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3,317,430

DETERGENT COMPOSITIONS

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This invention relates to a process of increasing the stability of foams produced on agitating detergent solutions in the presence of greasy soil. The invention further relates to detergent compositions containing small amounts of certain amine oxides as foam stabilizing additives.

It is common practice to include foam stabilizers in proprietary detergent compositions to improve the persistence and stability of the foam produced by agitation of solutions containing the detergent composition. These foam stabilizers are added both to conventional soaps and to detergent compositions based upon organic non-soap synthetic detergent compositions.

The present invention is concerned with the problem of stabilizing the foam produced on agitation of an aqueous solution containing a suds-producing organic synthetic detergent in the presence of soil. Foam persistence is generally used by the housewife as an index of the cleansing ability of the solution. Once the foam has collapsed, the housewife believes that the fat emulsifying and other cleansing abilities of the solution have been used up. This is not necessarily true, however, as the foam may collapse before the cleansing ability of the solution has been consumed. The problems of stabilizing the foam of aqueous solutions of detergent compositions and of correlating foam collapse with loss of detergent action are thus important ones, and ones which have received considerable attention by workers in the field.

In addition to stability, several other characteristics of the foam are involved. The original amount of foam produced on agitation of the aqueous solution is an important consideration. Furthermore, the texture of the foam, i.e., whether it is open and coarse, or of a very fine dense character, together with the ability of the foam to rinse cleanly and quickly from the articles being washed are factors which must be taken into consideration.

The prior art compounds which function as foam stabilizers in detergent systems depend upon well known foam stabilizing functional linkages such as the amide, alcoholic, and phenolic hydroxyl groups. Examples of these materials include fatty alcohols such as lauric alcohol, and fatty acid substituted amides such as lauric diethanol amide and lauric isopropanol amide. Parahydroxy laurophenone is an example of a foam stabilizing compound containing a phenolic hydroxyl group.

These prior art foam stabilizers have some degree of specificity, i.e., they are suitable for use in stabilizing the foams produced in aqueous solutions of certain suds-producing organic detergent compounds. For example, parahydroxy laurophenone is effective only with sodium lauryl sulfate or mixtures of this with other compatible active detergents. Also, the above-mentioned amides are generally suitable for use with alkyl aryl sulfonates, and lauryl alcohol is generally limited to use with alkyl sulfates.

Amine oxides have long been known to have surface active and germicidal characteristics. United States Patent 2,169,976 to Guenther et al. discloses a series of amine oxides and processes used in preparing the oxides.

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The patent further discloses that these compositions are useful generally as surface active agents and further that they may be used in combination with other surface active agents such as sulfuric acid esters of aliphatic alcohols of high molecular weight and reaction products of fatty acids with hydroxyalkyl or aminoalkyl sulfonic acids. All of the specific examples of the patent are limited to various amine oxides and a showing of their usefulness per se as foaming, wetting and washing compositions.

It is well known in the detergent art that merely because a substance is a surface active agent and further that it forms a foam in aqueous solution does not indicate that the composition is useful in stabilizing foams formed by agitating solutions of other surface active agents. For example, the soap of sodium laurate forms a foam in solution but when added to a synthetic detergent mixture, acts as a suds depressor. Saponin foams in the presence of water but in the presence of synthetic detergents has no effect.

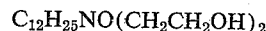
It has now been found that the presence of certain amine oxides improves the stability of the foam produced by agitating aqueous solutions of suds-producing organic synthetic detergents. The use of the amine oxides appears to result in a synergistic effect, in that the foam stability obtained is considerably greater than the stability of the foam obtained by using either the amide oxide or the foam-producing detergent material alone. In addition, the amine oxides are water-soluble, stable to bleach and are compatible with anionic detergents such as sulfated fatty alcohols and alkyl aryl sulfonates and are also effective with many nonionic detergents. This combination of properties is rarely found in suds stabilizing agents and is unexpected in the use of amine oxides.

The amine oxides found useful according to this invention are those having the formula



wherein R_1 is selected from the group consisting of straight chain alkyl and alkoxy alkyl radicals having from 8 to 18 carbon atoms and R_2 and R_3 each represent a radical selected from the group consisting of short chain aliphatic groups having 1 to 4 carbon atoms and mononuclear aromatic groups, or R_2 and R_3 may together form a heterocyclic structure.

Examples of suitable amine oxides falling within the above formula include N,N-dimethyldodecylamine oxide, $C_{12}H_{25}NO(CH_3)_2$; N-benzyl-N'-methyldodecylamine oxide, $C_{12}H_{25}NO(CH_3)CH_2C_6H_5$; N,N-dimethyloctylamine oxide, $C_8H_{17}NO(CH_3)_2$; N,N-dimethyldecylamine oxide, $C_{10}H_{21}NO(CH_3)_2$; N,N-dimethyltetradecylamine oxide, $C_{14}H_{29}NO(CH_3)_2$; N,N-dimethylhexadecylamine oxide, $C_{16}H_{33}NO(CH_3)_2$; the monododecyl ether of triethanolamine oxide, $C_{12}H_{25}OCH_2CH_2NO(CH_2CH_2OH)_2$; N,N-bis(2-hydroxyethyl) dodecylamine oxide,



and dodecylmorpholine oxide, $C_{12}H_{25}NOC_4H_8O$.

Most of the compounds described above are readily prepared from "practical" grade raw materials. Slightly improved results may be obtained by using compounds of greater purity, although the improved results may be offset by the additional processing costs. Products obtained from naturally occurring mixtures of fatty acids may also be used. For example, hydroxyethylated amine oxides

obtained from amine-2 mole ethylene oxide adducts of octadecyl, tallow and soya oil are suitable.

A preferred compound of the above-described class is N,N-dimethyldodecylamine oxide. This compound is practically odorless and is effective as a foam stabilizing additive in a wide range of detergent compositions. It can replace lauric diethanolamide in liquid detergents based on ammonium dodecyl benzene sulfonate. In addition, it can replace lauryl alcohol in formulations containing sodium lauryl sulfate. It can also be used in detergents in powdered form, paste form, or any other of the conventional forms employed in marketing present day synthetic detergent compositions. In each instance, the foam stabilizing effect of the amine oxide is exceptionally good, particularly in the presence of fatty soils.

It should be noted that all of the amine oxides of this invention decompose at about 100° C. and therefore cannot be added to a crutcher slurry and spray-dried to form a powdered detergent.

The term "suds-producing organic synthetic detergent" as employed herein and in the claims is intended to include those compounds which are commonly employed as the essential active ingredient of suds-producing synthetic detergent compositions. Examples of suds-producing organic synthetic detergents which are benefited according to this invention include both anionic and non-ionic materials.

Suitable detergents include the alkyl aryl sulfonates such as sodium dodecyl benzene sulfonate, ammonium dodecyl benzene sulfonate, potassium dodecyl benzene sulfonate, or ammonium pentadecyl benzene sulfonate and the methyl taurates such as Igepon TK-32, a sodium N-methyl-N-"tall oil acid" taurate, manufactured by General Aniline and Film Corporation. Also included are the sulfated fatty alcohols, such as sodium lauryl sulfate; the polyethylene oxide esters of resins or fatty acids, such as the ammonium salt of sulfated nonyl phenol condensed with four moles of ethylene oxide and the ammonium salt of sulfated dodecyl phenol condensed with six moles of ethylene oxide; Oronite NI-8589, a dodecyl phenol condensed with more than 10, i.e., 20 to 30 moles of ethylene oxide, sold by the Oronite Chemical Company; Triton X100, an alkyl aryl polyether alcohol manufactured by Rohm & Haas Company; and Tergitol NP-14, an alkyl phenol polyethylene glycol ether manufactured by Carbide & Carbon Chemicals Company. Optimum results according to this invention have been obtained with mixtures of the amine oxides with the alkyl aryl sulfonates, the sulfated fatty alcohols and mixtures of alkyl aryl sulfonates and the polyethylene oxide esters of resins or fatty acids. These mixtures are preferred.

Conventional soaps and inorganic "builder" salts, such as the phosphates, silicates, sulfates and the like, are not included within the term "suds-producing organic synthetic detergent" as used herein, although they may be used as auxiliary ingredients in the compositions of this invention. Also excluded from this class are the amine oxides described above, although these materials are described in the Guenther patent as being suitable for use as essential active ingredients in synthetic detergent compositions. The benefits of this invention are not obtained by merely increasing the concentration of the amine oxide employed in the detergent composition of this invention.

It is also noted that the amine oxides of this invention have a distinct advantage over the fatty acid substituted amides in that the latter tend to hydrolyze and become partially ineffective in alkaline liquid detergent compositions, causing a drop in pH with consequent formation of silica and reduction in anti-corrosion properties. The amine oxides do not suffer from this disadvantage.

As mentioned above, a strong synergistic effect is noted in the compositions of this invention. The Guenther patent mentioned above discloses that amine oxides possess good foaming properties in water solution. This is true,

however, only in the absence of soil. When soil is present, amine oxide solutions, like many other synthetic detergent solutions, cease to foam. This effect, together with the synergistic effect obtained with the compositions of this invention, are shown in Tables I, II, III and IV below. Table I summarizes the results of Terg-O-Tometer Tests conducted with a solution of standard synthetic detergent, a solution of the preferred amine oxide of this invention, and a solution containing both ingredients.

Terg-O-Tometer Tests involve empirical measurement of the amount of foam produced under simulated fabric washing conditions. The ratings given in this test are set forth in Table II. Stated sizes of cloth are placed in a miniature washing machine and are laundered in the presence of a measured amount of a standard soil preparation and water of a standard hardness. In these experiments, twelve pieces of cloth 6.5 inches by 4.25 inches, 1.75 grams of vacuum cleaner soil, and water of 50 p.p.m. hardness were employed. Table III shows the results obtained in comparing the suds stability of solutions containing an alkyl aryl sulfonate, an amine oxide and mixtures of the two over a range of proportions. Table IV presents similar data obtained when comparing solutions of a fatty alcohol sulfate, an amine oxide and mixtures of the two over a range of proportions. The results in each table are expressed in terms of the Dishpan Suds Stability Test.

The Dishpan Suds Stability Test is a standard test for determining the stability of suds in the presence of suds-destroying agents. In conducting the test, 16 grams of the detergent sample is dissolved in six quarts of tap water (90 p.p.m. hardness) at 115° F. in a dishpan of standard size. 20 grams of tallow containing 15% of free fatty acids are added and the solution is agitated for 30 seconds. The time for the suds to completely disappear is then determined in seconds, and these are the values given. It is noted that fatty acids are particularly effective in destroying foam and that for this reason the test employs a tallow having a high free fatty acid content.

TABLE I

| Ingredient | 10 Min. of Agitation | 20 Min. of Agitation ¹ |
|--|----------------------|-----------------------------------|
| Sodium dodecylbenzene sulfonate, 0.4 g./liter | + | + |
| Sodium dodecylbenzene sulfonate, 0.4 g. and N,N-dimethyldodecylamine oxide, 0.1 g./liter | 1/2 | 1 |
| Sodium lauryl sulfate, 0.4 g./liter | 1/2 | 1 1/2 |
| Sodium lauryl sulfate, 0.4 g./liter and N,N-dimethyldodecylamine oxide, 0.1 g./liter | 1 1/2 | 2 |
| N,N-dimethyldodecylamine oxide, 0.1 g./liter | 0 | 0 |

¹ Bleach added after 10 minutes.

The values given in Table I are taken from the standard values given in Table II below.

TABLE II.—TERG-O-TOMETER READINGS

| | |
|-------|-----------------------------------|
| 0 | No bubbles. |
| + | Trace. |
| 1/2 | Trace to 25% of surface coverage. |
| 1 | 25 to 50% surface coverage. |
| 1 1/2 | 50 to 100% surface coverage. |
| 2 | Complete surface coverage. |

The data of Table I indicates that the amine oxide at a level of 0.1 gram per liter in the presence of soil possesses no foaming ability whatsoever. Similarly, the sodium dodecylbenzene sulfonate and the sodium lauryl sulfate possess very little foaming power in the presence of soil. However, when the sulfonate or sulfate is mixed with the amine oxide, the foaming of the mixture in the presence of soil is greatly increased, thus demonstrating a large synergistic effect.

TABLE III.—SUDS STABILITY OF MIXTURES OF AMMONIUM DODECYLBENZENE SULFONATE AND N,N-DIMETHYL DODECYLAMINE OXIDE

| Formula..... | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|--|------------|------------|------------|------------|------------|----------|----------|------------|
| Percent ammonium dodecylbenzene sulfonate, active..... | 20.0 | 19.0 | 17.0 | 10.0 | 5.0 | ----- | 6.0 | 40.0 |
| Percent N,N-dimethyl dodecylamine oxide, active..... | ----- | 1.0 | 3.0 | 10.0 | 15.0 | 20.0 | 2.0 | 6.0 |
| Percent ethyl alcohol, 100%..... | 15.0 | 15.0 | 15.0 | 15.0 | 15.0 | 15.0 | 15.0 | 15.0 |
| Percent water and miscellaneous ingredients..... | 65.0 | 65.0 | 65.0 | 65.0 | 65.0 | 65.0 | 77.0 | 39.0 |
| | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| Dishpan Suds Stability Test—16 grams detergent, 20 grams tallow, 6 qts. 90 p.p.m. hardness water at 115° F. Agitated for 30 seconds. Time for suds to break, in seconds. Seconds (duplicate determinations)..... | { 25 30 | { 30 30 | { 65 60 | { 40 35 | { 40 35 | { 0 0 | { 0 0 | { 70 75 |

TABLE IV.—SUDS STABILITY OF MIXTURES OF SODIUM LAURYL SULFATE AND N,N-DIMETHYL DODECYLAMINE OXIDE

| Formula..... | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|--|------------|------------|------------|------------|------------|----------|----------|------------|
| Percent sodium lauryl sulfate, active..... | 15.0 | 14.0 | 12.0 | 7.5 | 6.0 | ----- | 6.0 | 30.0 |
| Percent N,N-dimethyl dodecylamine oxide, active..... | ----- | 1.0 | 3.0 | 7.5 | 9.0 | 15.0 | 2.0 | 6.0 |
| Percent ethyl alcohol, 100%..... | 15.0 | 15.0 | 15.0 | 15.0 | 15.0 | 15.0 | 15.0 | 20.0 |
| Percent water and miscellaneous ingredients..... | 70.0 | 70.0 | 70.0 | 70.0 | 70.0 | 70.0 | 77.0 | 44.0 |
| | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| Dishpan Suds Stability Test—16 grams detergent, 20 grams tallow, 6 qts. 90 p.p.m. hardness water at 115° F. Agitated for 30 seconds. Time for suds to break, in seconds. Seconds (duplicate determinations)..... | { 20 25 | { 40 45 | { 40 40 | { 30 35 | { 20 15 | { 0 0 | { 0 0 | { 65 70 |

Tables III and IV give data comparing the suds stability of mixtures of N,N-dimethyl dodecylamine oxide with ammonium dodecyl benzene sulfonate, in one case, and with sodium lauryl sulfate in the other case. The suds stability of solutions of the individual components of the mixtures is also given. Each test was conducted in the presence of a standard level of tallow containing 15% of free fatty acids.

From Table III it is noted that mixtures of the sulfonate and amine oxide in the ratios of 6:1 to 0.3:1 provided considerably improved suds stability over the use of either the sulfonate or the amine oxide alone. The amine oxide alone provided no sudsing under the conditions of the test.

From Table IV it can be seen that the sulfate and amine oxide mixtures in ratios ranging from 14:1 to 1:1 provided better suds stability than either component of the mixture.

As the total level of detergent and amine oxide was constant in each case, synergistic results are clearly shown by the data.

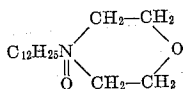
In the compositions of this invention, the level of amine oxides required to provide optimum foam stability depends to some extent upon the particular organic synthetic detergent employed and upon the nature of the amine oxide. Generally speaking, synergistic results are obtained when the amine oxides are present at a level ranging from 2 to 100% by weight of the suds-producing synthetic organic detergent. In other words, the synthetic detergent-amine oxide ratio should range from about 50:1 to 1:1. At levels below this range, little if any benefit is obtained. At levels above this range, the amine oxides are either less effective or their use does not provide additional benefit. This is shown in Tables III and IV above, and Table V below, which give data obtained by evaluating a light duty liquid detergent in terms of its suds stability in the presence of foam destroying agents. In this instance, the Dishpan Suds Stability Test was conducted with 10 grams of the detergent sample and the water temperature was 120° F. The conditions were otherwise the same as those described above.

TABLE V.—DISHPAN SUDS STABILITY TEST

| Detergent Compositions | | | Time for Suds to Break (Seconds) | | | |
|---|-----------------------|-------------------------|--|-----------------------------|---|---------------------------|
| Percent N,N-dimethyl dodecylamine Oxide | Percent Ethyl Alcohol | Percent Water and Misc. | 29.1% Ammonium Dodecyl Benzene Sulfonate | 29.1% Sodium Lauryl Sulfate | 17.14% Ammonium Dodecyl Benzene Sulfonate plus 11.87% Alipal ¹ | 29.1% Alipal ¹ |
| None | 14.8 | 56.1 | 105 | 5 | 35 | 25 |
| .50 | 14.8 | 55.6 | 100 | 5 | 80 | 25 |
| 1.00 | 14.8 | 55.1 | 105 | 5 | 90 | 25 |
| 2.00 | 14.8 | 54.1 | 105 | 5 | 100 | 30 |
| 3.00 | 14.8 | 53.1 | 130 | 15 | 150 | 35 |
| 4.00 | 14.8 | 52.1 | 300 | 35 | 280 | 40 |
| 5.00 | 14.8 | 51.1 | 370 | 35 | 335 | 50 |
| 6.00 | 14.8 | 50.1 | 390 | 30 | 330 | 50 |
| Lauric Diethanolamine | | | | | | |
| 6.00 | 14.8 | 50.19 | ----- | ----- | 80 | ----- |

¹ Ammonium salt of sulfated nonyl phenol condensed with 4 moles of ethylene oxide (29.1% is on active basis).

N,N-dimethyldodecylamine oxide, the preferred alkyl amine oxide for use according to this invention, may be prepared according to any of the well-known procedures. Suitable methods for preparation are found for example in the aforementioned Guenther et al. Patent No. 2,169,976. In one typical method, a mixture of 100 grams of N,N-dimethyldodecylamine of a practical grade having a melting point range of -21 to -11° C. was mixed with 200 grams of 30% hydrogen peroxide and 400 ml. of 95% ethyl alcohol and allowed to stand overnight at room temperature. The following day 0.1 gram of manganese dioxide were added with cooling in order to destroy excess hydrogen peroxide. The mixture was then stirred mechanically until no more oxygen gas was evolved, i.e., about three hours. The solution was then filtered from the manganese dioxide and the filtrate was subjected to vacuum distillation in a water bath warmed to $40-45^{\circ}$ C. When the concentrated solution started to foam, 100 ml. of 95% ethyl alcohol were added. The vacuum distillation was resumed until foaming again became troublesome, when it was again counteracted by another 100 ml. of 95% ethyl alcohol. The vacuum distillation was continued until no more liquid emerged from the condenser. The residue weighed 187 grams. 100 grams of the amine yields 107.5 grams of the oxide, and the residue was found to contain 57.5% of N,N-dimethyldodecylamine oxide. The solvent was removed from a portion of the product by spreading the amine oxide in a thin layer in a vacuum desiccator charged with fresh concentrated sulfuric acid. The hydrated form of the amine oxide was thus obtained. The melting point of the picrate was 81° C. The starting material, N,N-dimethyldodecylamine, formed a picrate which melted at 51° C. N-dodecylmorpholine oxide



was prepared in the same manner as described above.

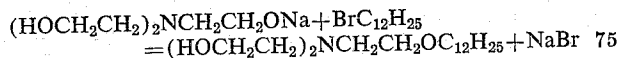
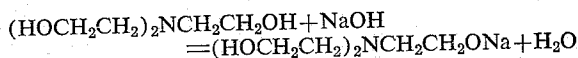
The N-benzyl-N'-methyldodecylamine oxide described above may be prepared by the method of Jerchel and Jung (Berichte 85, 1135 (1952)). This procedure yields the hydrate, $\text{C}_{12}\text{H}_{25}\text{NO}(\text{CH}_3)\text{CH}_2\text{C}_6\text{H}_5 \cdot \text{H}_2\text{O}$.

The N,N-bis(2-hydroxyethyl)dodecylamine oxide may be prepared according to a process similar to that described above for the preparation of dimethyldodecylamine oxide. Where products of high purity are desired, N,N-bis(2-hydroxyethyl)dodecylamine may be prepared from (1) dodecyl bromide and diethanol amine (U.S. Patent 2,541,088), or (2) from dodecylamine and 2 moles of ethylene chlorohydrin, and this material used as a starting material. Other suitable starting materials are obtained by the adding on of 2 moles of ethylene oxide to mixtures of long chain amines obtained from natural fats. The Ethomeens, sold by Armour and Company, are products of this type, and are derived from coconut oil, tallow or soya. Ethomeen C-12 is a coconut oil amine and is stated to have the structure



The 18 carbon hydroxyethylated amines (octadecylamine, tallow and soya) are satisfactory. These commercial products may generally be used as starting materials.

The monododecyl ether of triethanolamine oxide was prepared according to the following:



The following examples illustrate the process and product of this invention.

Example 1

| Ingredient: | Percent |
|---|---------|
| Ammonium dodecylbenzene sulfonate | 17.14 |
| Ammonium salt of sulfated nonyl phenol condensed with 4 moles of ethylene oxide | 11.87 |
| N,N-dimethyldodecylamine oxide | 6.00 |
| Denatured ethyl alcohol (100%) | 14.80 |
| Perfume | .20 |
| Water and miscellaneous ingredients | 49.99 |
| | 100.00 |

Example 1 is a light duty liquid detergent prepared according to this invention. Its performance in dishwashing and light duty laundering is excellent. The foam produced during agitation of a washing solution containing the usual level of this detergent is of medium fine open texture and remains stable in the presence of soil until the fat emulsifying and cleaning ability of the solution is exhausted. In addition, the foam on the washing solution remains stable for an exceptionally long period of time where other detergent foams tend to break and disappear a short time after agitation of the solution ceases.

Example 2

Table VI below shows the comparative effectiveness of two prior art detergent compositions and the composition of Example 1 in a Standard Dishpan Suds Stability Test and a Standard Dishwashing Test.

The standard dishwashing test employed measures the number of artificially soiled dinner plates washed with a solution of the detergent under standard conditions. The standard soil employed is a uniform blend of 9 parts by weight of emulsifier-free vegetable shortening, 8 parts by weight of bread flour and green color. A teaspoonful of the standard soil is spread evenly over each plate. 6 quarts of water of the desired hardness is adjusted to 116° F. and a measured amount of detergent is added. The number of standardly soiled plates washed in this solution according to a standardized washing technique gives an indication of the effectiveness of the solution. The end point is reached when the foam no longer completely covers the surface of the washing solution.

The Standard Dishpan Suds Stability Test is conducted in the same manner as that described above with reference to the data in Table I. The results are expressed in a time required, in seconds, for the suds to break.

TABLE VI

| Light Duty Liquid Detergent | Percent | | |
|---|---------|----------|--------|
| | 1 | 2 | 3 |
| Ammonium dodecylbenzene sulfonate | 17.14 | 17.14 | 17.14 |
| Alipal 1 (active) | 11.87 | 11.87 | 11.87 |
| Lauric diethanolamine | 6.00 | | |
| N,N-dimethyldodecylamine oxide | | 6.00 | |
| Ethyl alcohol (100%) | 14.80 | 14.80 | 14.80 |
| Perfume | .20 | .20 | .20 |
| Water and miscellaneous ingredients | 49.99 | 49.99 | 55.99 |
| | 100.00 | 100.00 | 100.00 |
| Standard Dishwashing Test Data: | | | |
| Number of plates washed in 120 p.p.m. water at— | | | |
| 3 grams (duplicate determinations) | 19, 20 | 21, 21 | 17, 18 |
| 6 grams (duplicate determinations) | 37, 37 | 38, 38 | 34, 35 |
| Standard Dishpan Suds Stability Test: | | | |
| Time for suds to break (seconds) (duplicate determinations) | 80, 85 | 345, 350 | 30, 35 |

¹ Ammonium salt of sulfated nonyl phenol condensed with 4 moles of ethylene oxide.

The above data show that the addition of an amine oxide to the detergent system of column 3 provides a considerable improvement in dishwashing ability. The degree of improvement obtained with N,N-dimethyldodecylamine oxide also represents an improvement over the prior art lauric diethanolamide. The stability of the suds obtained with the amine oxide-containing composition shows a marked improvement over the prior art amide.

The following examples are illustrative of further detergent compositions prepared according to this invention.

Example 3

| Ingredient: | Percent |
|--|---------|
| Dodecyl benzene sulfonic acid, 90% ----- | 10.0 |
| Sodium xylene sulfonate (37% active) ----- | 21.6 |
| Sodium silicate (37.5%) ----- | 7.0 |
| Potassium hydroxide ----- | 3.2 |
| N,N-dimethyldodecylamine oxide (50%) ---- | 7.0 |
| Tetrapotassium pyrophosphate ----- | 20.0 |
| Water ----- | 31.2 |
| | 100.0 |

Example 3 represents a heavy duty liquid detergent prepared according to this invention. These detergents

Example 5

| | |
|--|-------|
| Sodium tetrapropylene benzene sulfonate_ | 18.0 |
| N,N-dimethyldodecylamine oxide ----- | 3.5 |
| Sodium toluene sulfonate ----- | 2.5 |
| Tetrasodium pyrophosphate ----- | 25.0 |
| Pentasodium tripolyphosphate ----- | 15.0 |
| Sodium silicate ----- | 6.0 |
| Sodium carboxyl methyl cellulose ----- | 0.5 |
| Water ----- | 7.0 |
| Sodium sulfate and miscellaneous ----- | 22.5 |
| | 100.0 |

Examples 4 and 5 are powdered detergent compositions containing N,N-dimethyldodecylamine oxide and N-dodecylmorpholine oxide as foam stabilizing additives. The volume of foam produced in aqueous solutions of these compositions is equal or superior to that obtained with prior art foam stabilizers. In addition, the foam produced remains stable for a longer period of time.

Example 6

Three samples of N,N-di(2-hydroxyethyl) dodecylamine oxide, $C_{12}H_{25}NO(CH_2CH_2OH)_2$, were tested as a suds stabilizer in a light duty liquid detergent formulation. The results of this test are given in the following table.

TABLE VII

| Light Duty Liquid Detergent Ingredient | Percent | | | | |
|--|---------|--------|--------|--------|--------|
| | 1 | 2 | 3 | 4 | 5 |
| Ammonium dodecylbenzene sulfonate..... | 17.14 | 17.14 | 17.14 | 17.14 | 17.14 |
| Alpal 1 (active)..... | 11.87 | 11.87 | 11.87 | 11.87 | 11.87 |
| Lauric diethanolamide..... | | | | | 6.00 |
| $C_{12}H_{25}NO(CH_2CH_2OH)_2$ (a)..... | 6.00 | | | | |
| $C_{12}H_{25}NO(CH_2CH_2OH)_2$ (b)..... | | 6.00 | | | |
| $C_{12}H_{25}NO(CH_2CH_2OH)_2$ (c)..... | | | 6.00 | | |
| Ethyl alcohol, 100%..... | 12.00 | 12.00 | 12.00 | 12.00 | 12.00 |
| Perfume..... | .20 | .20 | .20 | .20 | .20 |
| Water and miscellaneous ingredients..... | 52.79 | 52.79 | 52.79 | 58.79 | 52.79 |
| | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |
| Standard Dishwashing Test Data: Number of plates washed in 120 p.p.m. water at detergent level of— | | | | | |
| 3 grams (duplicate determinations)..... | 22, 23 | 18, 18 | 18, 20 | 12, 13 | 19, 21 |
| 6 grams (duplicate determinations)..... | 42, 42 | 37, 38 | 37, 38 | 25, 26 | 37, 39 |

¹ Ammonium salt of sulfated nonyl phenol condensed with 4 moles of ethylene oxide.

give excellent results in dishwashing tests. The composition of Example 3 is equivalent in dishwashing characteristics to a similar composition containing 7% of N-substituted fatty acid amides, but is slightly less effective in regard to the amount of suds produced.

Example 4

| Ingredient: | Percent |
|--|---------|
| Sodium dodecyl benzene sulfonate ----- | 18.0 |
| Sodium toluene sulfonate ----- | 2.5 |
| Sodium silicate ----- | 6.0 |
| N-dodecylmorpholine oxide ----- | 3.5 |
| Sodium carboxymethylcellulose ----- | 0.5 |
| Tetrasodium pyrophosphate ----- | 25.0 |
| Pentasodium tripolyphosphate ----- | 15.0 |
| Water ----- | 7.0 |
| Sodium sulfate and miscellaneous ----- | 22.5 |
| | 100.0 |

The above data show that the addition of N,N-di(2-hydroxyethyl) dodecylamine oxide to the detergent system provides a considerable improvement in dishwashing ability. Of the three samples, sample (a) was of the highest purity and provided the greatest improvement in results.

Example 7

Tables VIII and IX below describe a series of tests conducted on N,N-dimethyl alkyl amine oxides where the alkyl (R_1) radical varies from 8 to 18 carbon atoms in length. In Table IX it will be noted that the dishwashing results of the C_{16} and C_{18} compounds are poor. However, these same compounds give improved suds stability in the presence of tallow as evidenced by the suds stability data.

TABLE VIII.—SUDS STABILITY OF MIXTURES OF POTASSIUM DODECYLBENZENE SULFONATE AND N,N-DIMETHYL-ALKYLAMINE OXIDES

| Light Duty Liquid Detergent Ingredient | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|------------|------------|----------|------------|----------|------------|----------|------------|----------|------------|----------|
| Percent Potassium dodecylbenzene sulfonate, active..... | 20.0 | 16.0 | ----- | 16.0 | ----- | 16.0 | ----- | 16.0 | ----- | 16.0 | ----- |
| Percent N,N-dimethyl octylamine oxide, C ₈ H ₁₇ NO-(CH ₃) ₂ , active..... | ----- | 4.0 | 20.0 | ----- | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| Percent N,N-dimethyl decylamine oxide C ₁₀ H ₂₁ NO-(CH ₃) ₂ , active..... | ----- | ----- | ----- | 4.0 | 20.0 | ----- | ----- | ----- | ----- | ----- | ----- |
| Percent N,N-dimethyl tetradecylamine oxide C ₁₄ H ₂₉ NO-(CH ₃) ₂ , active..... | ----- | ----- | ----- | ----- | ----- | 4.0 | 20.0 | ----- | ----- | ----- | ----- |
| Percent N,N-dimethyl hexadecylamine oxide C ₁₆ H ₃₃ NO-(CH ₃) ₂ , active..... | ----- | ----- | ----- | ----- | ----- | ----- | ----- | 4.0 | 20.0 | ----- | ----- |
| Percent Armeen DMS oxide (Soya dimethylamine oxide)..... | ----- | ----- | ----- | ----- | ----- | ----- | ----- | ----- | ----- | 4.0 | 20.0 |
| Percent Alcohol 3A..... | 15.0 | 15.0 | 15.0 | 15.0 | 15.0 | 15.0 | 15.0 | 15.0 | 15.0 | 15.0 | 15.0 |
| Percent Water, etc..... | 65.0 | 65.0 | 65.0 | 65.0 | 65.0 | 65.0 | 65.0 | 65.0 | 65.0 | 65.0 | 65.0 |
| Dishpan Suds Stability Test: 16 grams detergent, 20 grams tallow, 6 qts. 90 p.p.m. hardness water at 115° F. Agitated for 30 seconds. Time for suds to break, in seconds. Seconds (duplicate determinations)..... | { 30 30 | { 40 40 | { 0 0 | { 50 55 | { 0 0 | { 40 45 | { 0 0 | { 35 40 | { 0 0 | { 40 45 | { 0 0 |

TABLE IX.—EVALUATION OF N,N-DIMETHYL-ALKYLAMINE OXIDES AS A SUBSTITUTE FOR LAURIC DIETHANOLAMIDE IN LIGHT DUTY LIQUID DETERGENT

| Formula..... | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|--|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|------------------|
| Percent Ammonium dodecylbenzene sulfonate, active..... | 17.28 | 17.28 | 17.28 | 17.28 | 17.28 | 17.28 | 17.28 | 17.28 |
| Percent Ammonium salt of sulfated dodecylphenol condensed with 6 moles ethylene oxide, active..... | 11.87 | 11.87 | 11.87 | 11.87 | 11.87 | 11.87 | 11.87 | 11.87 |
| Percent N,N-dimethyl octylamine oxide, C ₈ H ₁₇ NO(CH ₃) ₂ , active..... | 5.00 | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| Percent N,N-dimethyl decylamine oxide C ₁₀ H ₂₁ NO(CH ₃) ₂ , active..... | ----- | 5.00 | ----- | ----- | ----- | ----- | ----- | ----- |
| Percent Ethomeed C ₁₂ amine oxide C ₁₂ H ₂₅ NO(CH ₂ CH ₂ OH) ₂ , active..... | ----- | ----- | 5.00 | ----- | ----- | ----- | ----- | ----- |
| Percent N,N-dimethyl tetradecylamine oxide, C ₁₄ H ₂₉ NO(CH ₃) ₂ , active..... | ----- | ----- | ----- | 5.00 | ----- | ----- | ----- | ----- |
| Percent N,N-dimethyl hexadecylamine oxide, C ₁₆ H ₃₃ NO(CH ₃) ₂ , active..... | ----- | ----- | ----- | ----- | 5.00 | ----- | ----- | ----- |
| Percent Soya dimethylamine oxide..... | ----- | ----- | ----- | ----- | ----- | 5.00 | ----- | ----- |
| Percent Lauric diethanolamide..... | ----- | ----- | ----- | ----- | ----- | ----- | 5.00 | ----- |
| Percent Alcohol 3A..... | 14.80 | 14.80 | 14.80 | 14.80 | 14.80 | 14.80 | 14.80 | 14.80 |
| Percent Water, NH ₄ OH, etc..... | 51.05 | 51.05 | 51.05 | 51.05 | 51.05 | 51.05 | 51.05 | 51.05 |
| Dishwashing Test Data: Number of plates washed in 120 p.p.m. water at the level of— | | | | | | | | |
| 3 grams..... | 21, 21 | 20, 21 | 19, 20 | 17, 19 | 12, 14 | 13, 14 | 18, 18 | 17, 18 |
| 6 grams..... | 34, 34 | 34, 35 | 33, 34 | 32, 32 | 23, 26 | 22, 25 | 37, 38 | 29, 30 |
| Dishpan Suds Stability Test: 10 grams detergent, 20 grams tallow, 6 qts. 90 p.p.m. hardness water at 115° F. Agitated for 30 seconds. Time for suds to break, in seconds. Seconds (triplicate determinations)..... | { 160 180 170 | { 580 550 580 | { 730 740 710 | { 560 580 570 | { 240 220 240 | { 490 510 500 | { 125 130 130 | { 50 60 60 |

Example 3

| | | |
|--|---------|----|
| Ingredient: | Percent | |
| Sodium tetrapropylene benzene sulfonate | 18.0 | 50 |
| Monododecyl ether of triethanolamine oxide | 3.5 | |
| Sodium toluene sulfonate | 2.5 | |
| Tetrasodium pyrophosphate | 25.0 | |
| Pentasodium tripolyphosphate | 15.0 | 55 |
| Sodium silicate | 6.0 | |
| Sodium carboxy methyl cellulose | .5 | |
| Water | 7.0 | |
| Sodium sulfate and miscellaneous ingredients | 22.5 | |
| | 100.0 | 60 |

This example is a powdered detergent composition containing the monododecyl ether of triethanolamine oxide as a foam-stabilizing additive. The volume of foam produced in aqueous solutions of this composition is equal or superior to that obtained with prior art foam stabilizers. In addition, the foam stabilizer is stable in the presence of a bleaching agent.

We claim:

1. An improved detergent composition comprising an organic suds-producing synthetic detergent selected from the group consisting of anionic-nonsoap detergents and nonionic detergents and as a foam stabilizer an amine oxide selected from the group consisting of N,N-bis(2-hydroxyethyl) dodecylamine oxide and N-benzyl-N-methyl

dodecylamine oxide, the amine oxide being present at a level ranging from 2% to 100% by weight of the synthetic detergent.

2. The detergent composition of claim 1 wherein the amine oxide is N,N-bis(2-hydroxyethyl) dodecylamine

3. The detergent composition of claim 1 wherein the amine oxide is N-benzyl-N-methyl dodecylamine oxide.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,317,430

May 2, 1967

Hill M. Priestley et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 12, line 52, after "dodecylamine" insert -- oxide
--.

Signed and sealed this 21st day of November 1967.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents