parts of 10% sulfuric acid to form the sulfuric acid addition product or salt of N-glucyl-N-methyl cetyl amine.

Example VI

The product of Example I was added to distilled water and the resultant treatment bath was tested by washing woolen felt, oiled as described by Rhodes and Brainard, Journal of Industrial and Engineering Chemistry, 21, 60 (1929), in an ordinary launderometer and judging the degree of cleanliness optically. N-glucyl-N-methyl cetyl amine was found to be as effective a detergent as soap in distilled water at the same concentration.

Example VII

A treatment bath was prepared by adding 25 parts of the product of Example I to 10,000 parts of water containing about 4 parts of calcium chloride, and the resultant liquid was tested for detergent power as described in Example VI. It was found that the N-glucyl-N-methyl cetyl amine was as effective in the calcium chloride solution as in distilled water, whereas soap gave no cleansing whatever.

Example VIII

A treatment liquid was prepared by adding 2.5 parts of N-glucyl-N-methyl cetyl amine to 1000 parts of water containing about 2 parts of sulfuric acid (100%), and the resultant bath was tested as described in Example VI. It was found that the acidic treatment liquid, to which N-glucyl-N-methyl cetyl amine had been added, was as effective as the bath prepared from distilled water, whereas a similar acidic bath containing soap in the same concentration had no cleansing effect.

Example IX

The product of Example II was tested as in Example VI and was found to have good detergent power but to be slightly less effective as a detergent than the product of Example I. Its action was not decreased by the presence of mineral acids or calcium chloride.

According to the general procedure of Examples I to V inclusive, a similar process can be carried out by using in place of a glucyl amine,

any other sugar amine in which the mono-saccharide radical contains 5 or 6 carbon atoms. The amines may be prepared in any suitable manner from mono-saccharides of the ketose or aldose type containing 5 or 6 carbon atoms. Thus, instead of a glucyl amine, that is, an amine prepared from glucose, amines prepared from arabinose, ribose, lyxose, xylose, gulose, mannose, idose, allose, galactose, altrose, talose, d'-fructose and the like may be used. A method of preparing such amines is described in a co-pending application of Robert B. Flint and Paul L. Salzberg, Serial No. 635,045, in which sugars containing 5 or 6 carbon atoms are reacted with a primary or secondary amine and hydrogen under elevated pressure and at an elevated temperature in the presence of a hydrogenating catalyst. Included among the specific products described are N-methyl-glucamine, N-methyl-xylamine, N-butyl-xylamine, N-ethyl-glucamine, N-hydroxy-ethyl-glucamine, N-methyl-galactamine, N-methyl-fructamine and the like. Any of the primary or secondary amines of the character described are applicable for use in the present invention as starting materials.

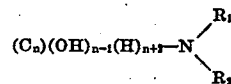
The method of combining the primary or secondary amine with the alkyl halide to form the new secondary or tertiary amines is subject to considerable variation and may vary widely in details of a character well known in the art. The process is preferably carried out by reacting the primary or secondary amine and the alkyl halide in the presence of an acid-binding agent as, for example, sodium carbonate, magnesium oxide, calcium carbonate, potassium carbonate, potassium acetate, sodium acetate, and the like. It is preferable also to effect the reaction in a solvent such as, for example, an alcohol-benzene mixture or an aqueous alcohol solution. In general, any inert solvent may be used. It is further desirable to employ a condensation catalyst such as, for example potassium iodide or sodium iodide.

The proportions of alkyl halide, primary or secondary amine, acid-binding agent, solvent and catalyst may vary within relatively wide limits depending largely upon the results desired. Generally speaking, it is desirable to use at least a sufficient amount of the acid-binding agent to react with all of the hydrogen halide liberated by the reaction.

The temperature may vary within relatively wide limits, but should preferably be sufficiently high to enable the reaction to proceed smoothly and quickly but insufficiently high to cause the formation of decomposition products. In general temperatures within the range of about 100° C. to 200° C. give desirable results.

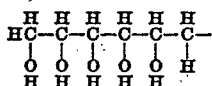
In the formation of the acid addition products (salts) of the new secondary and tertiary amines, the secondary and tertiary amines may be combined with any suitable acids, as for example, hydrochloric, sulfuric, phosphoric, acetic and formic.

In general, the products which are preferably employed as detergents are those which have the formula



and acid addition products thereof, wherein n is 5 or 6, R_1 is a radical having 8 or more carbon atoms (e. g., capryl, lauryl, myristyl, cetyl, stearyl ($-C_{18}H_{37}$), cerotyl, oleyl ($-C_{18}H_{35}$), erucyl, linoleyl, linolenyl, ricinoleyl, and the like), and R_2 is hydrogen or an aliphatic radical such

that the compound is water-soluble (e. g., methyl, ethyl, propyl, butyl, allyl, hydroxy ethyl, dihydroxy propyl, and substituted aliphatic radicals containing as substituents such groups as the sulfate or sulfonic acid groups). Very highly advantageous results have been obtained in the use of compounds having the foregoing general formula, in which the poly-hydroxy aliphatic radical is a normal radical having 6 carbon atoms, and the following general formula.



(generally referred to as the glucyl group). It is further desirable that the compound be one in which, according to the general formula, R_1 is a straight chain or normal alkyl radical having 8 or more carbon atoms. For the application of the products as detergents in aqueous baths, it is preferable that R_2 of the general formula be a lower aliphatic radical, preferably an alkyl radical containing not more than 4 carbon atoms (cf. Examples I, II and III) or a substituted alkyl radical containing not more than 4 carbon atoms, as for example, N-cetyl-N-glucyl ethanolamine, or N-cetyl-N-glucyl-2:3-propane diol-1-amine.

The new class of compounds described may be used in cleansing materials of all kinds and, as previously indicated, are particularly valuable for use in acidic aqueous solutions or aqueous solutions containing metallic salts in which ordinary soaps are ineffective. While the invention is not limited to any theory, it is believed that the excellent properties of the products and the advantages they possess over ordinary soaps can be traced to the fact that these new products contain no carboxyl groups on the long chain alkyl group, such as is the case with ordinary soaps. Apparently, another reason why these products have given such good results lies in the fact that they contain the amino group, the acid salts of which have a neutral or slightly acid reaction rather than a slight alkaline reaction as in the case of soaps. Because of their great effective cleansing power in acidic solutions, the new products are particularly valuable in cleaning silk, wool and other materials which are detrimentally affected by alkaline solutions, but which may be cleaned in acidic solutions.

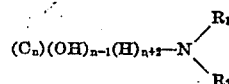
The treatment baths prepared in accordance with the invention may contain, in addition to the products herein described, other compounds which are surface active or possess cleaning, wetting, penetrating or dispersing properties. As examples of additional materials possessing washing, cleansing, emulsifying and wetting power may be mentioned Turkey red oils, ordinary soaps (in neutral solutions), aromatic sulfonic acid (such as alkylated naphthalene sulfonic acids), mineral oil sulfonic acids, sulfonated derivatives of abietic acid, higher alkyl sulfuric esters, saponin, and aliphatic and aromatic acid amides, such as sodium taurocholate or sodium salts of analogous acid amides. The products of the invention may also be employed in combination with neutral or acid salts, such as, for example, sodium sulfate, sodium chloride, sodium bisulfate, sodium bicarbonate, and similar compounds of the other alkali metals or of ammonium. In a like manner, they may be employed with magnesium sulfate, magnesium chloride, magnesium acetate, zinc chloride and zinc acetate. Other additional materials with which the

products of the invention may be combined are bleaching and disinfectant agents, such as persulfates, percarbonates and perborates; filling materials such as talc, marble-dust and starch; adsorbing materials such as suitable clays, e. g., fuller's earth; protective colloids or dispersing agents such as gum tragacanth, gall acids and their derivatives, agar-agar, glue, methyl cellulose, sulfite cellulose lyes, calcium saccharate, albumin, sodium cellulose glycolate, gelatin, natural and artificial resins, derivatives of cholesterol, phosphatides, gelloes, natural and artificial waxes, wool waxes, solvent and softening agents, organic bases and their salts such as alkylamine salts and quaternary ammonium compounds, inorganic colloids; and scouring materials such as kieselsguhr, powdered pumice, sulfur, flour, china clay, salt and the like. Desirable results for many purposes may also be obtained by employing the secondary or tertiary amines or salts thereof, produced as herein described, in combination with the various acyclic, mono-cyclic or complex cyclic terpenes or derivatives thereof such as, for example, limonene, dipentene, terpinolene, terpinene, phellandrene, sylvestrene, pinene, borylene, sabinene and their alcoholic, ketonic and aldehydic derivatives. It will be apparent, furthermore, that our new products may be combined with a wide variety of other additional materials which possess washing, cleansing, emulsifying, wetting, dispersing, adsorbing, lathering, bleaching, germicidal and bactericidal powers. They may likewise have incorporated therewith artificial or natural perfuming substances, many of which in themselves possess detergent properties of some value.

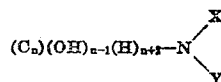
As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that we do not limit ourselves to the specific embodiments thereof except as defined in the following claims.

We claim:

1. In a process of producing chemical compounds having the following formula

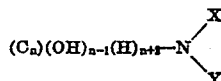


wherein n is 5 or 6, R_1 is an aliphatic radical having an open chain of at least eight carbon atoms, and R_2 is hydrogen or an aliphatic radical, the step which comprises reacting an amine having the formula.



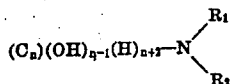
in which n is 5 or 6, X is hydrogen, and Y is hydrogen or an aliphatic radical, with an aliphatic halide having an open chain of at least eight carbon atoms.

2. In a process of producing new chemical compounds, the step which comprises reacting an amine having the formula

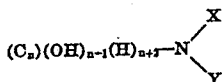


in which n is 5 or 6, X is hydrogen, and Y is hydrogen or an aliphatic radical, with an alkyl halide having at least eight carbon atoms, and further combining the resultant product with an acid.

3. In a process of producing chemical compounds having the following formula

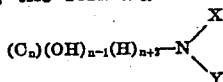


wherein n is 5 or 6, R_1 is an alkyl radical having at least eight carbon atoms, and R_2 is hydrogen or an aliphatic radical such that the compound is water-soluble, the step which comprises reacting an amine having the formula



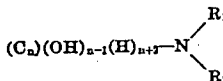
in which n is 5 or 6, X is hydrogen, and Y is hydrogen or a lower aliphatic radical, with an alkyl halide having at least eight carbon atoms.

4. In a process of producing new chemical compounds, the step which comprises reacting an amine having the formula



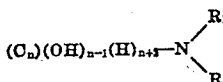
in which n is 5 or 6, X is hydrogen, and Y is hydrogen or a lower aliphatic radical, with an aliphatic halide having at least eight carbon atoms, and further combining the resultant product with an acid.

5. Compounds of the group consisting of compounds having the following formula



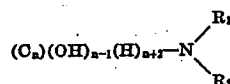
and the acid addition products thereof, in which n is 5 or 6, R_1 is an aliphatic radical having an open chain of at least eight carbon atoms, and R_2 is hydrogen or an aliphatic radical.

6. Compounds of the group consisting of compounds having the following formula



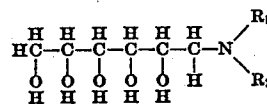
and the acid addition products thereof, in which n is 5 or 6, R_1 is an alkyl radical having at least eight carbon atoms, and R_2 is hydrogen or an aliphatic radical such that the compound is water-soluble.

7. Compounds of the group consisting of compounds having the following formula



and the acid addition products thereof, in which n is 5 or 6, R_1 is an alkyl radical having at least eight carbon atoms, and R_2 is hydrogen, an alkyl radical having not more than four carbon atoms, or a hydroxy alkyl radical having not more than four carbon atoms.

8. A compound having the following general formula:



wherein R_1 is a straight chain alkyl radical having at least eight carbon atoms, and R_2 is an alkyl radical having not more than four carbon atoms.

9. N-glucyl-N-methyl cetyl amine.

10. A tertiary aliphatic glucamine in which one of the aliphatic groups attached to the nitrogen atom is a higher aliphatic hydrocarbon radical containing eight to eighteen carbon atoms inclusive, and the other is a lower aliphatic hydrocarbon radical.

11. An N:N-dialkyl-glucamine in which one of the alkyl radicals is a higher alkyl radical containing at least eight carbon atoms and the other is a lower alkyl radical having not more than four carbon atoms.

WILLIAM S. CALCOTT.
RICHARD G. CLARKSON.

Certificate of Correction

October 8, 1935.

Patent No. 2,016,956.

WILLIAM STANSFIELD CALCOTT ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 33, for "oiled" read *soiled*; and page 4, first column, line 45, for "R" read *R₂*; 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 17th day of December, 1935.

[Seal]

LESLIE FRAZER,
Acting Commissioner of Patents.