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LIQUID SYNTHETIC DETERGENT

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 No Drawing. Filed Oct. 3, 1966, Ser. No. 583,920
 Int. Cl. C11d 1/18, 1/20, 7/08

U.S. Cl. 252—152

6 Claims

ABSTRACT OF THE DISCLOSURE

A process for the production of essentially neutral, non-aqueous, detergent concentrates is set forth. The concentrates are produced by reacting a cosmetic-type acid with an alkylol amine in the presence of a fatty amide and an alkyl aryl sulfonate.

This invention relates to fluid detergent concentrates which are essentially non-aqueous in character, possessing substantially a neutral pH and consisting essentially of 100% solids. More specifically, the fluid detergent concentrates of this invention are neutral blends of fatty alkylolamides and alkylolammonium alkyl aryl sulfonates which may be encapsulated in plasticized gelatin capsules without swelling or otherwise rendering the encapsulating material useless.

The preparation of aqueous or highly alkaline blends of fatty alkylolamides and alkylolammonium alkyl aryl sulfonates is well-known in the detergent industry. Generally speaking, in one prior art method of preparing such blends, equal parts by weight of an alkylolamine having at least one acylatable hydrogen atom in the amino group and a fatty acylating substance are allowed to condense for a few hours under a high vacuum with agitation. Normally, the acylating substance is immiscible with the alkylolamine. During the reaction period the emulsion originally formed when the mutually insoluble alkylolamine and acylating agent are blended together eventually breaks and the mixture becomes a homogeneous fluid. In the prior art processes the vacuum is not essential to the production of material, but it helps in keeping color bodies and other undesirable extraneous material at a low level.

The condensation material thus prepared by the reaction of the excess alkylolamine and acylating substance is then combined with an alkyl aryl sulfonic acid. The excess alkylolamine which was not consumed in the preparation of the condensation product then reacts with the sulfonic acid to form the alkylolammonium sulfonate which is the anionic portion of the detergent. In the prior art processes, the reaction of the sulfonic acid consumes about half of the excess of the alkylolamine present adventitiously from the initial condensation reaction.

At this point, since there is an excess of alkylolamine present, the pH of aqueous solutions of the detergent concentrate is in the neighborhood of about 8-10. Since the pH of the human epithelial tissue is usually in the neighborhood of about 5 to about 6, use of the blends of fatty alkylolamides and alkylolammonium alkyl aryl sulfonates in shampoos and other cleaning preparations which come in contact with the skin can cause dermatitis in certain individuals. It, therefore, is desirable to have a material exhibiting a pH at or near neutrality. Further, the material must not set up into a pasty semi-solid. It can also be mentioned at this time that lower pH values are necessary to prevent "tanning" of the gelatin capsules used to encase the detergent concentrate.

The fluid detergent concentrate must possess a neutral pH, and cannot contain, generally speaking, more than

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about 10% water if they are to be used in gelatin encapsulating systems. More specifically, the water content should be less than about 5% so as to prevent swelling of the gelatin capsule. As discussed above, it is the current practice in the trade to prepare materials having an excess of the alkylolamine which are, of necessity, alkaline in nature. If at this point, in order to neutralize the composition, one adds sufficient sulfonic acid to neutralize the excess alkylolamine present in the fatty alkylolamide-alkylolammonium alkyl aryl sulfonate blend, the material sets up into an unworkable pasty solid having little commercial utility.

On the other hand, if alkylolamine salts of the sulfonic acid containing excess amine are prepared and neutralized with mineral acids so that the formulation is neutral, the resulting material is a solid opaque paste and is totally useless as far as encapsulation or other use in concerned. When water was added to this solid opaque paste, a water content up to 10% (the maximum tolerated in gelatin encapsulation) had little, if any, effect on the product. Increase in the concentration of water up to about 50% of the formulation appeared to start to thin out the composition; however, this concentration of water is greatly in excess of that which could be tolerated by gelatin capsules.

Accordingly, it is an object of this invention to provide a method whereby fluid detergent concentrates possessing a neutral pH may be produced.

It is another object of this invention to provide neutral blends of fatty alkylolamides and alkylolammonium alkyl aryl sulfonates having an essentially neutral pH.

Another object of this invention is the manufacture of non-aqueous, essentially neutral pH, fluid detergent concentrate suitable for gelatin encapsulation.

Additional objects, if not specifically set forth herein, will be readily apparent to those skilled in the art from the detailed description of the invention which follows.

In general, it has now been discovered that unique, fluid, 100% active detergent concentrates possessing essentially a neutral pH can be prepared if the excess alkylolamine is neutralized with a member of a specific class of acids. As discussed above, additional alkyl aryl sulfonic acid cannot be added since it results in the formation of an unworkable pasty solid. However, the fatty alkylolamide-alkylolammonium alkyl aryl sulfonate blends can be rendered neutral and as well as remaining fluid by combining therewith a cosmetic type acid.

In general, the novel detergent composition of this invention comprises the condensation product of an alkylolamine having at least one acylatable hydrogen atom in the amino group and a fatty acylating substance having an average of between about 12 and about 20 carbons in the fatty acid group, an alkylolammonium alkyl aryl sulfonate, and a cosmetic acid salt of the alkylolamine.

The condensate may be defined as comprising essentially fatty acid amides of an alkylolamine with a non-performance affecting amount of fatty acid monoester of the alkylolamine. While not preferred, the percentage of the ester, based on the weight of the alkylolamide, can vary from about 5% to about 40% without substantially affecting the foam stabilizing properties as well as the crystal inhibiting properties of the fatty alkylolamide. Depending upon the acylating agent utilized to acylate the alkylolamine, glycerine may or may not be present in the final composition. The overall glycerine content should not be in excess of that present in the gelatin capsule for plasticization purposes. The acylating substance is normally a monocarboxylic acid or derivative thereof having an average of about 10 to about 18 carbons in the acyl portion. By "acylating substance" is meant any substance

which is capable of formation or introduction of an acyl radical into the alkylolamine and includes carboxylic acids, carboxylic acid halides, carboxylic acid esters and anhydrides. In regard to the esters, the term is meant to cover both esters of monohydric alcohols and esters of polyhydric alcohols such as the glycerol esters. Typical glycerol esters include coconut oil, soybean oil, glycerol trioleate, trilaurin, trimyristin, palm kernel oil, butterfat and the like.

More in detail as to the description of the various components, the condensate is formed by reacting the excess alkylolamine having at least one acylatable hydrogen atom in the amino group with a fatty acylating substance at a temperature ranging between about 130° and about 165° C. for about ½ to about 6 hours. The reaction can also be carried out at 70–130° C. in the presence of sodium methylate or other sodium alcohol salts, soda amide, or potassium alcoholates, amides or hydroxide for ¼ to 3 hours. Among the preferred organic sulfonic acids useful in the practice of the invention are the alkyl or polyalkyl aryl sulfonic acids containing from about 8 to about 22 carbon atoms in the alkyl portion of the molecule. Generally speaking, these aromatic sulfonic acids are well-known in the art. They may be mononuclear or polynuclear in structure. More particularly, the aromatic nucleus may be derived from benzene, toluene, xylene, naphthalene, phenol, cresols, etc. The alkyl substituent on the aromatic nucleus may vary widely, as long as the desired detergent power of the active ingredient is preserved. While the number of sulfonic acid groups present in the nucleus may vary, it is usual to have one such group present in order to preserve as much as possible the balance between the hydrophilic and hydrophobic portions in the molecule. Specific examples of suitable alkyl aromatic sulfonic acids are the higher alkyl aromatic sulfonic acids wherein the higher alkyl substituent on the aromatic nucleus may be branched or straight-chained in structure. They comprise such groups as decyl, dodecyl, keryl, pentadecyl, hexadecyl, mixed long-chain alkyls derived from long-chain fatty material, cracked paraffin wax, olefins, polymers of lower mono-olefins, etc. Preferred examples of this class are the higher alkyl mononuclear aryl sulfonic acids wherein the alkyl group is about 8 to about 22 carbons and preferably about 12 to 18 carbons. When combined with the alkylolamine, they form the alkylolamine sulfonate and said sulfonate is present in the fluid detergent concentrates of this invention generally in an amount at least about 5% and usually between about 20% to about 60% although it is preferred to use from about 25% to about 40% by weight of the composition.

In forming either the alkylolamide or the alkyl aryl sulfonic acid alkylolamine sulfonate, it is preferred that a lower alkylolamine be utilized. This low alkylolamine may be either a primary, or a secondary alkylolamine and may have up to about 4 carbon atoms in each radical. Preferred are the alkylolamines such as mono-, and di-, ethanolamine and isopropanolamine. Commercial mixtures containing mono-, di-, and triethanolamines wherein the alkylene portion contains from 2 to 4 carbons may also be utilized. Such materials include aminomethylpropanol, monobutanolamine, dibutanolamine, propanolamine, dipropanolamine, N-ethylpropanolamine, ethanolamine, N-methylethanolamine, N-ethylethanolamine, diethanolamine and structurally isomeric materials such as diglycolamine.

In the neutralization step, certain classes of acids may be used advantageously. Generally speaking, these acids may be classified as the cosmetic type acids. These are normally the aliphatic carboxylic acids or hydroxy-containing carboxylic acids, and may generally be defined as those acids having a molecular weight of less than 150. Examples include lactic acid, glacial acetic acid, glycolic acid, citric acid, tartaric acid, trichloroacetic acid, phosphoric acid, diethylorthophosphate, p-toluene sulfonic acid, methane sulfonic acid,

In preparing the alkylolamides of the alkylolamines, it is preferred to react about 25 to about 75 parts of the fat acylating agent with about 75 to about 25 parts of the alkylolamine and heat the mixture to temperatures between about 130° C. and about 165° C. for about 1 to about 6 hours. The resulting mixture may then be cooled; and, to 50 parts of the said mixture about 10 to about 50 parts of an alkyl aryl aromatic sulfonic acid may be added. The alkyl radicals on the aromatic portion of sulfonic acid may contain an average of about 8 to 22 carbons. The sulfonic acid forms the sulfonate with the unreacted alkylolamine from the initial condensation. The resulting blend consists of about 10 to about 50 parts condensate, about 10 to about 60 parts of alkyl aryl sulfonate, and about 5 to about 30 parts of free alkylolamine and glycerin. The resulting mixture is then blended with a sufficient quantity of the cosmetic type acid to produce the desired neutral pH. This can be accomplished at ambient temperatures although the reaction is slightly exothermic. The final reaction system is essentially neutral, fluid, and consisting of about 100% solids.

Perhaps at this time it is proper to define what is considered substantially anhydrous as far as an interpretation of the instant invention is concerned. Following the procedure described in the specification, one can prepare essentially 100% active material. As will be described later on, this material is encapsulated in gelatin capsules for direct sale to consumers in concentrated form. As the gelatin capsules normally contain from 5% to 10% moisture, it is desirable in certain instances to add perhaps up to 10% water in the concentrate so as to render the composition in moisture equilibrium with the gelatin capsule. Accordingly, for purposes of this invention, substantially anhydrous, is to be taken as less than about 10% moisture.

The capsules are produced by any of the common methods used with plasticized gelatin. One embodiment of this process involves producing a pair of plasticized gelatin films and feeding them into a rotary die. The detergent is fed between the sheets as the dies rotate and the capsule is produced as the dies press the sheets together. The capsule is formed around the metered amount of detergent provided.

The following examples are presented to illustrate the invention. It will be understood that these examples are illustrative only and should not be taken in any manner as limiting the invention as defined by the appended claims.

EXAMPLE I

In order to form the fatty alkylolamide portion of the detergent, 37.5 parts of diethanolamine was reacted with 37.5 parts of coconut oil for 4 hours at 150° C. under a vacuum of 29 inches of mercury gauge with agitation. During this period of time the emulsion originally formed by the mutually insoluble diethylolamine and coconut oil when blended together eventually breaks and the mixture becomes a homogeneous fluid. The vacuum was not essential to the production of the material but it helps in keeping color bodies and other undesirable extraneous material at a low level. The reaction mass thus prepared was then cooled to 80° C. and treated with 25 parts of dodecyl benzene sulfonic acid followed by ½ hour of mixing to assure homogeneity. The diethanolamine which was not consumed in the preparation of the diethanolamine condensate of the coconut oil reacted with the sulfonic acid to form the diethanolammonium sulfonate, which is the anionic component of the fluid detergent. It was then determined that this second reaction consumed about half of the excess diethanolamine which was present adventitiously from the initial condensation reaction. At this point, a portion of the reaction mass was treated with sufficient dodecyl benzene sulfonic acid to neutralize the alkylolamine present in the material. The resulting material set up into an unworkable pasty solid having little commercial utility. As to the other aliquot portion, 88% food grade lactic acid, in an amount of 11% based on the

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reaction mass, was added to substantially neutralize the reaction material. It was surprisingly found that the material remained completely fluid without possessing high viscosity and was suitably employed in the preparation of detergent concentrations which were encapsulated in gelatin capsules.

EXAMPLES II TO X

The procedure of Example I was carried out using other low molecular weight cosmetic type acids. Those found to be desirable and their amounts required are set forth below:

| Acid used for neutralization | Amount required, percent | Final pH of product | Type of finished product |
|------------------------------|--------------------------|---------------------|--------------------------|
| Glacial acetic acid..... | 5 | 7.0 | Liquid. |
| Glycolic acid..... | 8 | 7.0 | Do. |
| Citric acid..... | 6 | 6.8 | Do. |
| Tartaric acid..... | 6 | 7.2 | Do. |
| Trichloroacetic acid..... | 7 | 6.0 | Do. |
| Phosphoric acid..... | 8 | 7.4 | Do. |
| Diethylorthophosphate..... | 6.5 | 7.0 | Do. |
| p-Toluene sulfonic acid..... | 14 | 7.0 | Do. |
| Methane sulfonic acid..... | 8.5 | 6.5 | Do. |

In some formulations, perhaps due to low amide levels, crystallization takes place. It has been found that 2-amino-2 methyl-1-propanol, in an amount of about 5% to about 14%, based on the total detergent concentrate, will inhibit crystallization of the formulation.

EXAMPLE XI

A specific embodiment of the invention is as follows:

| | Percent |
|---|---------|
| Solar CO (a 50:50 diethanolamine-coconut oil condensate prepared in accordance with the method of Example I.....) | 7.35 |
| Mixed isopropanolamine..... | 19.00 |
| 2-amino-2 methyl-1-propanol..... | 9.00 |
| n-dodecylbenzene sulfonic acid..... | 54.65 |
| 88% lactic acid..... | 10.00 |

Ingredient number 3 was found to be a necessary substitute for part of ingredient number 2 as it functions as a crystallization inhibitor. After the preparation of the condensate as per the procedure of Example I, all the other ingredients were merely mixed in. Gelatin capsules filled with the above formulation did not swell nor "tan."

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A process for preparing a fluid, essentially neutral, detergent concentrate which comprises: reacting, at a temperature between about 130° C. and about 165° C., an excess of a lower alkylolamine having at least one acylatable

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hydrogen atom in the amine group with a fatty acylating agent having about 12-20 carbons in the fatty chain so as to form a fatty lower alkylolamide, cooling and reacting some of the remaining lower alkylolamine with a higher alkyl aryl sulfonic acid selected from the group consisting of higher alkyl benzene sulfonic acid and higher alkyl naphthalene sulfonic acid so as to form a lower alkylolammonium higher alkyl aryl sulfonate in an amount such that the reaction mixture contains about 10 to about 50 parts of the said fatty lower alkylolamide, about 10 to about 60 parts of the said lower alkylolammonium higher alkyl aryl sulfonate and about 5 to about 30 parts of the said lower alkylolamine, and adding to the reaction mixture, at about ambient temperature, a cosmetic-type acid selected from the group consisting of lactic acid, glacial acetic acid, glycolic acid, citric acid, tartaric acid, trichloroacetic acid, phosphoric acid, diethylorthophosphate, p-toluene sulfonic acid, and methane sulfonic acid to form the cosmetic-type acid salt of said lower alkylolamine.

2. The process of claim 1 wherein the higher alkyl aryl sulfonic acid contains about 8 to about 22 carbon atoms in the alkyl portion of the molecule.

3. The process of claim 1 wherein the lower alkylolamine is selected from the group consisting of monoethanolamine, diethanolamine, mono-isopropanolamine, di-isopropanolamine and mixtures thereof.

4. The process of claim 1 wherein the fatty acylating agent is coconut oil.

5. The process of claim 1 wherein the sulfonic acid is selected from the group consisting of decyl benzene sulfonic acid, dodecyl benzene sulfonic acid, keryl benzene sulfonic acid, pentadecyl benzene sulfonic acid and hexadecyl benzene sulfonic acid.

6. The product produced by the process of claim 1.

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252-137