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2,880,219

PRODUCTION OF N-ACYL TAURIDES

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This invention relates to improvements in the produc-tion of amide-type anionic surface active sulfonates, more particularly N-higher acyl taurine salts.

The reaction of higher fatty acids, fatty acid chlorides and fatty acid esters with 2-aminoalkane sulfonic acids (taurines) and the alkali metal salts thereof to yield anionic surface active materials useful as wetting, cleans-ing, softening and dispersing agents is well known. In U.S. Patent 1,932,180, several processes are described for the preparation of such surface active materials, but the only process which has up to the present been em-ployed commercially is that wherein an acid chloride is reacted in aqueous medium with a 2-aminoalkane sulfonic acid in the presence of an acid neutralizer such as caustic soda. The preparation of the acid chloride employed as an intermediate is not only hazardous but time-consuming and costly, since it employs phosphorus trichloride and requires at least one additional step. In addition, when the acid chloride is treated with a taurine or a taurine salt, an anionic surface active agent is ob-tained containing a considerable quantity of salt, e.g. sodium chloride, which is highly undesirable when said surface active agent is employed in detergent and built soap formulations. The presence of sodium chloride in such formulations imparts thereto an unduly high hy-groscopicity and its removal therefrom is very expensive.

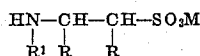
In order to overcome these shortcomings, it has been heretofore proposed to obtain a salt-free product by condensing presumably one mole of a free fatty acid with one mole of a taurine salt, but no additional advantage was found over the acid chloride method. As a matter of fact, it was found that considerable taurine decom-position occurred, a separation of ammonia or methyl-amine from the taurine was unavoidable, and the yield and quality of the products (odoriferous and discolored) were not as had been hoped for.

It is an object of this invention to provide a new and improved process for the production of high quality salt-free N-higher acyl taurine salts. Other objects and advantages will appear as the description proceeds.

The attainment of the above objects is made possible by the instant invention which comprises heating prefer-ably in the absence of a solvent at least 1.2 moles of an acylating agent selected from the group consisting

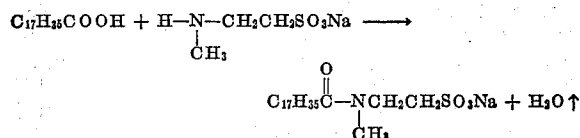
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of aliphatic and alicyclic carboxylic acids of at least 8 carbon atoms with one mole of a taurine salt of the formula



wherein R¹ is selected from the group consisting of H and hydrocarbon radicals of 1 to 20 carbon atoms, R is selected from the group consisting of H and lower alkyl, and M is a salt-forming radical selected from the group consisting of alkali metals and alkaline earth metals, in an inert atmosphere at a temperature of about 200 to 320° C. while removing the water formed during the reaction.

The reaction which takes place may be illustrated by the following equation wherein stearic acid is employed as the acylating agent and the sodium salt of N-methyl taurine as the taurine salt:



The process of this invention eliminates the necessity for first preparing the fatty acid chloride as a step pre-liminary to its subsequent reaction with the taurine, and yields a salt-free product. It has also been found that this process requires a much shorter reaction time, and makes possible the attainment of excellent yields of a product in the form of a solid instead of a slurry or dilute solution. The product thus obtained is, further, of excellent quality relative to purity and lack of dis-coloration and odor. While the exact reason for the im-proved results is not known, it is thought that the excess free carboxylic acid in the reaction mixture stabilizes the taurine salt, minimizing its decomposition, increas-ing yields and reducing the formation of odoriferous and discolored by-products. In most cases, the use of the ex-cess carboxylic acid acylating agent simultaneously ef-fects a highly desirable reduction in the viscosity of the reaction mixtures.

Inasmuch as an excess of carboxylic acid is employed, the final product will inherently contain some free car-boxylic acid which may if desired be removed by com-mon extraction or superheated steam distillation pro-cedures. As a further feature of this invention, it has been found that such product may be treated with an inorganic or organic base such as the alkali metals or amines such as triethanolamine or the like to saponify the carboxylic acid and produce its soap in situ. The resulting mixture of soap and N-higher acyl tauride may be employed either directly or after addition of other ingredients in the production of detergent compositions

in liquid or solid form. The use of such compositions for the formation of solid detergent compositions in particulate or bar form is exceedingly advantageous. These compositions may also be employed in the production of skin creams, lotions, salves, and in food products as foaming agents in addition to other uses wherein the presence of a mineral acid salt of an alkali metal, alkaline earth metal or ammonia or amine is undesirable.

The duration of the reaction is generally inversely proportional to the temperature employed, the rate of reaction increasing as the temperature increases. However, at higher temperatures, there is a tendency for much of the taurine salt to decompose, while at unduly low temperatures such as below 180° C., the reaction is too slow for practical purposes. The temperature employed in any particular instance will be limited by the acid employed, particularly its molecular weight, degree of unsaturation, and reactivity. Thus, lower temperatures may be employed where lauric acid is the acylating agent than where stearic acid is employed. The maximum temperature is defined by the relationship between taurine decomposition (darkening, odor, etc.) and yield. In general while 200 to 320° C. define the extreme limits of operation, a range of 200 to 260° C. will be found to yield excellent results in most instances. Within this range, temperatures of about 220 to 240° C. have been found to yield optimum results when employing the most usual reactants. At temperatures within the aforementioned ranges, the reaction is usually complete in about 10 hours, although the duration required for completion of the reaction may range in any particular instance from about ½ to 15 hours.

In order to prevent excessive discoloration of the product, especially in the case of oleic acid and other acids containing unsaturated components, it is necessary to exclude air from contact with the reaction mixture. Accordingly, an inert atmosphere such as nitrogen or vacuum should be maintained over the mixture during the reaction. When employing reduced pressures, 10 to 200 mm. mercury absolute pressures are preferred. Pressures less than 10 mm. mercury may be employed if the acid is not too volatile. The extent of vacuum will therefore depend on the volatility of the acid and the reaction temperature. If the inert atmosphere is maintained by use of an inert gas such as nitrogen, the gas is preferably passed in continuous manner over the reaction mixture to assist in removal of the water formed during the reaction.

The reaction may under certain circumstances be conducted in a suitable high boiling solvent such as chlorobenzene, dichlorobenzene, nitrobenzene, chlorinated paraffins, tetrachloroethylene, trichloroethane, ethylene dichloride, propylene dichloride, toluene, xylene, alkyl benzenes, alkyl naphthalenes and the like. The use of such solvents, however, generally has the disadvantages of higher cost due to the initial cost of the solvent itself, and the expense of solvent recovery and replacement of losses. Further, the reaction rate in most cases is detrimentally affected by the insolubility of most sulfonic acid salts in these solvents.

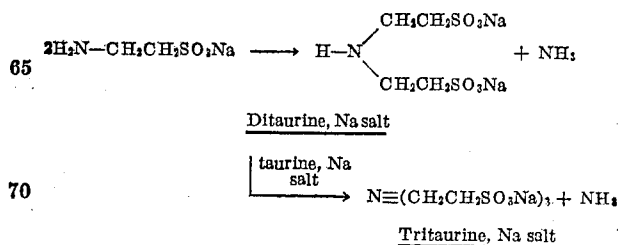
The use of at least 1.2 moles of the carboxylic acid acylating agent for each mole of taurine salt is essential to the attainment of the desired results in carrying out the process of this invention. In general, proportions of about 1.5 to 2 moles of the acid per mole of taurine salt have been found sufficient in most instances. If desired, the reaction mixture may contain a larger excess of the acid, such as up to 6 to 10 moles or more per mole of taurine salt, where a product containing a higher free carboxylic acid content is desired. Treatment of such a product with caustic soda or potash, or an organic base, to saponify the free carboxylic acid would then yield in situ a detergent mixture containing soap and N-higher acyl taurine in any desired proportions. However, any increase in the amount of excess carboxylic acid em-

ployed in the reaction mixture, while to some extent aiding in stabilizing the taurine salt, at the same time tends to increase the cost of the product due to greater heat requirements and increased carboxylic acid losses.

As carboxylic acid acylating agents of at least 8 carbon atoms which may be employed in the instant invention, those preferred are of the aliphatic or alicyclic type although aromatic acids may be used. Particularly preferred are the higher fatty acids. As representative of higher aliphatic and alicyclic carboxylic acids operative in the instant invention, there may be mentioned caprylic acid, pelargonic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, ricinoleic acid, linoleic acid, undecylenic acid, tall oil acid, acid mixtures from various natural plant and animal oils such as olive, tallow, castor, peanut, coconut, soybean, cotton seed, ucahuba, linseed, cod, herring, menhaden, neat's-foot, sperm, palm, corn, butter, babassu, kapok, hempseed, mustard, rubberseed, rape, safflower, sesame, acids from the oxidation fractions of petroleum, and from oxo-aldehydes, naphthenic acids, abietic acids, and the hydrogenated derivatives of such acids and acid mixtures. Other acids which may be employed include alkyl benzoic acids such as dodecyl benzoic acid, nonyl benzoic acid, octyl benzoic acid, alkyl naphthoic acids such as nonyl naphthoic acid, and the like.

In the formula given above for the taurine salts operative in the instant invention, R may represent hydrogen, methyl, ethyl, isopropyl or the like; R¹ may represent either hydrogen or a hydrocarbon radical of 1 to 20 carbon atoms such as methyl, ethyl, isopropyl, butyl, heptyl, isooctyl, dodecyl, pentadecyl, stearyl, abietinyl, oleyl, cyclohexyl, phenyl, or the like, and M may represent an alkali metal such as sodium, potassium, or lithium, an alkaline earth metal such as calcium, magnesium, barium, or the like, or a tertiary or hindered amine such as dicyclohexyl amine, tributyl amine, trioctyl amine, triethanolamine, N,N-diphenyl methylamine, N,N-dimethyl octadecylamine, tetrahydroxyethylene diamine, or the like. Thus, by way of example only, the following specific 2-aminoalkane sulfonic acids may be employed in the form of their salts with a salt-forming group having one of the values given above for M: taurine, ditaurine, N-methyl taurine, N-methyl ditaurine, N-ethyl taurine, N-propyl taurine, N-isopropyl taurine, N-butyl taurine, N-isobutyl taurine, N-tertiary butyl taurine, N-amyl taurine, N-hexyl taurine, N-cyclohexyl taurine, N-phenyl taurine, N-methyl-2-methyl taurine, N-methyl-2-ethyl taurine, N-methyl-1,2-dimethyl taurine, N-octyl taurine, N-dodecyl taurine, N-stearyl taurine, and the like.

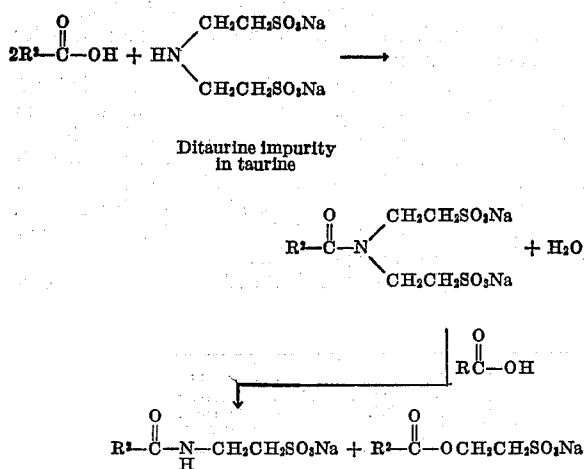
The taurine salts are preferably employed in the form of dried powders, but they may also be employed as aqueous solutions since the water is removed during the reaction. In addition to lowering the viscosity of the reaction mixture in many cases, the carboxylic acid as noted above aids in stabilizing the taurine salts. In the absence of carboxylic acid, heating taurines at high temperature tends to cause evolution of an amine or ammonia to form ditaurines or tritaurines:



In view of the high yields obtained by the process of the instant invention, the following reactions are also

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believed to occur with ditaurine salt in addition to the main reaction of the carboxylic acid with the taurine salt:



Similarly, tritaurine could react to form one molecule of amide anionic, two molecules of ester anionic and one molecule of water.

The products obtained by this process are valuable anionic surface active agents and have many varied commercial uses. The most conspicuous property of these products is their great activity at surfaces and interfaces which promotes their use in a large field of the technical arts. For instance, they can be used as wetting, frothing, or washing agents in the treating and processing of textiles; for converting liquid or solid substances which per se are insoluble in water (such as hydrocarbons, higher alcohols, oils, fats, waxes, and resins) into creamy emulsions, clear solutions or fine stable dispersions; for carbonizing, for dyeing; for the pasting of dyestuffs; for fulling, sizing, impregnating and bleaching treatments; as cleansing agents in hard water; in tanning and mordanting processes; for dyeing acetate with insoluble dyestuffs; for the preparation of dyestuffs in finely divided form; for dispersible dye powders; for producing foam for fire extinguishers; as a means for improving the absorptive power of fibrous bodies; and as an aid in softening hides and skins.

In addition, these products are valuable emulsifiers, wetting agents and dispersants for agricultural compositions containing insecticides, fungicides, bactericides, or other pesticidal substances, herbicides, plant growth regulators, fertilizers and/or soil conditioners, or the like, or mixtures thereof, in solid or liquid form.

These products are also valuable for use as additives to petroleum products, such as fuel oils, lubricating oils, greases, and as additives to the water or brine used for oil recovery from oil-bearing strata by flooding techniques.

Other valuable uses are in metal cleaning compositions; dry cleaning compositions; additives for rubber latices; foam inhibitors for synthetic rubber latex emulsions; froth flotation agents; additives for road building materials; as air entraining agents for concrete or cement; additives to asphalt compositions; plasticizers and modifiers for vinyl plastics, alkyl resins, phenolformaldehyde resins and other types of polymeric-type plastic materials; for incorporation into adhesives, paint, linoleum; for use in bonding agents used in various insulating and building materials; as refining aids in wood digesters to prepare pulp, as additives to pulp slurries in beating operations to prevent foaming and also to aid the beating operation in paper-making; and as aids in the preparation of viscose dope.

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The products are also useful as emulsifiers for emulsion polymerization, as mercerizing assistants, wetting agents, rewetting agents, dispersing agents, detergents, penetrating agents, softening agents, lime soaps dispersants, dishwashing agents, anti-static agents, disinfectants, insecticides, moth-proofing agents, bactericides, fungicides and biocides. They are valuable as anti-fogging agents for use on glass and other surfaces where the accumulation of an aqueous fog is detrimental. They are useful in the rayon industry as additives to the dope or to the spinning bath and as aids in clarifying viscose rayon. They are of value in hydraulic fluids to improve viscosity characteristics.

The products are especially useful in breaking petroleum emulsions. They may be used to break emulsions of crude petroleum and salt water as obtained from oil wells, or to prevent water-in-oil emulsions resulting from acidization of oil wells by introducing the agent into the well, or to break or prevent emulsions which would result from a water flooding process for recovering oil from oil-bearing strata. They may also be used to break emulsions encountered in a petroleum refining process.

They are useful as corrosion inhibitors, as rust inhibitors, in the protection of metals especially ferrous metals, in acid pickling baths, in acid cleaning compositions, and in electro-plating baths. Other valuable uses are as solvents or in solvent compositions, as cleaning agents for paint brushes, as additives for paints, lacquers, and varnishes; as lubricants, as greases and stuffing agents.

The products may be employed in the preparation of skin creams, lotions, salves and other cosmetic preparations such as home hair-wave sets, shaving creams, shampoos, toothpastes, etc. They may also be employed in food products as foaming agents, emulsifying agents, and softening agents.

They may be used as aids in conditioning of soil; as aids in the grinding, milling or cutting of metals either in aqueous solution, emulsions or in oils; as aids in the fixing of dyes to leather and natural or synthetic fibers; as aids in level dyeing of fibers; as aids in stimulating plant growth; as an additive to cement to improve the strength of the resulting concrete or to improve its hardening time or its resistance to freezing and thawing or scaling; and as curing aids and penetrants for use in fertilizer.

The following examples are illustrative of certain preferred embodiments of the instant invention and are not to be regarded as limitative. Parts are by weight unless otherwise indicated.

EXAMPLE 1

In a 250 cc. 3-neck flask equipped with a mechanical stirrer, stopper and exit to aspirator vacuum, were placed 11.8 g. dry sodium salt of N-methyl taurine (85% purity; .062 mole), and 35.2 g. stearic acid (.124 mole). The flask was then placed in an oil bath which was thermostatically controlled at 220° C. and held there for 10 hours under aspirator vacuum (approximately 15 to 20 mm. of mercury pressure), while the mixture was stirred.

The product (molten at 220° C.) was cooled and the resultant brittle waxy tan mass chipped out. This product had the odor of stearic acid, but no objectionable amine odor was noticed.

Wgt.=45.5 g. Direct analysis for product indicated an activity of 54% or yield of 93% based on N-methyl taurine.

The product was an excellent cotton detergent when mixed with sodium tripolyphosphate, soda ash, and the reaction product of Example 8 below. This mixture was effective in hard water and no lime soap curd was produced.

Analysis of product:	Percent
N-stearoyl-N-methyl taurine, sodium salt	¹ 54
Stearic acid	² 36.2
N-methyl taurine, sodium salt	³ 1.5
Inert extractable material	⁴ 3.0
Other (by difference)	⁵ 5.3

¹ Analysis by methylene blue method described in Nature 160, 759 (1947) and Trans. Faraday Soc. 44, 226-239 (1948).

² By extraction with petroleum ether and titration of petroleum ether residue.

³ By titration of solution which had been extracted with petroleum ether to remove fatty acid.

⁴ From weight of petroleum ether residue subtracting stearic acid.⁵ May contain stearic acid anhydride, high molecular weight ketones, etc.

⁵ Includes moisture and impurities present in technical N-methyl taurine.

The following table records the results of experiments carried out in the same manner as Example 1 above:

Table

Ex.	Acylating Agent	Taurine Used	Mole Ratio of Acylating Agent to Taurine	Temp., °C.	Time, hours	Yield Based on Taurine, percent
2	Stearic acid	N-methyl taurine, Na salt	1.5:1	220	10	90
3	do	do	1:1	220	10	62
4	do	do	2:1	240	10	92.5
5	do	do	2:1	180	10	35
6	do	do	2:1	260	2	87
7	Lauric acid	do	3:1	200	10	91.75
8	do	do	2:1	200	10	90
9	Oleic acid	Taurine, Na salt	2:1	220	10	91
10	do	do	6:1	220	10	92.6
11	Palmitic acid	N-methyl taurine, Na salt	2:1	220	10	90
12	Stearic acid	N-butyl taurine, Na salt	2:1	220	10	90
13	Oleic Acid, Na salt	N-methyl taurine, Na salt	1:1	220	10	2.8
14	do	do	2:1	220	10	8
15	Stearic acid+0.5 moles NaOH per 2 moles acid	do	² 2:1	220	10	92.8
16	Stearic acid+1.5 moles NaOH per 2 moles acid	do	³ 2:1	220	10	61.3
17	Stearic acid	Taurine, inner salt	1.5:1	220	10	10
18	Tall oil	N-methyl taurine, Na salt	2:1	220	10	73
19	Distilled tall oil	do	2:1	220	10	87
20	Naphthenic acid fraction (molecular weight=330-350)	do	2:1	220	10	81
21 ¹	Stearic acid	do	2:1	220	10	94

¹ In this example the reaction was carried out at atmospheric pressure under nitrogen which was passed through the flask in a slow stream during the heating period. ² 1.5 free acid:1. ³ 0.5 free acid:1.

Examples 3, 13 and 16 are included in the table to illustrate the importance of employing an excess of the carboxylic acid acylating agent in the instant process. Example 5 is included to illustrate the importance of operating within the range of temperature disclosed hereinabove. Examples 13, 14 and 16 additionally show the importance of employing the acylating agent in the form of its free carboxylic acid, in excess of the amount of taurine salt, instead of in the form of its sodium salt. Examples 15 and 16 show that the sodium salt of the fatty acid does not interfere with the reaction as long as there remains the required amount of excess free carboxylic acid in the reaction mixture. Example 17 is included to illustrate the importance in employing the taurine in the form of its salt instead of in the form of the free sulfonic acid inner salt. The product of Example 8 was converted to an excellent liquid shampoo by saponifying the excess lauric acid with triethanolamine. The product of Example 9 was a good cotton detergent when the excess oleic acid was saponified with caustic. It foamed well in a Maytag agitator type washing machine. It also formed a soap-detergent bar with excellent lathering and lime soap dispersing properties.

EXAMPLE 22

Using equipment described in Example 1, 92 g. (0.324 mole) of oleic acid was mixed with 30 g. (0.162 mole) of 87% N-methyl taurine, sodium salt. The mixture was stirred and heated in an oil bath at 220° C. for 4 hours. Moderate foaming was observed during the first part of the heating period due to the evolution of water. The opaque slurry gradually changed to a clear, yellow melt. The melt was cooled to 95° C. and the excess oleic acid was neutralized by adding a solution of 6.5 g.

(0.162 mole) sodium hydroxide in a small amount of water. The pH was brought to 9¹ by adding a small additional amount of caustic. The paste was then dried in a vacuum oven to a light yellow solid weighing 113 g. Analysis showed that this product contained 43% of N-oleoyl-N-methyl taurine, sodium salt. The remainder was mainly sodium oleate.

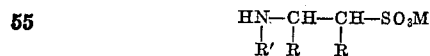
The product was then run through a meat grinder 5 times and processed in a soap die to form a small soap bar containing the taurine derivative. This bar showed good lathering and cleaning action even when used with hard water. The dirty wash water did not leave a soap and scum on the sides of the wash basin but rinsed clean. This was due to the powerful lime soap dispersing action of the N-oleoyl-N-methyl taurine.

This invention has been disclosed with respect to cer-

tain preferred embodiments, and various modifications and variations thereof will become obvious to the person skilled in the art. It is to be understood that such modifications and variations are included within the spirit and purview of this application and the scope of the appended claims.

We claim:

1. A process comprising heating at least 1.2 moles of an acylating agent selected from the group consisting of free aliphatic and alicyclic carboxylic acids of at least 8 carbon atoms with one mole of a taurine salt of the formula



wherein R¹ is selected from the group consisting of H and hydrocarbon radicals of 1 to 20 carbon atoms, R is selected from the group consisting of H and lower alkyl, and M is a salt-forming radical selected from the group consisting of alkali metals and alkaline earth metals, in an inert atmosphere at a temperature of about 200 to 320° C. while removing the water formed during the reaction.

2. A process as defined in claim 1 wherein the acylating agent is a higher fatty acid.
3. A process as defined in claim 2 wherein the acylating agent is stearic acid.
4. A process as defined in claim 2 wherein the acylating agent is palmitic acid.
5. A process as defined in claim 2 wherein the acylating agent is oleic acid.

¹ The pH was measured on a 1% aqueous solution of a small portion of the reaction mixture.

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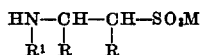
6. A process as defined in claim 2 wherein the acylating agent is lauric acid.

7. A process as defined in claim 2 wherein the acylating agent is tallow acid.

8. A process as defined in claim 1 wherein the taurine salt is the sodium salt of taurine.

9. A process as defined in claim 1 wherein the taurine salt is the sodium salt of N-methyl taurine.

10. A process comprising heating at least 1.2 moles of an acylating agent selected from the group consisting of free aliphatic and alicyclic carboxylic acids of at least 8 carbon atoms with one mole of a taurine salt of the formula



wherein R^1 is selected from the group consisting of H and hydrocarbon radicals of 1 to 20 carbon atoms, R is selected from the group consisting of H and lower alkyl, and M is a salt-forming radical selected from the group consisting of alkali metals and alkaline earth metals, in an inert atmosphere at a temperature of about 200 to 320° C. while removing the water formed during the reaction, and then saponifying the excess acylating agent in the reaction product in situ.

11. A process as defined in claim 10 wherein the acylating agent is a higher fatty acid.

12. A process as defined in claim 11 wherein the acylating agent is stearic acid.

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13. A process as defined in claim 11 wherein the acylating agent is palmitic acid.

14. A process as defined in claim 11 wherein the acylating agent is oleic acid.

15. A process as defined in claim 11 wherein the acylating agent is lauric acid.

16. A process as defined in claim 11 wherein the acylating agent is tallow acid.

17. A process as defined in claim 10 wherein the taurine salt is the sodium salt of taurine.

18. A process as defined in claim 10 wherein the taurine salt is the sodium salt of N-methyl taurine.

19. A process as defined in claim 10 wherein the excess acylating agent is saponified with sodium hydroxide.

20. A process as defined in claim 10 wherein the excess acylating agent is saponified with potassium hydroxide.

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